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Luciano de Andrade Gomes

STUDIES ON URBAN SEWAGE SLUDGE DRYING PROCESS AIDED BY ADJUVANTS FOR PRODUCING SOIL AMENDMENTS

March - 2020

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Studies on Urban Sewage Sludge Drying Process Aided by Adjuvants for Producing Soil Amendments

Ph.D. Thesis in the scientific area of Environmental Engineering, submitted to the Department of Civil Engineering, Faculty of Science and Technology, University of Coimbra, Portugal

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"Se você quer transformar o mundo, experimente primeiro promover o seu aperfeiçoamento pessoal e realizar inovações no seu próprio interior. Estas atitudes se refletirão em mudanças positivas no seu ambiente familiar. Deste ponto em diante, as mudanças se expandirão em proporções cada vez maiores. Tudo o que fazemos produz efeito, causa algum impacto."

- Dalai Lama

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ABSTRACT

Sewage sludge (SS) formed during the purification of urban effluents in wastewater treatment plants (WWTP) is produced in high quantities in Portugal (around 300 kt year^{-1} on a dry basis) and in all developed countries. Thus, the management of this waste is expensive due to the high moisture content (greater than 80%), transportation costs, and all the logistics to the final destination. The main constituents of WWTP sludge are water, biomass (microorganisms, including some pathogens), inorganic solids, fats, macronutrients (N, P, K), Ca, Mg, Fe, and minor quantities of potentially toxic metals (PTM) such as Cr, Ni, Cu, Pb, Zn, and Cd. Due to its high organic matter (OM) content and nutrients, its application in the soil is a possible management route.

In the context of the circular economy, this thesis aimed to study the isothermal sludge drying process, aided by other industrial residues, with a view to agronomic recovery. The studies involved sludge from anaerobic digestion and various industrial residues (weathered coal fly ash collected in a landfill - CFA; green liquor dregs - GLD; eggshell - ES and rice husk - RH) used as adjuvants. Experimental tests were carried out by drying small cylinders with an initial moisture content of about 80% at different isothermal conditions (70, 85, 100, 115, and 130 ºC). After the initial physical and chemical characterization of several samples of sludge and adjuvants, multiple drying studies were performed. Sludge samples were mixed with different proportions of adjuvants, where the most used dosage was 0.15 g g^{-1} of SS (wet basis).

Initially, the characterization of soil and sludge samples revealed that the concentration of PTM of the soil complies with the lowest constraints in at least 90% of the Portuguese territory. However, if more restrictive limits were adopted (such as those adopted in Sweden), the concentrations of Ni, Zn and Cd would hamper the application of sludge in the soil. The ecological risk assessment showed that the geoaccumulation index (I$_{geo}$) for Cd, Cu and Zn corresponds to a moderate to the high pollution level. However, the pollution index (PI) and the potential ecological risk index (PERI) revealed that there is no contamination, and the ecological risk is low for the six metals studied.

Drying kinetics demonstrated that different periods could be identified: Period 0 (warm-up), Period I (free water removal) and Period II (interstitial water removal), which represent the heating phase, constant drying period, and non-linear drying period, respectively. The temperature increase led to faster drying. For example, the control sample at 70 °C required about 64 minutes to achieve a moisture ratio (MR) of 0.30, while at 130 °C the same dryness level was reached in approximately 17 minutes. The positive effect of the use of adjuvants on the diffusion coefficient (D_{eff}), for example at 100 ºC in Period I, compared to the control sample, was 1.11; 16 and 19%, for CFA, ES, and RH, respectively. However, GLD decreased the D_{eff} by about 7%. Additionally, the experimental drying data can be well described by the second Fick's Law (Period I) and by the thin-layer model (Period II).

Regarding the properties of adjuvants, the acid neutralization capacity of GLD and ES played an important role in increasing the pH of the soil from 6.7 to 7.8 and 8.0, respectively. GLD was the only

adjuvant that decreased the pathogenic microorganisms (86%), although it did not improve the drying process. Thus, the studies carried out allowed to identify three decisive parameters in the selection of an adjuvant for the drying process: reduction of pathogenic microorganisms, acid neutralization capacity, and influence on the germination index.

Germination study with *Lepidium Sativum L.* (garden cress) indicated that the sludge mixed with CFA and ES reduces the phytotoxicity effect of the sludge, reduces the acidity and increases the OM content in the soil. The SS: adjuvant mixture reduced the concentration that induces 50% of inhibition - EC_{50} by 66%, 60% and 80% for CFA, GLD, and ES, respectively, when compared with the effect of the SS without any adjuvant. Additionally, the tests in pots with garden cress revealed that the effect of the sludge with and without the different adjuvants did not present a deleterious effect on the plants.

Finally, through a multicriteria approach involving environmental, technical and economic aspects, it was possible to conclude that the sludge drying using GLD at 130 ºC is the best option in terms of adjuvant type and temperature. However, ES at 130 ºC and GLD at 70 ºC can also be considered. Therefore, the incorporation of these residues as SS drying adjuvants can bring environmental and social gains, in addition to promoting the value chain in new routes for waste management, thus closing the loop of these anthropogenic materials in the environment.

RESUMO

As lamas formadas na depuração de efluentes urbanos em Estações de tratamento de águas residuais (ETAR) são produzidas em elevadas quantidades em Portugal (em torno de 300 kt ano^{-1} em base seca) e em todos os países desenvolvidos. Devido ao elevado teor de humidade (superior a 80%), aos custos de transporte, e a toda a logística até ao destino final, a gestão destes resíduos é por isso dispendiosa. Os principais constituintes da lama de ETAR são a água, biomassa (microrganismos, incluindo alguns agentes patogénicos), sólidos inorgânicos, gorduras, macronutrientes (N, P, K), Ca, Mg, Fe e quantidades menores de metais potencialmente tóxicos (*PTM*) como por exemplo Cr, Ni, Cu, Pb, Zn e Cd. Devido ao seu elevado teor em matéria orgânica (*OM*) e nutrientes, a sua utilização no solo tem sido uma via possível para gerir este resíduo.

No contexto da economia circular, esta tese teve como objetivo estudar o processo de secagem isotérmica de lama, coadjuvado com outros resíduos industriais, tendo em vista a valorização agronómica. Os estudos envolveram lamas de digestão anaeróbia, bem como diversos resíduos industriais (cinzas de carvão coletadas num aterro – CFA; *Dregs* de licor verde – GLD; casca de ovo – ES e casca de arroz – RH). Os ensaios foram realizados com recurso à secagem de pequenos cilindros com humidade inicial de aproximadamente 80%, para diferentes condições isotérmicas (70, 85, 100, 115, e 130 °C). Após uma fase inicial de caracterização física e química de diversas amostras de lamas e dos adjuvantes, foram realizados múltiplos estudos de secagem. As amostras de lamas foram misturadas com diversas taxas de aditivos, sendo a mais utilizada 0,15 g g^{-1} de lama (base húmida).

Inicialmente, o estudo da caracterização das amostras de solo e lama, revelou que a concentração de *PTM* do solo cumpre as restrições mais baixas em cerca de 90% do território português, e que os limites impostos à lama na legislação portuguesa não foram ultrapassados em nenhuma amostra. No entanto, se fossem adotados limites mais restritivos (como por exemplo os praticados pela Suécia), as concentrações de Ni, Zn e Cd poderiam ser impeditivas para aplicar lama ao solo. A avaliação do risco ecológico mostrou que o índice de geoacumulação (I$_{geo}$) para Cd, Cu e Zn corresponde a um nível de poluição moderado a alto. No entanto, o índice de poluição *(PI)* e o índice potencial de risco ecológico *(PERI)* revelaram que não há contaminação e o risco ecológico é baixo para os seis metais estudados.

A cinética de secagem demonstrou que podem ser identificados diferentes períodos de secagem: Período 0 *(warm-up)*, Período I *(free water removal)* e Período II *(interstitial water removal)*, os quais representam a fase de aquecimento, período de secagem constante e o período não linear de secagem, respetivamente. O aumento na temperatura levou a uma secagem mais rápida. Por exemplo, a amostra de controlo a 70 °C exigiu cerca de 64 minutos para atingir uma razão de humidade *(MR)* de 0,30, enquanto que a 130 °C o mesmo nível de secagem foi alcançado em aproximadamente 17 minutos. O efeito positivo do uso dos adjuvantes no coeficiente de difusão (D_{eff}), por exemplo a 100 °C, no Período I, face à amostra controlo, foi 1,11; 16 e 19 %, para o CFA, ES e RH, respetivamente. Entretanto, o uso de GLD diminuiu o D_{eff} em ~ 7%. Também foi possível verificar que os dados experimentais da

secagem podem ser bem descritos pelo modelo baseado na segunda Lei de Fick (Período I) e pelo modelo da fina-camada (Período II).

Relativamente às propriedades dos adjuvantes, a capacidade de neutralização ácida do GLD e da ES assumiu papel importante no aumento do pH do solo de 6,7 para 7,8 e 8,0, respetivamente. O GLD foi o único adjuvante que influenciou na diminuição dos microrganismos patogénicos (86%), embora não tenha melhorado o processo de secagem. Assim, os estudos realizados permitiram identificar três parâmetros decisivos na escolha de um adjuvante para o processo de secagem: diminuição de microrganismos patogénicos, capacidade de neutralização ácida e influência no índice de germinação.

O estudo de germinação com *Lepidium Sativum L.* (agrião de jardim) indicou que a lama misturada com CFA e com ES reduz o seu efeito fitotóxico e a acidez e aumenta o conteúdo de MO no solo. A mistura lama: adjuvante reduziu a concentração que induz 50% de inibição - EC_{50} em 66%, 60% e 80% para CFA, GLD e ES, respetivamente, quando comparado com o efeito da lama sem adição de qualquer adjuvante. Adicionalmente, os testes em vasos com agrião de jardim revelaram que a lama com e sem os diferentes adjuvantes não apresenta efeito deletério para as plantas testadas.

Finalmente, através de uma abordagem multicritério envolvendo aspetos ambientais, técnicos e económicos, foi possível concluir que a secagem de lama utilizando GLD a 130 ℃ é a melhor opção em termos de adjuvante e temperatura. No entanto, ES a 130 ℃ e GLD a 70 ℃ também podem ser opções consideradas. Assim, a incorporação destes resíduos como adjuvantes de secagem de lamas pode trazer ganhos ambientais e sociais e promover a cadeia de valor, que se traduz em novas rotas de gestão de resíduos, fechando o ciclo destes materiais antropogénicos no ambiente.

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ABBREVIATIONS AND ACRONYMS

AD	Anaerobic digestion
ANC	Acid neutralization capacity
AOX	Absorbable organic halogens
APA	Portuguese environmental agency
AP	Alkylphenol
ASR	Agricultural soil receptor
CFA	Coal fly ash
CFC	Colony-forming cells
CONAMA	Conselho nacional do meio ambiente
CRF	Code of federal regulations
CRITIC	Intercriteria correlation method
Db	Dry basis
DEHP	Di(2-ethylhexyl) phthalates
ECC	Commission of the European community
EPA	Environmental protection agency
ES	Eggshell
EU	European Union
EWC	European waste catalogue
FAAS	Flame atomic absorption spectrometry
GLD	Green liquor dregs
HHV	High heating value
ISO	International organization for standardization
IQ	Intelligence quotient
LAS	Linear alkylbenzene sulfonate
LHV	Low heating value
LOI	Loss on ignition
MCDM	Multi-criteria decision making
MOORA	Multi-objective optimization on basis of ratio analysis
OM	Organic matter
p.e	Population equivalent
PAE	Phthalate
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorobiphenyl
PCDD	Polychlorinated dibenzodioxin/furan
PFA	Hormone, perfluorinated acid
PHP	Pollutant including pharmaceutical product
PTM	Potentially toxic metal
PTr	Sludge primary treatment
RH	Rice husk
SMO	Sludge management operator
SS	Sewage sludge
STr	Sludge secondary treatment
TOPSIS	Technique for order preference by similarity to ideal solution
TS	Total solids
TT_r	Sludge tertiary treatment

USEPA	United States environmental protection agency
Wb	Wet base
WWTP	Wastewater treatment plant
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy

NOMENCLATURE

$\bar{L}_b$	Mean root length of the control sample	[cm]
$\bar{N}_b$	Mean number of germinated seeds in the control sample	[-]
D_{eff}	Effective diffusion coefficient	[m^2 min^{-1}]
E_r^i	Potential ecological factor	[-]
$\bar{L}$	Mean length of roots	[cm]
$\bar{N}$	Mean number of germination seeds	[-]
T_r^i	Biological toxicity factor	[-]
B_n	Background concentration of the toxic metal (n) in soil	[mg kg^{-1}]
C_0	Background concentration in the soil	[mg kg^{-1}]
CF	Coarse fraction soil	[mm]
C_i	Concentration of the metal (i)	[mg kg^{-1}]
C_n	Content of a specific metal (n)	[mg kg^{-1}]
D_0	Maximal diffusion coefficient at infinite temperature	[m^2 s^{-1}]
DR	Drying rate	[gH_2O min^{-1} kg^{-1} SS_{wb}]
E_a	Activation energy	[kJ mol^{-1}]
EC	Electrical conductivity	[mS cm^{-1}]
EC_{50}	Concentration that induces 50% of inhibition	[%]
FF	Fine fraction of soil	[mm]
GI	Germination index	[%]
HFF	Humic fraction of soil	[mm]
I_{geo}	Geoaccumulation index	[-]
k	Kinetic constant	[min^{-1}]
LED	Light-emitting diode	[μmol m^{-2} s^{-1}]
$M_{(t)}$	Moisture content at any t time	[gH_2O g^{-1} SS_{db}]
M_0	Initial moisture content	[gH_2O g^{-1} SS_{db}]
M_e	Moisture content at equilibrium	[gH_2O g^{-1} SS_{db}]
mM	Millimolar	[-]
MR	Moisture ratio	[-]
PERI	Potential ecological risk index	[-]
PI	Pollution index	[-]
r	Radius	[m]
R^2	Coefficient of determination	[-]
RMSE	Root mean square error	[%]
RRG	Relative root growth	[%]
RSG	Relative seed germination	[%]
S_i	Legal threshold to apply SS to agricultural soil	[mg kg^{-1}]
SS_CFA	Sewage sludge plus 0.15 g CFA	[g CFA g^{-1} SS_{wb}]
SS_ES	Sewage sludge plus 0.15 g ES	[g ES g^{-1} SS_{wb}]
SS_GLD	Sewage sludge plus 0.15 g GLD	[g GLD g^{-1} SS_{wb}]
SS_RH	Sewage sludge plus 0.15 g RH	[g RH g^{-1} SS_{wb}]
T	Temperature	[ºC]
t	Time	[min]
t_f	Time at the end of period I	[min]
TS	Total solids	[-]
WAC	Water absorption capacity	[g H_2O 100 g db^{-1}]

Wt	Weight	[%]
α_n	Roots of the Bessel function of zero-order	[-]
a	Parameter Thin-layer model	[-]

1. INTRODUCTION

1.1 Scope and motivation

In developed countries, a huge amount of wastewater generated must be depurated before it can be safely released back into the environment. The incorporation of environmental principles into wastewater treatment strategies is associated with efforts to promote water quality using efficient wastewater treatment plants (WWTP). The sewage sludge (SS) produced during this stage, requires separation from the liquid phase and further treatment before use in agriculture, composted, incinerated, or even disposed of in a landfill. In Europe, the production of SS is about 45-90 g dry basis (db) per person day^{-1} (Christodoulou and Stamatelatou, 2016; Mininni et al., 2015). By 2020, SS generated in the European Union (EU) will be about 13 Mt_{db} (Collard et al., 2017; Gomes et al., 2019). Figure 1.1 shows the average SS production (kt_{db} year^{-1}) in some EU countries in the period 2006 - 2015, according to data available from EuroStat (2019).
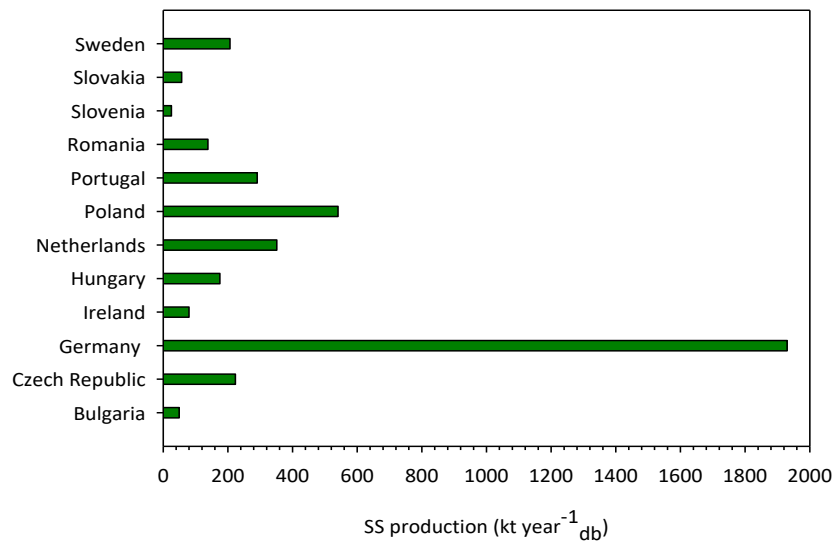
Figure 1.1 - Mean annual production of SS in some European countries (2006-2015).

The main constituents of SS are water (free, interstitial, surface, and bound), biomass (microorganisms including pathogens), inorganic solids, fats, salts, potentially toxic metals (PTM), polycyclic aromatic hydrocarbons (PAH), other organic matter (OM) and nutrients (Healy et al., 2016; Metcalf and Eddy, 2014). Figure 1.2 shows a schematic representation of secondary SS flakes formed in activated sludge systems. Several authors have been focused on determining the SS properties (Slepetiene et al., 2020). SS may be of interest for agriculture application due to the presence of nutrients such as nitrogen (N), phosphorus (P), potassium (K) (Alvarenga et al., 2016, 2015; Cerne et al., 2019; Sharma et al., 2017) and due to the carbon pool (Gomes et al., 2019). However, the main problem for managing SS is the significant amount of water, which is typically around 80 – 98% of the total weight

(Danish et al., 2016; Kacprzak et al., 2017; Zhang et al., 2019b, 2017, 2016). This moisture content increases transport costs and odour generation (Collard et al., 2017; Leila et al., 2017).
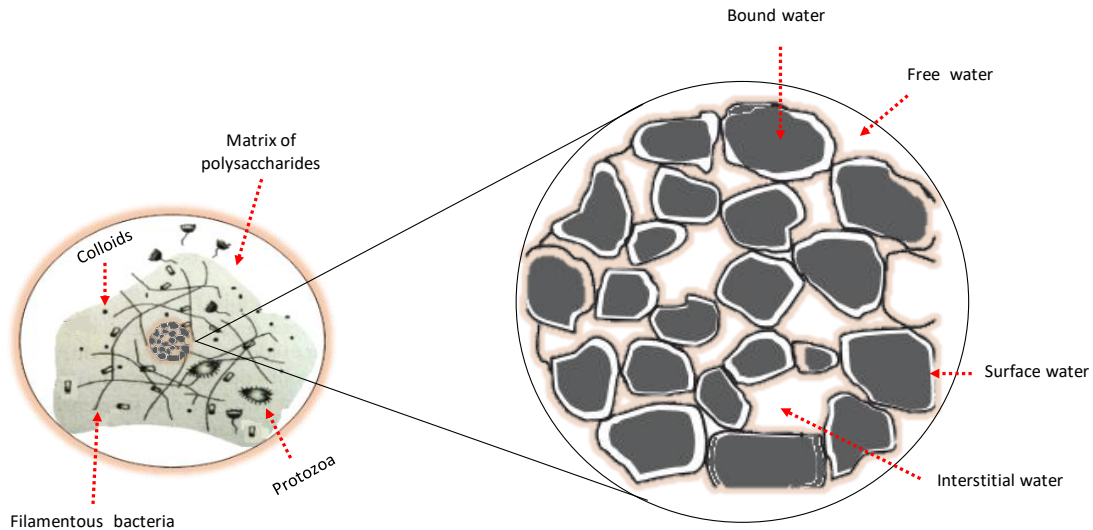
Figure 1.2 - Typical composition of a secondary sludge flake formed in an activated sludge system (Adapted from Syed-Hassan et al., 2017; von Sperling, 2008).

The application of SS to the soil should be controlled to avoid the nutrients excess, and thus to prevent the eutrophication of aquatic bodies (Stürmer et al., 2020). The legal limit for PTM and pathogenic microorganisms for the environment and public health safeguard should also be ensured (Singh et al., 2017). The usage of SS in agriculture is regulated in the EU by Directive 86/278/EEC, and in Portugal by *Decreto Lei Nº.* 276/2009.

The proper management of SS requires constant care throughout the global chain, i.e., from the generation, treatment, and disposal. The EU guidelines encourage the reduction, reuse, and recycling of waste. Thus, from the perspective of the circular economy, compactible residues can be used as *conditioners or adjuvants* for SS management process. These adjuvants may be used for specific purposes, such as to facilitate the migration of SS water throughout the solid phase content to surface during the drying process, which may represent a reduction in time and drying costs (Deng et al., 2017; Zhang et al., 2019a).

Some researchers have studied SS drying using sawdust (Li et al., 2016), hazelnut bark (Pehlivan et al., 2016), rice husk (RH) (Wang et al., 2019), coal fly ash (CFA), lignite, lime mud (Zhang et al., 2017), etc., in accordance with the principles of industrial ecology. In this context, the SS drying process aided with specific adjuvants will be investigated in this thesis.

1.2 Wastewater treatment and formation of sewage sludge

In Portugal, 1003 Mm^3 of treated water was supplied and 627 Mm^3 of wastewater was generated in 2015 (Gomes et al., 2019). About 80% of the Portuguese inhabitants have water supply and wastewater treatment services, and the production of SS is around 300 kt_{db} $year^{-1}$ (LeBlanc et al., 2008; RARSAP, 2016). SS generation is growing in most of the developed countries. Indeed, this is a global

problem that is being faced by EU countries. Legal guidelines must be updated for environmental protection and sustainability indicators must be calculated for monitoring purposes (Praspaliauskas and Pedišius, 2017).

The stages commonly present in WWTP for dealing with SS may include dewatering, thickening, stabilisation of OM (aerobic or anaerobic digestion), sanitation (pathogens inactivation), storage, drying and transport (Syed-Hassan et al., 2017). Figure 1.3 represents a typical layout of a WWTP in terms of primary (PTr), secondary (STr), and tertiary treatment (TTr).
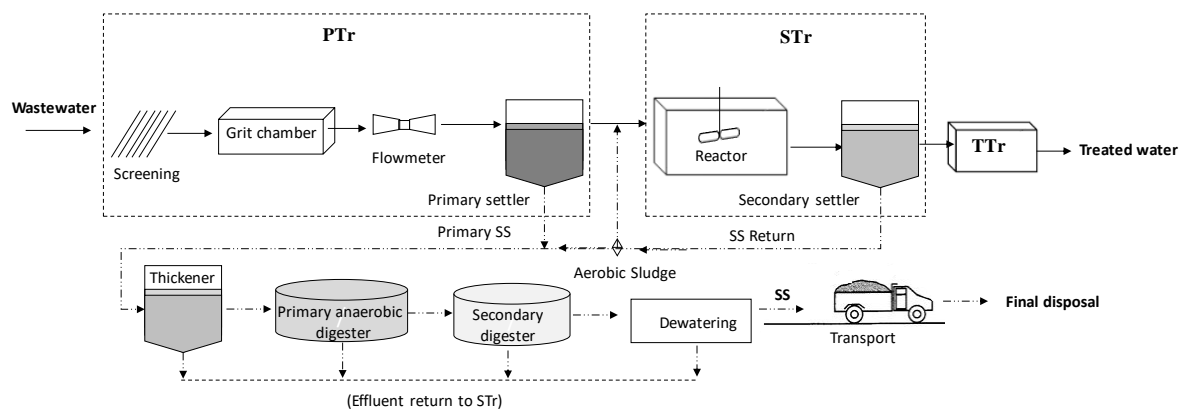
Figure 1.3 - Typical layout of a WWTP consisting of primary (PTr), secondary (STr), and tertiary treatment (TTr) (Adapted from Syed-Hassan et al. 2017; von Sperling, 2008).

In mainland Portugal, WWTP only with PTr represents 30.8% coverage, STr 58.1% and TTr accounts for 8.1% (https://rea.apambiente.pt/). The level of treatment appears to be balanced between aerobic and anaerobic processes, unlike other countries such as Finland, Spain, United Kingdom, Czech Republic, and Slovakia, where anaerobic digestion (AD) is predominant (Kelessidis and Stasinakis, 2012).

PTr may include a step for removal of grits, oil and grease, and a primary settler. Thus, PTr usually removes inorganic solid and particulate OM. These operations aim to reduce not only the organic load but also the energy consumption and hydraulic holding time in the later phase (secondary treatment). In this treatment stage, OM removal occurs mainly by physical mechanisms, where about 50-70% removal of suspended solid may be achieved (Syed-Hassan et al., 2017).

STr is normally based on a consortium of microorganisms that oxidise (aerobic) organic matter (Pathak et al., 2009). Microorganisms under appropriate environmental conditions (e.g., temperature, pH, oxygen, nutrients, and residence time) assimilate the dissolved OM, producing CO_2, H_2O, and additional microorganisms (biological growth). Both anaerobic and aerobic digestion mechanisms allow stabilisation of SS formed in WWTP. STr commonly integrates a secondary settler that promotes the sedimentation of the residual biomass. Part of this biomass can be returned to the aeration tank (activated sludge), and the excess is removed from the system.

Combining primary and secondary SS (named "mixed SS") originates one stream of SS in the WWTP, which facilitates its subsequent treatment. AD removes about 50 to 70% of OM, while in aerobic systems it is possible to reduce about 40-50%. SS production is 20% higher in aerobic than in anaerobic processes. Generally, undigested SS has a lower C/N (carbon/nitrogen) ratio, and nitrogen is in the organic form (Metcalf and Eddy, 2014). AD is considered an ecologically sound technology for SS volume reduction and stabilisation, which is able to produce biogas through the fermentation of OM (Zhang et al., 2019b). However, AD tends to increase ammonia (NH_4^+), and a post-treatment may be required (ammonification) (Metcalf and Eddy, 2014). The sludge dehydration stage is difficult, and to reach a moisture content of about 80%, centrifugation is required (Zhang et al., 2019b). The supernatant of STr can be polished in TTr for nutrient (N and P) and pathogen removal. This stage enables to reach high-quality water, which can be released safely into natural ecosystems.

1.3   Properties of sewage sludge

1.3.1   *Physical and chemical properties*

The composition of the SS may vary with seasonality, the weather conditions, the composition of the effluents and the level of treatment (Seiple et al., 2017). SS generated in WWTP may have high moisture content, namely 99% in unprocessed samples and 80-90% when dehydrated by centrifugation, or even 55% or less when subjected to thermal dehydration (Świerczek et al., 2018). This variability is also dependent on the different microorganism groups (facultative, aerobic, and anaerobic) including pathogens (viruses, protozoa, etc.) (Sharma et al., 2017). Table 1.1 presents some characteristics of the SS formed in primary and secondary treatments (PTr and STr), and involving aerobic or anaerobic metabolisms.

As shown in Table 1.1, the pH of SS may be in the range of 5 to 8. Moisture, OM and nutrients are significantly different for PTr and STr. Factors such as type of treatment, effluent contact time with microorganisms and organic load may determine the final effluent and sludge properties (Houdková et al., 2008; Metcalf and Eddy, 2014). SS contains high levels of nitrogen ($2\text{-}7\%_{db}$) and phosphorus ($1\text{-}5\%_{db}$) which in some cases can reach $15\%_{db}$, making it an excellent fertiliser for plants (Kacprzak et al., 2017; Świerczek et al., 2018). In general, a small amount of lignin or cellulose present in SS facilitates the stabilisation of SS. Moreover, SS from AD may be characterized by an HHV of about 12 MJ kg^{-1}_{db}, while mixed SS reaches up to 23 MJ kg^{-1}_{db}. Thus, the heat value on a dry basis is enough to select incineration as a management route for SS (Díaz et al., 2019). According to Syed-Hassan and co-workers, the use of SS as an energy source (11-22.10 MJ kg^{-1}_{db}) is interesting because it is comparable to lignite (11.80-21.90 MJ kg^{-1}_{db}) and other forms of biomass such as sawdust (11.80-20.40 MJ kg^{-1}_{db}) and bituminous coal (25.40-33.15 MJ kg^{-1}_{db}) (Syed-Hassan et al., 2017).

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Table 1.1 – Physical and chemical properties of primary (PTr) and secondary (STr) SS.

Parameter	[Ref. 1] [1]		[Ref. 2]		[Ref. 3] [2]	[Ref. 4] [3]	[Ref. 5]	
	PTr	STr	PTr	STr	STr	STr	PTr	STr
pH	6	7.1	5-8	6.5-8	7.12	5.5-6.8	6.5-7.5	6.5-8.0
EC (mS cm^{-1})	Ni	ni	Ni	ni	2.70	2.90	ni	ni
TS (%)	3	0.8	3.0-7.0	0.5-2.0	Ni	ni	6.0-12.0	0.83-1.16
OM (%TS)	75	70	60-80	50-60	80.4	72.0	30.0-60.0	59-88
N (%TS)	2.5	3.8	1.5-4	2.4-5	Ni	ni	1.6-6.0	2.4-5.0
P (P$_2$O$_5$ %TS)	1.6	5.5	0.8-2.8	0.5-0.7	6.3	1.36	1.5-4.0	2.8-11
K (K$_2$O %TS)	0.4	0.6	0-1	0.5-0.7	1.8	0.16	0.0-3.0	0.5-0.7
HHV (MJ kg$^{-1}_{db}$)	~25	~20	23-30	18-23	Ni	ni	4-6	8-10
Alkalinity (mg L^{-1} CaCO$_3$)	600	790	500-1,500	580-1,100	Ni	ni	2,500-3,500	580-1,100
Cellulose (%TS)	10	ni	ni	ni	Ni	ni	8.0-15.0	ni
Protein (%TS)	25	36	ni	ni	Ni	ni	15.0-20.0	32.0-41.0

[1] - Typical values of activated SS; [2] - Mixed SS; [3] – Anaerobic digestion; PTr – SS from primary treatment; STr – SS from secondary treatment; ni - not informed. Refs.: [1]- (Metcalf and Eddy, 2014); [2]- (Bennamoun et al., 2013a); [3]- (Alvarenga et al., 2017); [4]- (Alvarenga et al., 2008); [5]- (Fytili and Zabaniotou, 2008); HHV- higher heating value.

The organic elemental analysis of SS in terms of carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S) for several countries is presented in Table 1.2.

Table 1.2 - Comparison of elemental analysis of SS in several countries.

Country	Elemental content (wt%)							References
	C	H	O	N	S	Ash	M (%)	
China	35.5	6.1	19.0	4.6	1.1	33.7	50.0	[1]
Spain [1]	38.2	4.3	20.9	4.5	0.9	31.2	77.0	[2]
Spain [2]	22.7	3.3	15.5	3.1	1.6	53.8	74.0	
France	36.4	5.5	18.8	5.7	1.0	32.6	82.0	[3]
France	56.9	8.2	24.3	8.8	1.8	ni	ni	[4]
Lithuania	46.6	6.5	18.5	5.7	1.9	20.9	88.5	[5]
Singapore	44.0	6.5	30.1	3.9	5.3	10.3	79.0	[6]
Poland	28.5	4.1	18.4	3.6	1.3	44.1	ni	[7]
Turkey	36.4	4.4	17.3	5.3	1.1	35.5	79.7	[8]

Refs.: [1]- (Deng et al., 2017); [2]- (Otero et al., 2008); [3]- (Peregrina et al., 2014); [4]- (Charlou et al., 2015); [5]- (Praspaliauskas and Pedišius, 2017); [6]- (Chan and Wang, 2016); [7]- (Werle and Wilk, 2010); [8]- (Pehlivan et al., 2016); [1] - AD + thermal drying, from a city with low industrialisation; [2] - STr from the very industrialised city, M – moisture content; ni - not informed.

Table 1.2 shows that there is some variability in the carbon and ash content of the SS samples for the different countries. Also, it is possible to infer that the reuse of SS in soil applications may be of interest because of the high carbon content, especially for soils that are poor in bioavailable C and N.

1.3.2   Potentially toxic metals

The presence of PTM in SS formed in urban WWTP may be associated with the disposal of industrial effluents in the sewage domestic system. In the sewage sludge, PTM may appear associated with organic fragments, bacteria, inorganic particles, and colloids. Indeed, PTM may affect human health and the environment through soil and water pollution. The EU legislation (and the Portuguese as well) currently considers restrictions in SS composition for agricultural applications regarding the following PTM: cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn). Approximately 50-80% of the PTM content contained in the wastewater is fixed in the SS

during the wastewater treatment stages (Pathak et al., 2009). In a dry basis, the percentage of PTM in SS is approximately 0.5-2%, reaching values in the order of 6% in some cases. Table 1.3 presents the typical range of values for PTM in SS and the main effects on human health (Afroze and Sen, 2018; Fu and Wang, 2011; Metcalf and Eddy, 2014).

Table 1.3 - Typical PTM range in SS and the effects on human health.

PTM	Range (mg kg$^{-1}_{db}$)	Toxic effect
Arsenic (As) [1]	1.18-49.2	Carcinogenic, producing liver tumours, skin and gastrointestinal symptoms, disturbances of cardiovascular and nervous system functions, bone marrow depression, hemolysis, hepatomegaly, melanosis, polyneuropathy, and encephalopathy.
Cadmium (Cd)	0.21-11.8	Toxic to humans because it inhibits various enzyme systems, carcinogenic, renal disturbances, lung fibrosis, bone lesions, cancer, hypertension, and weight loss.
Chromium (Cr)	6.74-1160	Extremely toxic in its hexavalent form due to its strong oxidation properties. Human exposure to Cr (VI) compounds is suspected to be carcinogenic, mutagenic, teratogenic, epigastric pain nausea, vomiting, severe diarrhoea, producing lung tumours, and allergic dermatitis.
Copper (Cu)	115-2580	Long-term exposure causes fatigue, insomnia, osteoporosis, heart disease, cancer, migraine headaches, and seizures. Mental disorders include depression, anxiety, mood swings, phobias, panic attacks, and attention deficit disorders.
Lead (Pb)	5.81-450	Suspected carcinogen impacts the nervous system. Even low levels of lead can reduce IQ, stunt growth, and cause behaviour problems, damage the kidney, liver and reproductive system, basic cellular processes, and brain functions. The toxic symptoms are anaemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination, and renal damages.
Mercury (Hg)	0.17-8.3	Readily absorbed through the skin or inhalation of dust which contains residues; affects the immune system, alters genetic and enzyme systems, and damages the nervous system, cause impairment of pulmonary and kidney function, chest pain and dyspnoea.
Nickel (Ni)	7.44-526	Chronic bronchitis, reduced lung function, lung cancer, nasal sinus, and skin dermatitis.
Zinc (Zn)	216-8550	Causes short term "metal-fume fever", gastrointestinal distress, nausea, diarrhoea, and skin irritations.

[1] PTM no regulated under *Decreto Lei Nº. 276/2009*.

1.3.3 *Phosphorus content*

Phosphorus may be present in SS in dissolved or undissolved forms, or inside the cells of the microorganisms. The soluble P fraction is presented in the inorganic form (PO_4^{3-}, $H_2PO_4^-$, H_3PO_4, and HPO_4^{2-}) depending on the influence of the pH. In aqueous medium, for example at pH 5.0, the percentage of H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} is 0.1; 98; 2.0; and 7×10^{-8}, respectively. For pH > 7.0, there is a predominance of phosphorus in the form HPO_4^{2-} and PO_4^{3-}. For pH < 7.0, $H_2PO_4^-$ and HPO_4^{2-} are the predominant forms (Chao, 2006).

Figure 1.4 shows the most important flows of P from the mining phase to the dissipation, as well as the possible routes of recovery using SS in soil amendment (Ribarova et al., 2017).
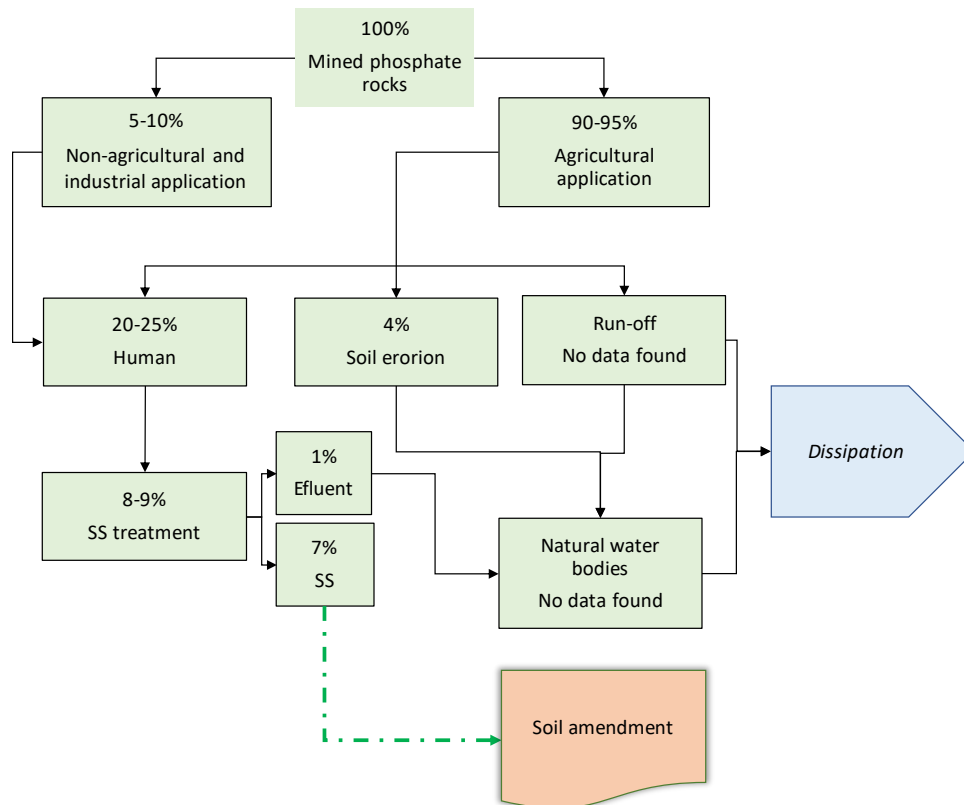
Figure 1.4 - Flows of phosphorus through anthropogenic activities (Adapted from Ribarova et al., 2017).

Agriculture represents about 90-95% of phosphorus consumption, and approximately 25% reaches the human food chain. Thus, it is possible to verify (Figure 1.4) the potential of P recovery, considering that ~ 7% is contained in SS and can be used in agriculture. The removal of phosphorus in the PTr is only about 5-10% of the amount entering WWTP (Smil, 2000). The standard STr with activated SS can remove around 15-40% (Chao, 2006). In general, in WWTP systems, it is only possible to retain the phosphorus in the organic form.

The recovery of phosphorus has gained technical and scientific interest in recent years due to the increasing consumption in fertilisers and the scarcity of phosphate rock. Nowadays, phosphorus is considered a critical raw material in the EU. The excessive discharge through effluents may cause eutrophication of aquatic bodies, thus the recovery of P from liquid or solid phases is of particular interest. Phosphorus can be removed from SS by leaching with mineral acids followed by precipitation as struvite ($MgNH_4PO_4.6H_2O$). Thermochemical processes can also be applied to SS for phosphorus accumulation in ashes and later on further use in the soil (Ribarova et al., 2017).

According to Li and co-workers (Li et al., 2014), the organic phosphorus fraction is transformed into inorganic phosphorus with the temperature increase, enhancing the bioavailability of P. The P in SS can be concentrated as apatite with an increase of temperature. In China, the average content of P in dried SS is 2.2 (wt%) but in some European countries reaches 15 (wt%) (Hoffmann et al., 2010).

1.4   Sewage sludge management

Environmental pressures caused by industrialisation and population growth require that the management of water resources and sludge production become an important topic. European legislation has encouraged safe recycling as a management route, raw material recovery, heat, and energy recovery (Cieślik et al., 2015). As aforementioned, the SS from WWTP generally contains high moisture content (~ 80%), which boosts management problems such as transportation costs, odours emissions, and storage difficulties. Therefore, SS management involves volume reduction and pathogenic microorganisms control. SS management options should consider technical, economic, legislative and environmental aspects (Đurđević et al., 2019). In general, the treatment of SS can cost between 20% and 60% of the total operating cost of a WWTP (Uggetti et al., 2010).

As shown in Figure 1.5, several SS management alternatives are possible, namely land application, thermal processes (e.g., incineration), bioprocessing (e.g., composting, vermicomposting, anaerobic digestion), landfill disposal and other applications. The following sections highlight some details about each of these processes, while more information is provided in Chapter 2.
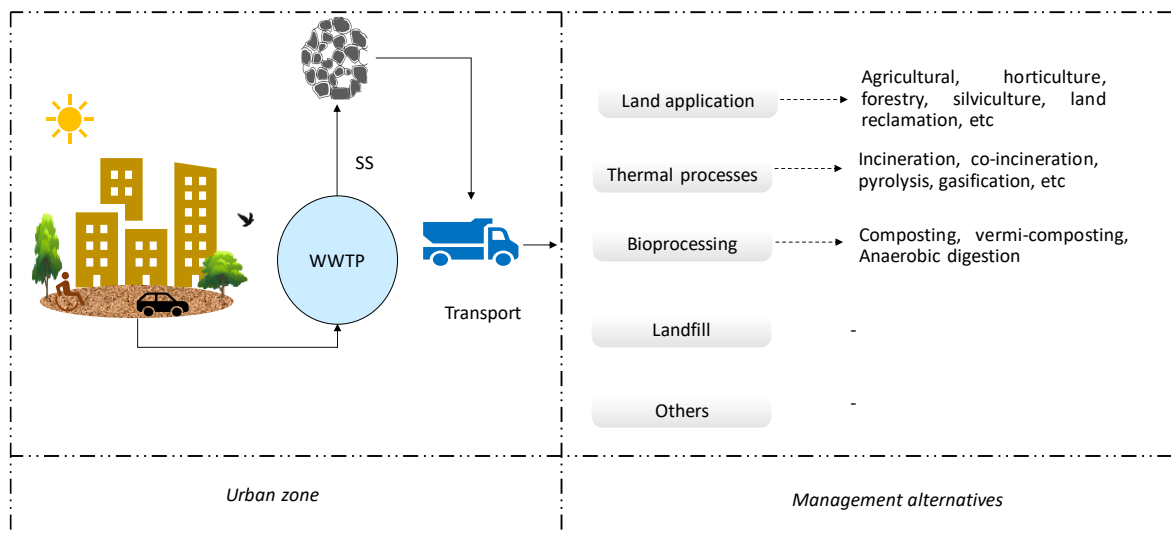
Figure 1.5 - Alternatives for SS management (Adapted from Sharma et al., 2017).

(i)   Agricultural application

The application of SS to soil should be a priority as a way of contributing to the circular economy. For this, SS must comply with the requirements of the European Union (Directive 86/278/EEC) and National legislation (e.g., *Decreto Lei Nº*. 276/2009 in Portugal) in terms of PTM, pathogenic microorganisms (*Escherichia coli* and *Salmonella* spp.) and organic compounds (polychlorinated biphenyl compounds, furans, polycyclic aromatic hydrocarbons, etc.). The soil application could be achieved directly or after stabilisation through composting. The concentrations of PTM in the final

product, are normally within the limits of the legislation (see Section 1.5). Organic content and the nutrients present in SS are particularly relevant to improve soil properties (Hamdi et al., 2019).

(ii) *Composting*

Composting is an economically viable and socially acceptable method for the treatment of SS, which involves the degradation of organic materials through the actions of microorganisms. OM is decomposed under controlled aerobic conditions to produce a stabilised material (i.e., humus). At the beginning C:N ratio must be 25:1 to 35:1. During the process, it is important to control moisture content (higher than 40% but lower than 80%), aeration conditions (oxygen concentration higher than 10%) and temperature. Reaching temperatures around 70 °C for at least 1-2 h is important for inactivation of pathogenic microorganisms (Du et al., 2019; WEF et al., 2010). This process allows the stabilisation of SS, which may be then used in a safer way for agronomic applications.

Mechanical solid-liquid separation devices (e.g., filters or centrifuges) do not guarantee complete dehydration of SS. To achieve a lower moisture level (< 30%), a thermal drying stage is required (Deng and Su, 2014). Thermal drying is considered a relatively simple technological operation which allows SS disinfection, but requires a significant amount of energy. This process can be applied before additional heat treatment: incineration or co-incineration with coal or other fuels, or pyrolysis (Cieślik et al., 2015).

(iii) *Incineration*

Incineration is an oxidation process of SS at high temperature (> 850 ºC) and the main products are flue gases (composed of CO_2 and H_2O), ashes and heat. This technique is attractive for the management of the SS because it reduces 90% of the volume and eliminates pathogenic microorganisms. However, a previous drying step is normally required. Inert material (about 30%$_{wt}$) remains at the end of incineration, which requires further management. Its use as a building material or for phosphorus recovery has been considered (Raheem et al., 2018).

(iv) *Final considerations*

The diversity of SS management options is highly desirable due to the limitations of soil application during rainy seasons (autumn and winter) as well as seasonality in the crops. For example, it is not possible to apply SS after sowing and before harvesting. Therefore, it is important to expand management options and seek new alternatives in SS management such as thermal drying, composting, and/or incineration.

Figure 1.6 shows the average values (kt year^{-1}) of the final SS management methods in some EU countries for the years 2006 to 2015, according to data available on EuroStat (2019). Except in Germany

and the Netherlands, where incineration appears to be the dominant route, agriculture and composting play an important role in other countries (Figure 1.6).
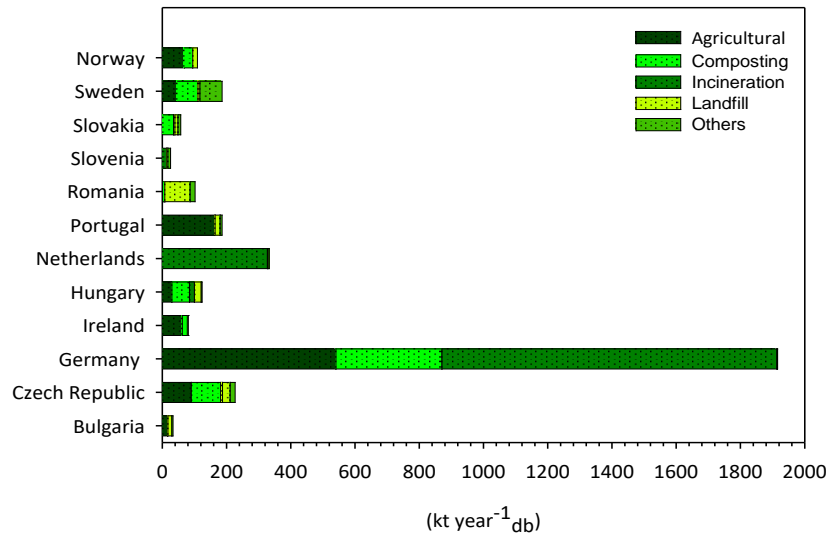
Figure 1.6 - Comparison between SS management methods in different EU countries to 2006-2015.

According to the literature, the final disposal routes for SS produced in the EU includes agricultural use (42.4%), incineration (26.9%), landfill (13.6%) and the rest (17.1%) stored for long periods for subsequent application in areas to be recovered (Đurđević et al., 2019). Among the main reasons to avoid landfill of SS, the following stand out:

(a) recycling of organic content (e.g., in agricultural soil or in degraded areas),

(b) nutrient recovery (P, N, K);

(c) energy production (in mono or co-incineration, pyrolysis or gasification).

The average recycling costs of raw SS in agriculture are estimated between 100 and 200 € t^{-1}_{db}. However, dehydrated and dried SS deposited in landfills, recovery areas, and incineration have a higher cost, between 200 and 400 € t^{-1}_{db} (Đurđević et al., 2019; Wiechmann et al., 2013).

1.5 Environmental legislation constraints

Several laws regulate the application of SS on agricultural soil. For instance, in the EU the relevant document is the Directive 86/278/EEC (EEC, 1986) and in the US is the 40 CFR Part 503 (US EPA, 1993). In general, the legislation recognizes that the SS should be subjected to biological, chemical, and/or heat treatment, stored for a long period of time or by another method to reduce health problems when applied to the soil (*Decreto Lei Nº.* 276/2009).

SS is classified in the European Waste Catalogue (EWC) with code 190805 (sludge from urban wastewater treatment) and 200304 (septic tank sludge), but there are also others with a similar composition (020305, 020403, 020502, 020603, 020705, and 030311).

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Within the regulatory framework for solid waste management/environmental protection, the main legal documents in the EU and Portugal are presented in Table 1.4.

Table 1.4 - Legal documents related to waste management in the EU and in Portugal with a focus on sewage sludge management and soil application.

Document	Objective
Directive 86/278/EEC	Stated, for the first time, the rules on how farmers should use sewage sludge as fertilisers.
Directive 91/271/EEC	Guides the collection, treatment and disposal of urban wastewater, and the treatment and discharge of wastewater from certain industrial sectors.
Directive 1999/31/EC	Provides operational and technical requirements on the waste and landfills, to prevent deleterious effects on the environment, in particular, the pollution of surface water, groundwater, soil, etc.
Decision 2006/799/EC	Establishes the revised ecological criteria and the related assessment and verification requirements for the award of the Community eco-label to soil improvers.
Directive 98/2008/EC	Establishes the measures to protect the environment and human health by preventing or reducing the adverse impacts of waste generation and management, reducing the overall impacts of resource use and improving the efficiency of use.
Decreto Lei Nº. 276/2009	The current instrument for the use of sewage sludge on agricultural land to avoid harmful effects on man, water, soil, vegetation, and animals by promoting their correct use.
Decreto Lei Nº. 103/2015	Establishes the rules governing the placing on the market of fertilising materials.
Commission Decision 2014/955/EC	The last amendment to the EWC, released previously by Commission Decision 2000/532/EC, which provides a wide common terminology for waste classification to ease waste management, including for hazardous waste. The assignment of codes serves in a broad variety of activities, including the transport of waste, installation permits, or as a basis for waste statistics.

Portugal has legislation in force (*Decreto Lei Nº*. 276/209) to regulate the application of SS on the soil whose purpose is to prevent contamination of the environment, human health, fauna, and flora. This legislation sets limits for PTM, organic contaminants and pathogenic microorganisms. Figure 1.7 presents a summary of the conditions for SS application in Portuguese soil, according to the guidelines of *Decreto Lei Nº*. 276/2009.

As illustrated in Figure 1.7, SS with similar composition as defined by the EWC may be managed by the SS operator, which must be registered according to *Decreto Lei Nº*. 178/2006. The SS Operator is responsible for the management and control of the sludge storage and/or treatment facility.
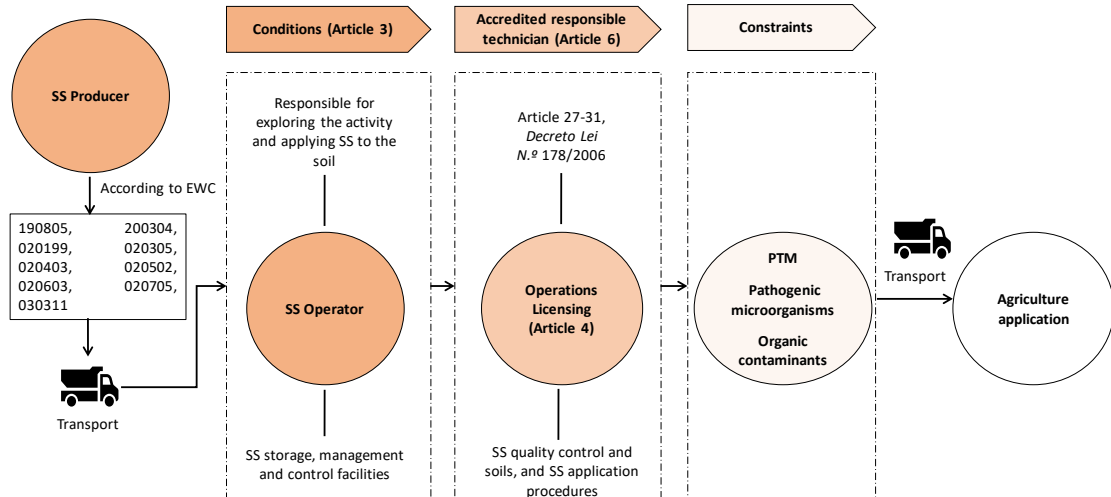
Figure 1.7 - Summary of the conditions for SS application in Portuguese soil.

1.5.1 Legal limits for soil SS application

The limits set by *Decreto Lei Nº*. 276/2009 regarding concentrations of PTM in soils that can receive SS as a function of the pH are shown in Figure 1.8 (a), and the limits in the SS are indicated in Figure 1.8 (b), both in logarithmic scale. PTM concentration set for SS application with pH > 7 can only occur in soils where crops are grown for commercial purposes and intended exclusively for animal consumption.

The control of soil contamination is a responsibility of the SS operator, who must provide the characterisation results whenever requested by the legal authorities. The limit values of the pathogenic microorganisms contained in SS are 1000 cells g^{-1} SS_{wb} for *Escherichia coli* and the absence of *Salmonella* ssp. in 50 g SS_{wb}. Regarding the limits of organic compounds present in SS, Table 1.5 describes the established values.

Nowadays, large quantities of organic chemicals are required to meet the needs of modern society. Consequently, some of these products are discharged to WWTP and, once present in the wastewater, end up concentrated in the SS. Research on organic SS contaminants has been carried out for over 30 years. According to Clarke and Smith (2011), most of the compounds studied do not endanger human health when biosolids are recycled to agricultural soil. A study conducted in Portugal by Alvarenga and co-authors confirmed that the presence of LAS, NPE, PCB, PAH, and PCDD/F displayed residual concentrations, all below the values set by *Decreto Lei Nº*. 276/2009 (Alvarenga et al., 2016). However, control is vital to prevent the accumulation of compounds that may interfere with ecosystems.
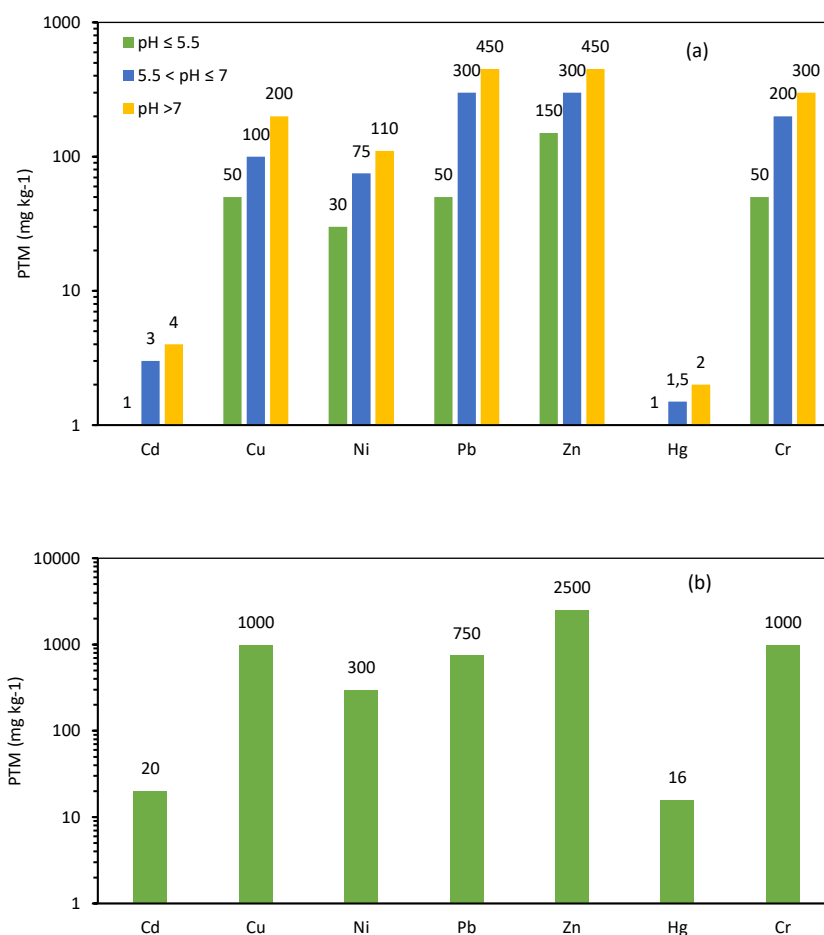
Figure 1.8 - Limits of concentrations of PTM (a) in soils with different pH and (b) in SS intended for application to agricultural soil.

Table 1.5 - Concentration limits of organic compounds in sludge intended for agriculture.

Organic compounds	Limit values (mg kg$^{-1}_{db}$)
LAS (Linear alkyl benzenesulfonates)	5 000
NPE (Ethoxylated nonylphenols and nonylphenols)	450
PAH (Polycyclic aromatic hydrocarbons)	6
PCB (Polychlorinated biphenyl)	0.8
PCDD (Polychlorinated dibenzo-p-dioxin)	100 [1]
PCDF (Polychlorinated dibenzofuran)	

[1] - ng TEQ kg^{-1}

1.6 Objectives of the thesis

In the context of the circular economy and seeking to meet EU targets for sustainability indicators, waste management research needs to be continuously improved. Therefore, incorporating waste into new production arrangements can bring environmental and social gains, and foster the value chain. Regarding this approach, this doctoral thesis aims to study the process of sewage sludge drying with

residues as adjuvants to obtain a product for agronomic applications. Hence, to achieve this main goal, the following specific objectives were considered:

I.   Characterization of SS and adjuvants samples to assess the main properties for agricultural purposes;

II.   Studies on experimental drying at different temperatures to evaluate the effect of sludge/adjuvant mixtures;

III. Selection of the best adjuvants for the drying process considering its performance and the quality of the final material for soil applications;

IV.   Modelling of the drying process to determine the relevant parameters, necessary for example, for the design and optimized operation of the dryer;

V.   Evaluate agronomic parameters at laboratory scale to predict the effect of the materials produced;

VI.   Screening of the performance of drying adjuvants, based on multicriteria (environmental, economic and technical).

1.7   Thesis structure

This thesis is organised into eight chapters.

Chapter 1 presents the scope and motivation of the thesis, including the general concerns about the amount of sewage sludge produced. The management difficulties due to the high moisture content following conventional wastewater treatment processes and sanitation of SS are highlighted. The options of EU and Portuguese legislation governing the disposal of SS in the soil are also summarised. Moreover, the aims and organisation of the work are also described.

Chapter 2 describes the theoretical background of the drying process and the mathematical models that describe moisture profiles during the drying phases. Two models are presented (Fick's law and Thin layer). Subsequently, an overview of the possible wastes/materials (adjuvants) that may improve the drying process is shown. Furthermore, a review focusing on the application of sewage sludge to the soil is also presented.

Chapter 3 presents an analysis of compliance with restrictions relative to PTM (e.g., Cd, Cr, Cu, Ni, Pb, and Zn) present in SS for application to Portuguese agricultural soil. The characterisation of SS samples, and the ecological risk assessment based on the geoaccumulation index (I_{geo}), pollution index (PI) and potential ecological risk index (PERI) for the referred PTM are also assessed.

Chapter 4 shows the results of drying small SS cylinders without and with 0.15 g adjuvant g^{-1} SS_{wb} using weathered coal fly ash (CFA) and dried at different temperatures (70, 85, 100, 115 and 130 °C). Both Fick's Second Law and the thin-layer models adequately described the moisture decay, and it was possible to identify the drying phases (rising-rate period, period I, and period II). Also, it is showed that the addition of CFA to SS facilitates the drying process and the final product can be potentially used

in agricultural soils. Germination tests with *Lepidium sativum L.* revealed a 66% improvement in EC_{50} for dry SS with CFA as well as improved shoot length.

Chapter 5 reveals that although the incorporation of green liquor dregs (GLD) at 0.15 g GLD g^{-1} SS_{wb} does not allow to improve SS drying performance at 70, 100 and 130 ºC, the disposal of both residues into the soil can be a good management strategy. GLD has a high acid neutralisation capacity and can be used as a liming agent to increase soil pH. The concentration of PTM in both wastes (SS and GLD) is not a problem for soil pellet applications. Isothermal kinetic data are modelled based on Fick's Second Law and the thin-layer model.

Chapter 6 presents the results of using eggshell (ES) as an adjuvant in the drying process. The results show that ES increased the drying rate compared to the control sample. An improvement for the drying rate from 9.0 and 16.3% to 70 and 100 ºC, respectively was observed. The final product (SS with 0.15 g ES g^{-1} SS_{wb}) is suitable for agricultural applications due to acid neutralisation capability. Furthermore, it is shown that the phytotoxicity of SS tested can be reduced by the addition of a small amount of ES (e.g., ~ 13% w/w). Finally, the models based on Fick's Second Law and thin-layer model adequately described moisture decay.

Chapter 7 provides a screening methodology based on environmental, technical, and economic criteria to select the best adjuvant (CFA, GLD, ES, and RH). Two multi-criteria decision making (MCDM) methods (MOORA and TOPSIS) are tested at two temperatures (70 and 130 ºC). According to the results obtained, the drying process at 130 ºC with GLD seems to be the best alternative. However, ES at 130 °C and GLD at 70 °C can also be considered. The worst options were CFA_70 and RH_70 in both methods applied. The most important criteria for decision making were the removal efficiency of pathogenic microorganisms, acid neutralisation capacity (ANC) and germination index (GI).

Finally, Chapter 8 presents the most relevant conclusions of the thesis and some suggestions for future research.

All scientific contributions of this thesis have been published in the following scientific publications (peer-reviewed international papers and papers at international conferences):

I. Gomes, L. A., Gabriel, N., Gando-Ferreira, L. M., Góis, J. C., Quina, M. J. 2019. Analysis of potentially toxic metal constraints to apply sewage sludge in Portuguese agricultural soils. *Environmental Science and Pollution Research*, 26(25), 26000–26014. doi:10.1007/s11356-019-05796-6

II. Gomes, L. A. Santos, A. F., Góis, J. C., Quina, M. J. 2020. Isothermal drying of sewage sludge with eggshell for soil applications, Wastes: Solutions, Treatments and Opportunities, vol III, CRC Press – Taylor & Francis Group, pg. 75-80, London, ISBN 978-0-367-25777-4.

III. Gomes, L. A. Santos, A. F., Góis, J. C., Quina, M. J. 2020. Impact of sewage sludge with eggshell on *Lepidium sativum L.* growth, Wastes: Solutions, Treatments and Opportunities, vol III, CRC Press – Taylor & Francis Group, pg. 119-124, London, ISBN 978-0-367-25777-4.

IV. Gomes, L. A., Santos, A. F., Lopes, R. J. A., Góis, J. C., Quina, M. J. 2019. Isothermal drying

kinetics of sewage sludge using weathered coal fly ash as an adjuvant for agronomic application. *Environmental Technology,* (in press). doi:<u>10.1080/09593330.2019.1700311</u>

V.   Gomes, L.A., Santos, A. F., Góis, J.C., Quina, M.J. 2020. Thermal dehydration of urban biosolids with green liquor dregs from pulp and paper mill. *Journal Environmental Management*. 261, 109944. doi:<u>10.1016/j.jenvman.2019.109944</u>

VI.   Gomes, L.A., Santos, A.F., Pinheiro C.T., Góis, J.C., Quina, M.J. 2020. Screening of waste materials as adjuvants for drying sewage sludge based on environmental, technical and economic criteria. *Journal of Cleaner Production*, 259, 120927. <u>doi: 10.1016/j.jclepro.2020.120927</u>

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2.   FUNDAMENTALS AND LITERATURE REVIEW

This chapter presents the fundamentals and the literature review regarding the drying process by the convective mechanism applied to the SS drying study. Moreover, some mathematical models are presented to describe the drying process. The most recent studies using adjuvants to improve the drying process are also summarized. The industrial technologies used for drying and the application of sewage sludge in soils as valorisation routes are also highlighted. The role of additives (adjuvants) in drying is emphasized, as well as the application of the final product to the soil, favouring circular economy from an industrial ecological perspective.

2.1   Drying process

Drying is a unit operation associated with the removal of liquid by evaporation from raw or processed materials (Domínguez, 2011). It is a complex operation involving mass and heat transfer under the influence of various factors such as physical (e.g., shrinkage) and chemical (odour, colour) transformations, that can promote changes in the material quality (Figure 2.1). This complexity creates difficulties in mathematical modelling to describe all the phenomena involved with the heat and mass transfer.
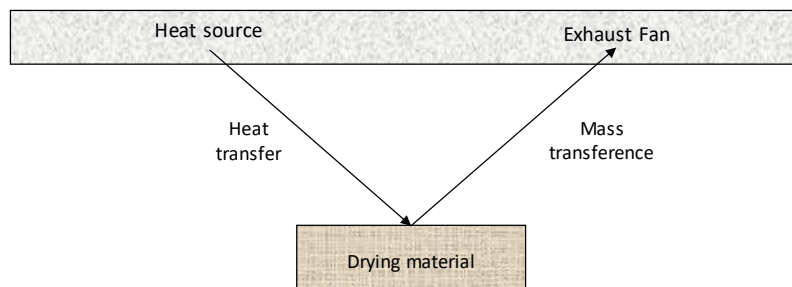
Figure 2.1 - Representative diagram of the drying process.

As shown in Figure 2.1, the vaporisation of the liquid contained in the material requires a heat supply for the drying process to take place. Then, the water is removed through mass transfer mechanisms to the exhaust system. Thus, drying can be considered a thermal separation process. However, drying can also be achieved by lyophilisation (or freeze-drying), wherein water removal occurs by sublimation of the frozen water (ice). In this process, the material is frozen and then exposed to a high vacuum, whereby the water sublimate (i.e., evaporates directly without melting) (Berk, 2013a). In contrast, the removal of liquids from solids without the application of heat, such as performed by centrifugation, is not seen as a strict drying (Mujumdar, 2014; Tsotsas et al., 2000).

The drying processes can be classified as natural or artificial. The heat from the sun or the wind represents the natural drying mechanism, while the others represent artificial drying. Air, inert gas or superheated steam are the main gases used to carry to promote drying of the material. This heat can be

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supplied by convection, conduction or radiation (e.g., microwave). Traditionally, most industrial dryers are convective, using hot air or direct combustion gases (Ivanov et al., 1972). However, sustainable development seeks to reduce energy use, avoid fossil fuel resources to reduce the carbon footprint and prevent climate change. Thus, any improvement in the drying process is welcome.

The moisture content of the material (M) can be expressed in g H_2O kg^{-1}_{wb} material. The mass flow of steam leaving the surface of the solid per unit of time is represented by the drying rate, |DR| (g H_2O m^{-2} min^{-1}). This parameter is usually obtained by measuring the change in moisture content over time, as shown by Eq.(2.1) (Tsotsas et al., 2000),

$$|DR| = \frac{M_{wb}}{A}\frac{\partial M}{\partial t} \qquad (2.1)$$

where M_{wb} is the mass wet of material (kg); *A* represents the surface area of the material, and *t* is time in min.

The DR is strongly dependent on the drying conditions (pressure, temperature, and moisture), material structure, and contact surface area. The study involving the drying process focuses on the flux of moisture content from the interior to the surface of the material. Some authors describe the flow of water inside the material as a combination of movements involving liquid and steam diffusion processes (Ivanov et al., 1972). Thus, the drying rate is an important parameter because it determines not only the costs but also the production capacity of a dryer (Berk, 2013b).

During the drying process, various mechanisms can favour the migration of moisture content. Due to the various types of water-binding contained in the material and due to the complexity of various phenomena, as illustrated in Figure 2.2, it is difficult to predict the beginning and the end of each drying phase (Ivanov et al., 1972).
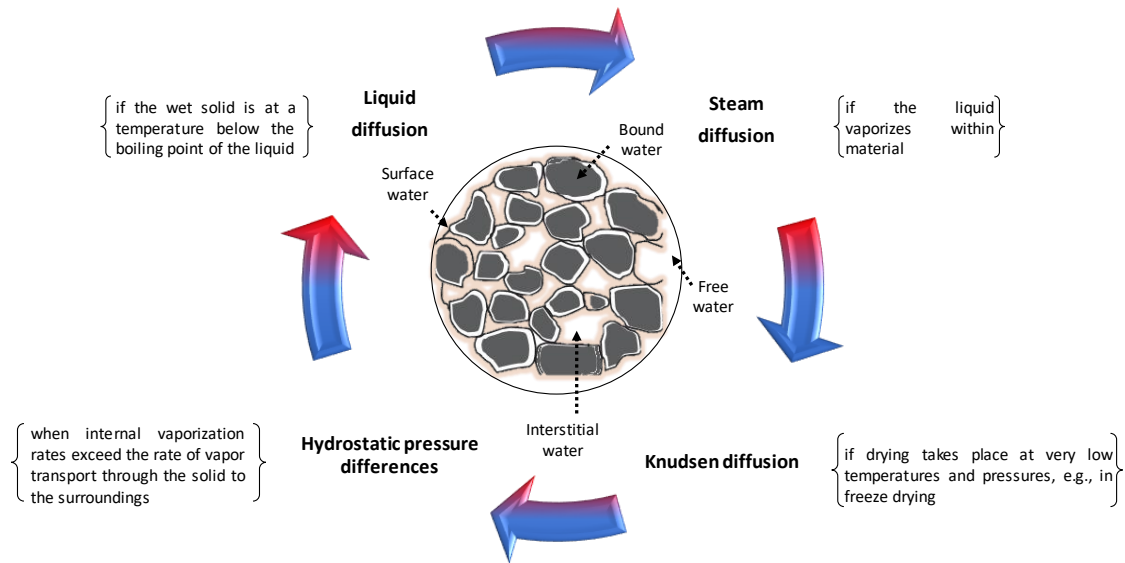
Figure 2.2 - Drying vaporization mechanisms (Adapted from Ivanov et al., 1972).

As a result of the complexity involved in the drying process, the predominant mechanisms of moisture transfer can change with the elapsed drying time due to the modification of the physical structure of the drying solid.

2.2   Main theories for the drying process in porous materials

Figure 2.3 summarizes the main theories about mass and heat transfer during the drying process (Pires, 2013; Srikiatden and Roberts, 2007). Dashed boxes represent the methodological approach used in this work.
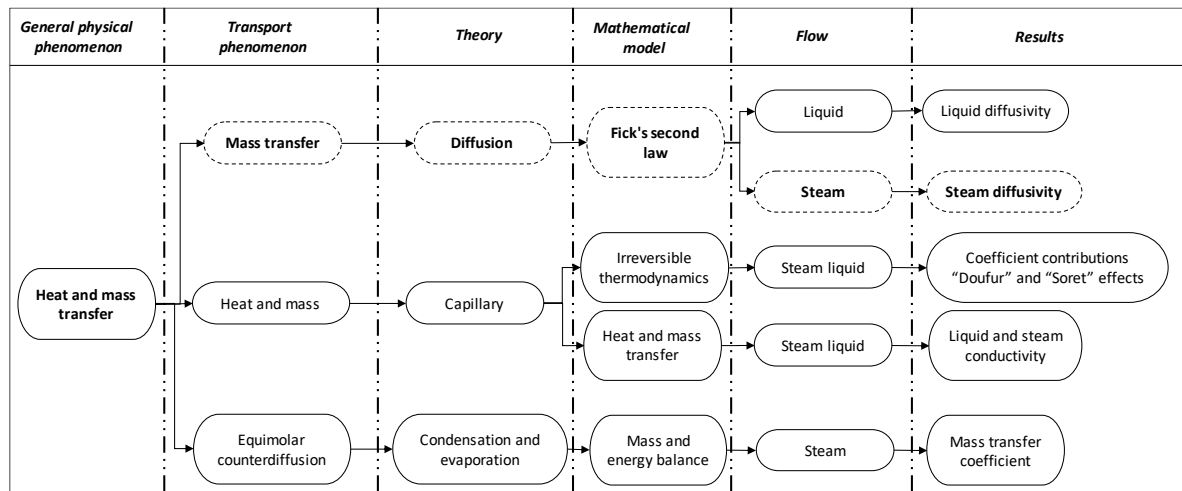
Figure 2.3 - Main theories to describe the drying process.

The phenomenon of heat and mass transfer can be supported by diffusion, capillarity and condensation, and evaporation theories. Different mathematical approaches (e.g., Fick's second law, mass and energy balance, etc.) can be applied to describe the drying phenomenon and to determine the diffusion coefficient (or diffusivity). This parameter is indicative of the diffusion mobility (of steam in the air).

Tripathy and Kumar (2009) and Barat and Grau (2016) described the flow of water within the material as a combination of movements involving liquid and steam diffusion processes that alternate throughout the drying stages. The diffusion, capillarity and evaporation-condensation theories that explain the mechanism of moisture transfer can be detailed as follows (Srikiatden and Roberts, 2007):

(i)   Diffusion

Diffusion is the process by which mass (e.g., moisture) is transported from one part of the system to another as a result of a concentration gradient (i.e., from high to a low concentration).

Fick recognized the similarity between heat and mass transfer. Thus, the diffusional flow, J_m, can be expressed by Fick's first law, Eq.(2.2),

$$J_m = -D\frac{\partial C}{\partial x} \tag{2.2}$$

where D is the diffusion coefficient or diffusivity (m² min⁻¹), C is the concentration of material (kg m⁻³), and x is the length (m). Thus, the flow of a solute through a plane will be proportional to the cross-sectional area (m²) and the concentration gradient, $-\partial C/\partial x$.

For a drying process, Eq.(2.2) can be rewritten as:

$$J_m = -D_{eff}\frac{\partial M}{\partial x} \tag{2.3}$$

where M is the moisture content (g H_2O kg⁻¹$_{wb}$ of material), and D_{eff} represents the effective diffusivity coefficient (m² min⁻¹).

The Fick's second law can be derived from the first law, Eq.(2.3), for predicting changes with respect to time over one dimension:

$$\frac{\partial M}{\partial t} = -D_{eff}\frac{\partial^2 M}{\partial x^2} \tag{2.4}$$

Further details will be described in Section 2.5.

(ii)   Capillarity

The capillarity theory describes the movement of liquid through the interconnecting capillary pores present in a solid. The bonding between the materials occurs by adhesion forces, which cause some liquids like water to migrate from the high to low concentration region. This theory suggests that capillary flow is responsible for water transport during the drying process of porous solid materials. Srikiatden and Roberts (2007) indicated the capillarity as the moisture rate-limiting mechanism at the beginning of drying and afterwards, steam diffusion is responsible for the last stages of drying.

The variation of moisture over time due to capillarity effects can be predicted according to Eq.(2.5), Srikiatden and Roberts (2007):

$$ln\left(\frac{M_t - M_e}{M_0 - M_e}\right) = \frac{h_s(T - T_s)}{\rho_s L \lambda (M_0 - M_e)}t \tag{2.5}$$

where M_t, M_e, and M_0, represent the moisture any time t (min), equilibrium moisture content and the initial moisture content, in g H_2O g⁻¹$_{db}$ of material, respectively (Danish et al., 2016); h_s is the surface heat transfer coefficient (W m⁻² K⁻¹), T and T_s is the initial and the saturation temperatures (K); t is the time (min), ρ_s is the mass concentration of solids (kg m⁻³), L is the characteristic dimension along the flow path (m), and λ is the latent heat (kJ kg⁻¹).

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(iii)   Evaporation-condensation

The evaporation-condensation theory was proposed by Henry in 1948 and considers the mass and heat transfer in an integrated manner. During the drying process, the weight loss is due to the mass transfer through the steam state, while heat gain occurs by condensation and subsequently is lost by evaporation. In porous systems, heat and mass transfer through evaporation-condensation is the dominant mechanism during the drop rate period (Srikiatden and Roberts, 2007).

The mechanisms of heat and mass transfer are responsible for the movement of water from the interior of the material to the surface (surrounding environment). The water transport within the material for a cylindrical shape is illustrated in Figure 2.4.

As shown in Figure 2.4, heat and mass transfer occur simultaneously during the drying process. Heat transfer promotes the removal of water from the solid. On the surface of the solid, heat is transferred by convection and radiation mechanisms, which promotes the evaporation of water. The direct contact of the internal part of the material with the drying environment promotes conductive heat transfer, which aids the formation of water steam gradients responsible for water diffusivity and capillary migration (Park, 1987, 2008).
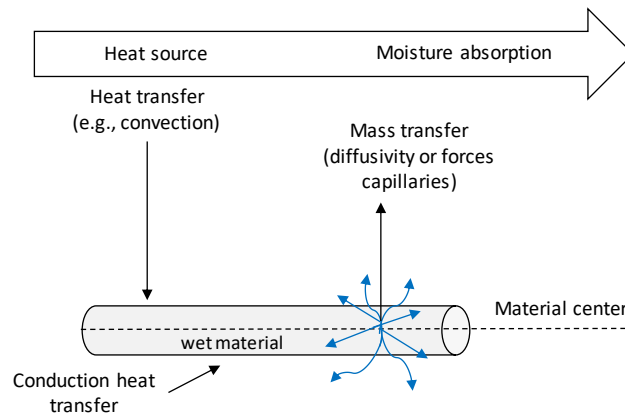
Figure 2.4 - Diagram of the moisture migration with emphasis on the intervening aspects of the drying process.

2.3   Thermal drying methods

Studies in the field of drying have evolved in recent years, which has diversified the methods of drying. Each technology can be based on one or more heat transfer mechanisms: convection, conduction, and radiation (e.g., solar drying). In convective drying, a hot and dry gas (usually air) provides the heat required for evaporation and for the removal of steam from the material surface. The convection mechanism can be classified as natural and forced. Natural convection corresponds to the movement of the fluid due to the floating forces within it, where the driving force is gravity. Forced convection is the flow of a fluid due to external forces imposed by fans, suction devices, etc.

In convective drying, both heat and mass exchanges between the gas and the particles are essentially convective transfer, although conduction and radiation may also be involved to some extent (Berk, 2013b). This widespread mode of drying is also known as air drying.

Conduction drying, also known as contact drying or conductive drying, is a process whereby heat is transferred to wet material from a heated surface in contact with it. For large capacities, convection dryers are often chosen. Convection dryers have much larger heat and mass coefficients due to higher transfer areas than conduction dryers. The construction of convection dryers is generally simpler than conduction dryers. Therefore, convection dryers are usually cheaper (van't Land, 2011). Solar drying is based on heat transfer by radiation, which is a limited alternative to conventional drying due to some specific limitations such as low efficiency, long residence time, and dependence on weather conditions (Tsotsas and Mujumdar, 2014). Figure 2.5 represents the different types of heat transfer during the drying process.
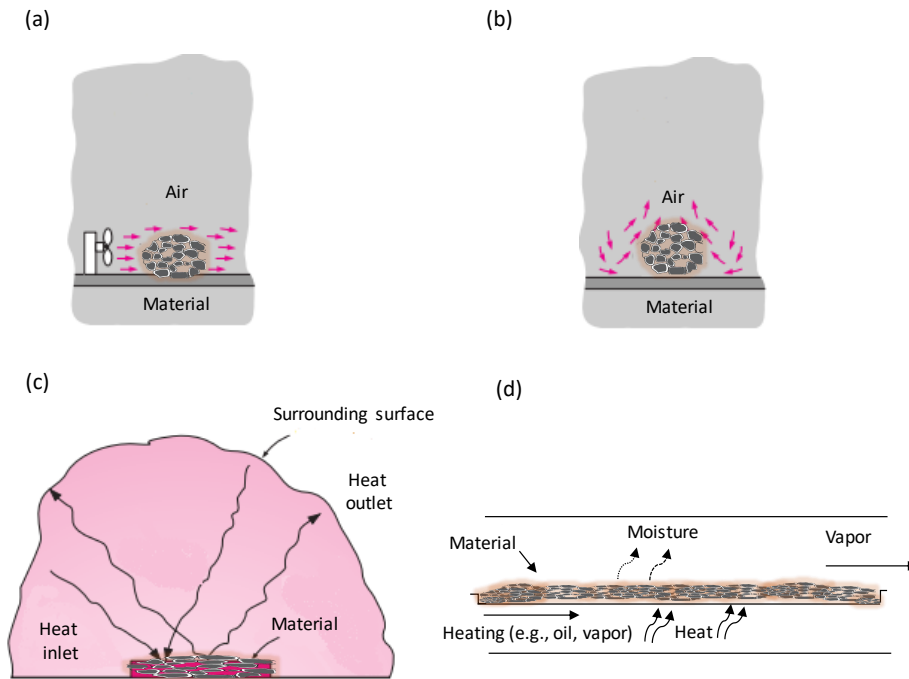
Figure 2.5 - Different mechanisms of heat transmission during the drying process (a) forced convection; (b) natural convection, (c) radiation, and (d) conduction (Adapted from Cengel, 2003).

Figure 2.6 shows an overview of the main drying methods, with emphasis on the thermal methods (Domínguez, 2011; Pires, 2013). Table 2.1 summarizes the different heat transfer mechanisms, describing the advantages and disadvantages of the drying process (Bennamoun et al., 2013a; Collard et al., 2017; Metcalf and Eddy, 2014; Tuncal and Uslu, 2014).
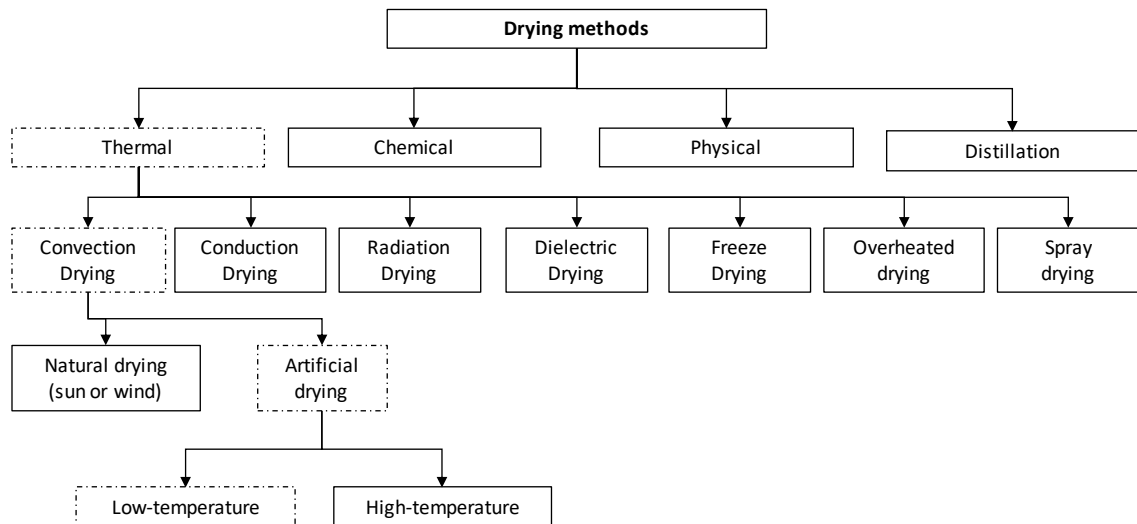
Figure 2.6 - Different methods for drying (Adapted from Bennamoun at al. 2013, and Collard et al., 2016). Dashed boxes represent the methodological approach used in this work.

The convective drying process normally uses dry air for water removal from the solid material. The drying rate depends mainly on two variables (Mujumdar, 2014; Vaxelaire and Cézac, 2004): air conditions (temperature, relative moisture, flow speed) and size and texture of the material. In the study of Bennamoun and co-workers, involving solar drying, the authors mention difficulties due to unstable operating conditions. Indeed, the drying rate increases during high radiation periods and decreases when conditions are unfavourable (Bennamoun et al., 2013a). Finally, it is important to note that drying can be performed in an integrated manner by combining different methods (e.g., hybrid dryers or combined dryers) (Bennamoun et al., 2013a).

Table 2.1 - Drying mechanisms and main characteristics involved (Adapted from Bennamoun et al., 2013a).

Mechanism of heat transfer	Advantages	Disadvantages	Characteristics	Specific energy consumption (kW h^{-1} t^{-1})	Specific drying rate (kg m^{-2} h^{-1})
Convection	- Easy operation	- Relatively long drying time - Bad odours - Gaseous emissions	Convective heat transfer occurs by direct contact of the air with the material	700-1400	0.2-30
Conduction	- No pollution of the heat carrying medium - Steam and odour confinement - Low concentration of VOC [1] - Reduced fire and explosion risks	- Relatively long drying time - Sticky phase hampers dryer performances	Heat transfer by conduction occurs through a wall separating the material from the heat transfer medium, usually thermal oil or steam	800-950	7.35

Table 2.1 (cont.) - Drying mechanisms and main characteristics involved (Adapted from Bennamoun et al., 2013a).

Mechanism of heat transfer	- Advantages	- Disadvantages	- Characteristics	Specific energy consumption (kW h^{-1} t^{-1})	Specific drying rate (kg m^{-2} h^{-1})
Radiation	- Use of free solar energy - Dried product at low cost for use in agriculture	- Depends on climatic conditions - Relatively long drying time (2 – 4 weeks) - High areas are needed	- Depends on climatic conditions (solar radiation, temperature, and velocity of the air) - Variable drying kinetics, even using open or closed tunnel greenhouses - Ventilation or wind is used to renew the air inside the house and the evacuation of the humidified air	30-200	-

[1] VOC - Volatile organic compounds

In each process, the drying rate can be influenced by several factors, namely (Bennamoun et al., 2013a; Deng and Su, 2014; Jamaleddine and Ray, 2010; Léonard et al., 2004; Vaxelaire and Cézac, 2004):

- mechanism of heat transfer;

- temperature;

- relative moisture;

- water content;

- rheological properties;

- crust formation;

- air flow;

- presence of chemical dehydration agents.

In terms of water removal from WWTP sludge, the residual moisture after conventional dewatering systems is higher or equal to 80% water. Therefore, to facilitate the management of SS, including soil application, reach a higher dryness degree may be important.

2.4   General characteristics of drying

2.4.1   Classification of materials

The materials with moisture content can be classified as (Strumillo and Tadeusz, 1986):

- *Colloidal:* tend to change size while preserving their elastic properties during drying (e.g., elastic gels);

- *Capillary-porous:* materials that can become brittle and shrink slightly during the drying process (e.g., sand, charcoal);

- *Colloidal-capillary-porous:* materials changed during the drying process, and the capillary walls are elastic and swell during water absorption (e.g., wood, leather).

Colloidal material having a very fine particle size (100 µm) can be considered a porous capillary material. Materials whose pore radius is less than 10^{-7} m are considered porous capillary with specific pore diameter distributions. In porous with a radius larger than 10^{-3} m, besides the capillary forces, gravitational forces must also be considered. In general, the analysis of the radius dimension is important to understand the absorption capacity of liquids due to steam in the pore walls.

2.4.2   *Moisture contained in solids*

As aforementioned, the drying process is considered a unitary operation that allows the modification of a material from liquid, semi-solid or solid-state into a solid product with low moisture content (Barat and Grau, 2016; Mujumdar, 2014). Table 2.2 presents the rheological classification of WWTP SS according to the total solid content (Tsotsas and Mujumdar, 2014).

Table 2.2 - Classification of rheological state with dryness.

	Total solids content (%)				
	< 10	10 - 40	40 – 60	60 - 90	> 90
State	Liquid	Viscous liquid, pasty	Glue phase	Granular solid	Dry solid

Most kinds of sludge have a pasty consistency and high-water content. Thus, the thermal drying process is usually an expensive process. During the drying process, mechanical-structural properties play an important role in the effectiveness of water removal. Thus, moisture can be present in the solid material in miscellaneous conditions, namely (Strumillo and Tadeusz, 1986):

- *Surface water:* located on the external film of the material due to surface tension effects.

- *Unbound, free or capillary (interstitial) water*: the moisture can be present in two forms: in the funicular state, where continuous fluid exists within the porous body; and in the pendular state, where the liquid is around and between the discrete particles, or in a discontinuous condition, or if the liquid water is interspersed by air bubbles.

- *Bound, hygroscopic or dissolved water*: represents the liquid that exerts steam pressure lower than pure liquid at the specified temperature (bounded in small pores, in solution, on the cell wall, or bounded by chemical and/or physical adsorption).

Figure 2.7 represents a flake of the material studied in this work (SS from WWTP), where the different conditions of water in the material are identified.

Accordingly, four types of water can be considered, namely free water between flakes, interstitial water, surface and bound (intracellular) water (Chen et al., 2002; Vaxelaire and Cézac, 2004). Therefore, the drying kinetics reveals different rates depending on the type of water that is being removed. Free water is easily removed by mechanical dehydration, but the others (interstitial, surface and intracellular) may be very difficult due to the strong bonds involved (Metcalf and Eddy, 2014; Deng and Su, 2014; Bennamoun et al., 2013).
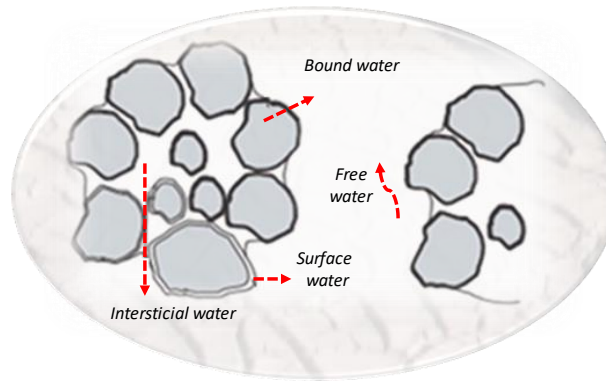
Figure 2.7 - Water distribution in SS flake (Adapted from Chen et al., 2002).

During the thermal drying process of SS, free water is also easily removed. Then, the migration of the interstitial and surface water occurs and finally, the bound water (intracellular) is removed. This process may be aided by increasing the porosity of the sludge with the addition of porous material or even dried sludge. The removal of water from SS is one of the most important processes that is promoted during primary and secondary treatment. This step aims to reduce the volume of sludge, which represents a cost savings (e.g., transport and final disposal). The SS collected in the primary and secondary settlers typically has moisture values around 98% (Evans, 2016; Tuncal and Uslu, 2014).

2.4.3   Theoretical aspects of drying kinetics

Typical kinetic curves of the drying process exhibit distinct regions, as depicted in Figure 2.8 (a-d) (Mujumdar, 2014). These regions may be termed as periods 0, I, II and III.

The region AB represents the heating phase (Period 0) where a fraction of the free water is removed. The drying rate increases, Figure 2.8 (b), as the temperature rises inside the solid material, Figure 2.8 (d). This phase is fast, and it may be possible to observe steam release from the material.

The next period I (BC region) is responsible for removing the free water (Lowe, 1995). At this stage, the drying rate remains almost constant, Figure 2.8 (b) as a consequence of the constant temperature inside the material (wet-bulb temperature), Figure 2.8 (d). The water steam released is conveyed from the moisture-saturated surface to the surrounding air.
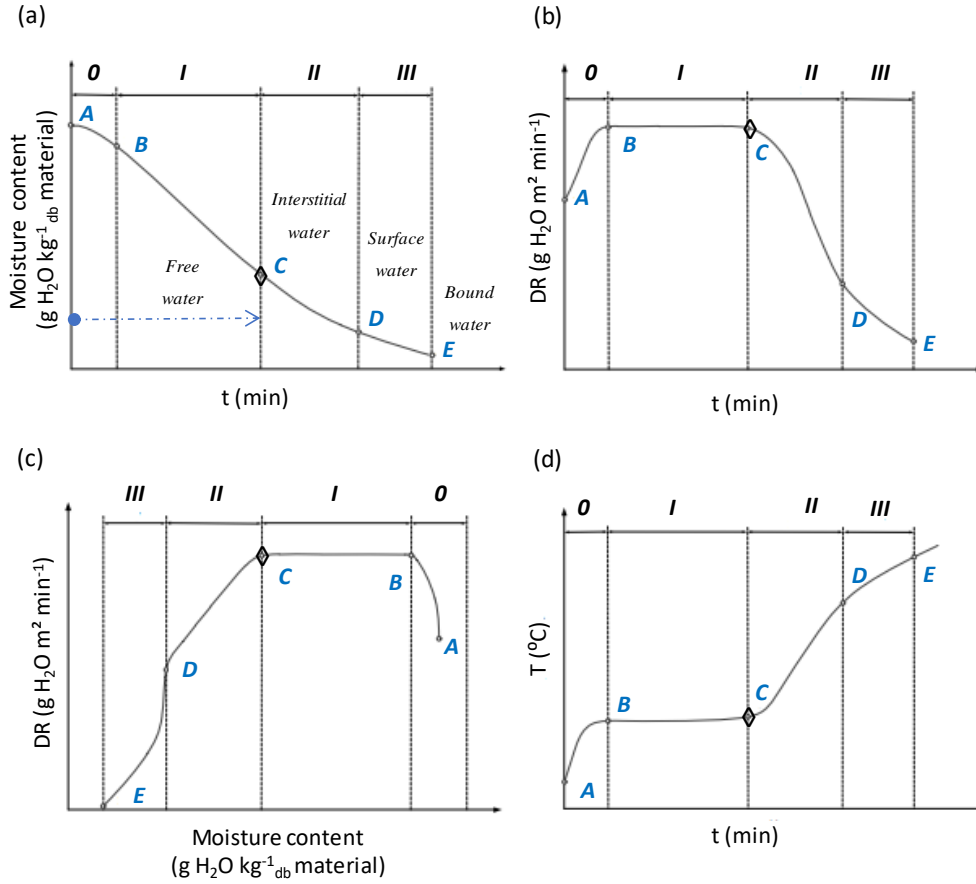
Figure 2.8 - Typical drying process curves: (a) moisture content over time; (b) drying rate as a function of time; (c) drying rate versus moisture content and (d) temperature inside the material as a function of time. The symbol ◊ represents the critical moisture of the process.

The water loss during Period I can be determined using Eq.(2.7) (Figueiredo et al., 2015):

$$\dot{m}_A = h_{m_A} A (C_{A_S} - C_{A\infty}) \tag{2.7}$$

where $\dot{m}_A$ is the mass flow of water (kg min^{-1}); h_{m_A} is the convection mass transfer coefficient (m min^{-1}); A is the area of mass transfer (m²); C_{A_S} and $C_{A\infty}$ represent the saturated and infinite steam concentration (kg m^{-3}), respectively.

The steam concentration at the surface corresponds to the value of the saturated steam concentration for the wet-bulb temperature. The difference between this value and the steam concentration in the air corresponds to the mass transfer driving force.

The stage CD (Period II) starts when it is reached certain moisture called "critical moisture content", M_c, (transition or inflexion point). The drying rate drops sharply as the interstitial water is removed (first falling rate period). At this drying stage, heat exchange is no longer compensated by evaporation of the water content. As a result, the temperature of the material increases and tends asymptotically to the air temperature.

Finally, the stage DE or Period III (second falling rate period) is observed when the material is dehydrated and reaches equilibrium temperature. At this time, the water still present in the SS is chemically bound to the material and difficult to remove. In the end, the partial steam pressure on the surface equals the steam pressure of the surrounding environment. Generally, this step is not considered in the calculation of the drying process since the flow is very low ($M = M_e$).

Similar drying phases were identified by Zhang et al., (2016), that tested the effect of lignite additives as drying adjuvant, in the temperature range of 60 - 80 °C. According to the authors, it was observed that the mixture of SS and lignite promoted a shorter warm-up period, followed by a constant rate and two distinct fall periods. The drying curve may vary depending on the type of sludge and the treatment levels adopted in the WWTP (Bennamoun et al., 2013a).

Therefore, in the constant rate step, the evaporation rate of surface water is equal to the diffusion rate of internal moisture. In the first period, the water flows through capillarity and molecular diffusion through the pores. In the second drop rate, the drying rates decrease slightly (Zhang et al., 2016). Moreover, Bennamoun et al., (2013a) identified three distinct drying phases: adaptation phase (Period 0), constant drying (Period I), and drying falling rate (Period II). Vaxelaire et al., (2000) mentioned that depending on the temperature and material properties, more than one falling period can be observed.

2.5   Modelling of drying process

The mathematical modelling of the drying kinetics is essential for the design of the drying equipment and optimization of the operating conditions. Regarding the drying of a wet solid under isothermal conditions, after an initial thermal adjustment period, the moisture content (M), decreases with time (t), Figure 2.8 (a). This period is followed by a nonlinear decrease (in g H_2O g^{-1}_{db} of material) in moisture over time, until the solid reaches the equilibrium moisture (M_e). The free moisture content (M_{free}) can be calculated by Eq.(2.8) (Pires, 2013):

$$M_{free} = (M_0 - M_e) \tag{2.8}$$

where M_0 and M_e represent the initial and equilibrium moisture content in g H_2O g^{-1}_{db} of material. The initial moisture content (M_0), the moisture content at any time (M_t), and the equilibrium moisture content (M_e) are defined by Eq.(2.9), (2.10), and (2.11), respectively. The moisture ratio (MR) is defined as indicated in Eq.(2.12) (Ameri et al., 2020; Danish et al., 2016):

$$M_0 = \frac{initial\ wt. - dried\ wt.}{dried\ wt} \tag{2.9}$$

$$M_t = \frac{wt.at\ anytime\ t - dried\ wt.}{dried\ wt} \tag{2.10}$$

$$M_e = \frac{wt.at\ equil. - dried\ wt.}{dried\ wt} \tag{2.11}$$

$$MR = \frac{M_t - M_e}{M_0 - M_e}$$

(2.12)

The drying rate (DR) can be expressed in gH_2O min^{-1} kg^{-1}_{wb} of the material and can be determined by Eq.(2.1), which results in Eq.(2.13).

$$DR = \frac{M_{wb}}{A} \frac{M_{t+\Delta t} - M_t}{\Delta t}$$

(2.13)

where $M_{t+\Delta t}$ and M_t represent the moisture content at $t+\Delta t$, and t is the time. For surrounding hot and dry air, the M_e can be considered negligible (Danish et al., 2016).

The mathematical modelling to describe the drying kinetics has been extensively studied by several researchers (Bennamoun et al., 2014; Cai et al., 2015; Danish et al., 2016). In this work, the approach used for modelling the drying kinetics is based on the considerations summarized in Figure 2.9, which shows the typical moisture decay profile for SS. The profile is divided into Period 0, I and II. Period 0 was neglected, Period I will be modelled by Fick's second law model and Period II by thin-layer drying model (Angelopoulos et al., 2016).
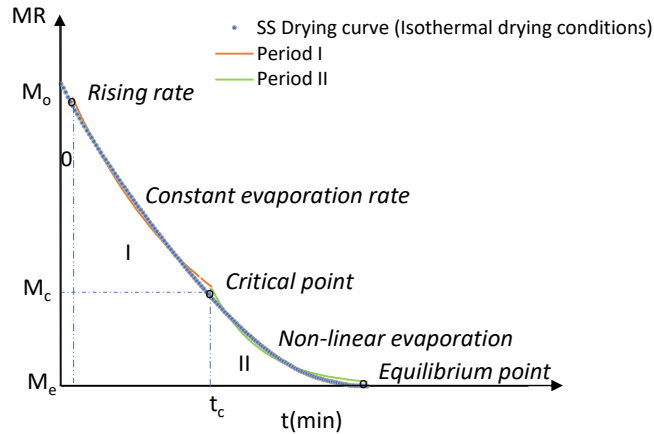
Figure 2.9 - Typical MR drying curve highlighting the application of Fick's second Law for Period I, and Thin-layer model for period II (Adapted from Lowe, 1995).

According to Figure 2.9, the period I is completed when the MR of the material reaches the critical value.

2.5.1 *Fick's law diffusion model*

As aforementioned, Fick's Law can be used to estimate diffusive flows in liquids and solids. The diffusional flow of a fluid contained in a material can be modelled as indicated in Eq. (2.14) (Srikiatden and Roberts, 2007),

$$\frac{\partial MR}{\partial t} = D_{eff}\left(\frac{\partial^2 MR}{\partial r^2} + \frac{n}{r}\frac{\partial MR}{\partial r}\right) \tag{2.14}$$

where t is the time (min), D_{eff} is the effective diffusivity coefficient (m² min⁻¹), r is the radius or semi-thickness of the studied geometry (m), n represents a constant equal to 0 for planar, 1 for cylindrical and 2 for spherical geometries. The initial and boundary conditions are:

$$t = 0 \quad MR\,(r, 0) = MR_i \tag{2.15}$$

$$r = 0 \quad \frac{\partial MR\,(0,t)}{\partial r} = 0 \tag{2.16}$$

$$r = R \quad MR\,(R, t) = MR_\infty \tag{2.17}$$

where R (m) represents radius at the surface.

In the literature, there are analytical solutions for different geometries (e.g., slab, cylinder and sphere) with different boundary conditions and with constant or variable diffusion coefficients (Figueiredo et al., 2015).

To solve Eq.(2.14) it can be assumed that (Ertekin and Firat, 2017; Srikiatden and Roberts, 2007):

   (a) The diffusion coefficient is independent of the moisture content for a given temperature;

   (b) The material is isothermal during drying;

   (c) The initial moisture is uniformly distributed throughout the material;

   (d) The surface moisture reaches equilibrium instantaneously with the surrounding air conditions;

   (e) The material size and geometry remain constant during drying;

   (f) There is no mass generation or depletion inside the material.

In the scope of this work, the geometry considered will be the infinite cylindrical shape. In the infinite cylinder, the lateral area is considered much larger than the radius (r) due to the longer length (L) of the cylinder. Thus, if $r \ll L$, the evaporation occurs predominantly through the lateral surface.

Figure 2.10 (a-b) illustrates an infinite cylinder and the following assumptions adopted:

   (a) diffusional flow occurs from the centre outwards unidirectionally;

   (b) diffusive flux inside the cylinder is equal to the convective flow on the surface;

   (c) there is radial symmetry;

   (d) heat and mass distribution is uniform within the cylinder.
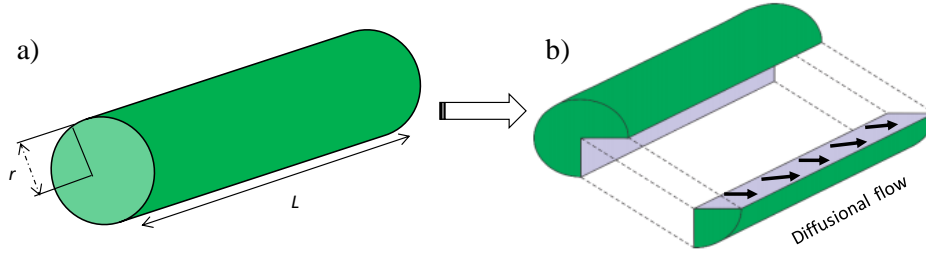
Figure 2.10 - (a) Illustration of an infinite cylinder (r << L), (b) radial symmetry with one-dimensional representation for the diffusional flow.

Thus, the solution of Fick's second law, (Eq.2.14), for the drying period I is indicated by Eq.(2.18) (Figueiredo et al., 2015; Srikiatden and Roberts, 2007).

$$MR = \frac{M(t)-M_e}{M_0-M_e} = \sum_{n=1}^{\infty} \frac{4}{r^2 \alpha_n^2} \ exp(-D_{eff} \ \alpha_n^2 t) \tag{2.18}$$

where the α_n parameter is the root of the Bessel function of zero-order, which can be determined by solving $J_o(r\alpha_n) = 0$.

The D_{eff} can be obtained by adjusting the mathematical model solution to the experimental values. Table 2.3 shows some D_{eff} values found in the literature for SS samples.

Table 2.3 - Effective diffusivity, D_{eff} , for SS with different adjuvants determined at varied drying temperatures.

Samples	Moisture (%)	T (ºC)	D_{eff} (m² min⁻¹)	Ref.
SS	75	122	1.95×10^{-6}	[1]
	75	160	2.71×10^{-6}	
SS:Slag [(1)]	72	120	1.71×10^{-6}	
	72	140	2.00×10^{-6}	
SS:Sawdust	85	80	4.66×10^{-6}	[2]
			4.21×10^{-7} [(2)]	
SS	86-88	70	6.30×10^{-6}	[3]
		80	1.05×10^{-5}	
		90	1.47×10^{-5}	
SS:NaClO [(3)]		70	8.40×10^{-6}	
		80	1.05×10^{-5}	
		90	1.26×10^{-5}	
SS:CaO [(4)]		70	1.68×10^{-5}	
		80	1.89×10^{-5}	
		90	1.89×10^{-5}	
SS	83	60	8.22×10^{-8}	[4]
		100	2.50×10^{-7}	
		140	4.95×10^{-7}	
SS:Lignite [(5)]		60	7.68×10^{-8}	
		100	2.11×10^{-7}	
		140	5.20×10^{-7}	

Refs.: [1]- (Bennamoun et al., 2013b); [2]- (Li et al., 2014); [3]- (Danish et al., 2016), [4]- (Zhang et al., 2016). [(1)] Ratio was not reported; [(2)] Ratio 4:6; [(3)] 30 ± 3 g SS with 0.10 mL NaClO g⁻¹ SS for 7 days; [(4)] 0.1g CaO to 30 ± 3 g SS for 7 days; [(5)] ratio of 10%.

Reyes et al., (2004) and Li et al., (2014) mentioned that the D_{eff} is not only influenced by the temperature but also by other factors, namely the thickness of the sludge layer, chemical composition, and heating method. According to these authors, for a layer thickness of 1 mm, the D_{eff} was 3.42×10^{-6} m^2 min^{-1}, while for 0.5 mm the coefficient was 2.28×10^{-6} m^2 min^{-1} for sludge from PTr.

Danish and co-works studied the drying process of SS and SS plus adjuvants (NaClO and CaO) at 70, 80, and 90 °C and found that D_{eff} was improved compared to untreated SS (Table 2.3). Moreover, an increase in DR was also observed, from 2.3 to 3.4 and 4.5 g H$_2$O min^{-1} kg^{-1} SS$_{wb}$ at 70 °C for SS, SS:NaClO and CaO, respectively. The authors also point out that three periods were observed during drying. According to the researchers, the first two periods were responsible for removing about 80-88% of the sample moisture (Danish et al., 2016).

2.5.2   *Thin-layer drying model*

The thin-layer drying model represents the moisture exchange between drying material (considered a thin-layer) and the surrounding air. The sensible heat from the air can be transferred by convection to wet material. In this case, the heated air contacts with the wet material, dragging out the evaporated water steam. Due to this thin structure, temperature distribution can be assumed as uniform (Ertekin and Firat, 2017; Kucuk et al., 2014). The drying period II mentioned above can be modelled by the thin-layer model (Figueiredo et al., 2015). This model is usually represented by a simple equation based on some drying parameters. These parameters account for the effects of various transport phenomena in the drying process, which can be determined by fitting to the experimental data (Tripathy and Kumar, 2009). The Lewis model (1921) is a common thin-layer model for predicting the MR represented by Eq.(2.19):

$$\frac{dM}{dt} = - k \ (M - M_e) \tag{2.19}$$

where k is the drying constant (min^{-1}). This is one of the simplest models, involving only one parameter for describing the drying process. By integration from *0* to *t* and assuming *k* as constant, and the initial condition as $M = M_0$ at *t = 0*, the solution of the equation is the Eq.(2.20), which is an exponential model (Ertekin and Firat, 2017):

$$MR = \frac{M(t) - M_e}{M_0 - M_e} = ae^{-kt} \tag{2.20}$$

where *a* is a parameter of the thin-layer model.

2.5.3   Relationship between D_{eff} and temperature

During the drying process, the diffusion of moisture content is strongly dependent on temperature and the total amount of water present in the material (Mujumdar, 2014). Factors such as porosity and tortuosity determine the diffusional processes. The dependence relationship between moisture diffusivity and temperature can be calculated by an Arrhenius-type equation (Angelopoulos et al., 2016),

$$ln(D_{eff}) = \ ln(D_0) - \frac{E_a}{RT} \tag{2.21}$$

where D_0 ($m^2 s^{-1}$) is the Arrhenius factor, E_a (kJ kmol^{-1}) is the activation energy for diffusion, R (kJ kmol^{-1} K^{-1}) the ideal gas constant, and T (K) is the temperature. The activation energy for diffusion can be determined from the slope of the linearized Arrhenius by plotting ln (D_{eff}) versus T^{-1}. The higher the activation energy, the greater the drying resistance of the material. Table 2.4 summarizes E_a values reported in the literature.

Table 2.4 – Activation energy (*E_a*), in SS samples.

Samples	E_a (kJ mol^{-1})	Ref.
SS (Control)	26.4	[1]
SS:Coal fly ash [1]	19.3	
SS:Lignite[1]	21.7	
SS:Potassium permanganate [1]	20.1	
SS:NaHCO$_3$ [1]	26.7	[2]
SS:CaO [2]	19.38	[3]
SS:NaClO [2]	36.7	

Refs.: [1]- (Zhang et al., 2017); [2]- (Zhou et al., 2017); [3]- (Danish et al., 2016). [1] 10% (w w^{-1}); [2] 30 ± 3 g SS with 0.10 L NaClO per g of SS; and 0.1g CaO to 30 ± 3 g SS for 7 days.

2.6   Industrial drying technologies

2.6.1   Types of dryers

To classify the dryers in groups, different approaches can be used, such as dryer feed process, heat transmission form, matter movement within the dryer, or energy source. Apart from this, the most common form to distinguished can be in terms of size, operating and initial costs. Figure 2.11 shows a classification of the dryers according to the operation methods, heat transfer processes and movement of materials inside the dryer, and Figure 2.12 according to the scale of production (Jamaleddine and Ray, 2010; Lee et al., 2012; Nonhebel et al., 1971; Tsotsas and Mujumdar, 2014).

Conductive drying using steam-heated rotary dryers began in 1830. Convection drying technology started only in 1890, when inexpensive electromotors to drive air blowers became commercially available. Spray drying started in the 20s of the last century. Freeze drying dates back to 1935 and microwave drying began in 1955 (van't Land, 2011).
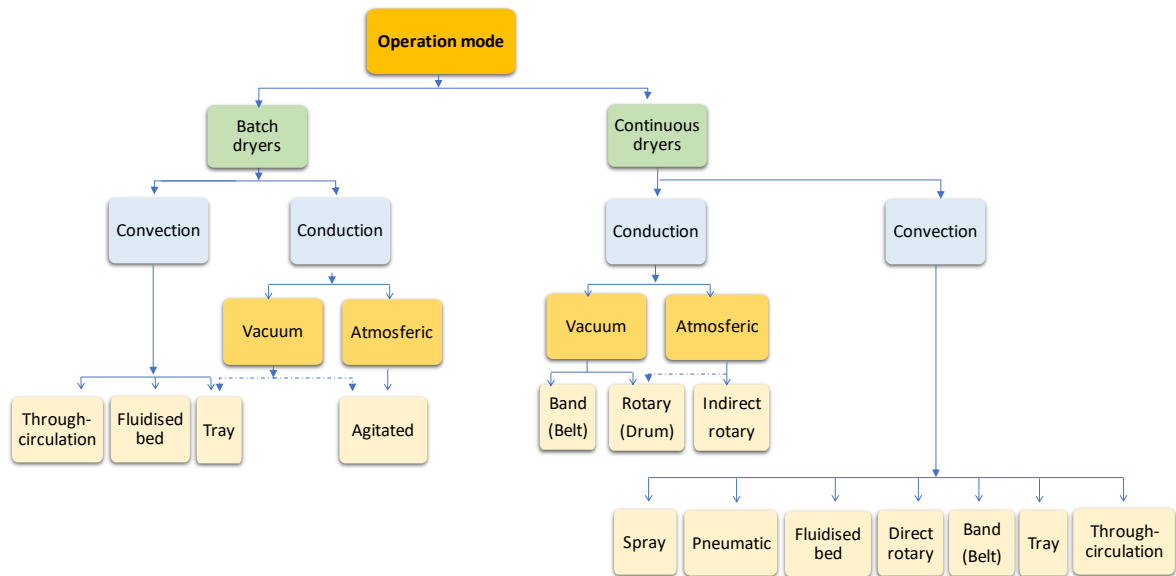
Figure 2.11 - Classification of dryers according to operation methods (Adapted from Nonhebel et al., 1971). Dotted arrows represent operational versatility.

The most used industrial convective dryers for SS are belt dryers, flash dryers, fluidized bed dryers and rotary dryers (Bennamoun et al., 2013a; Lowe, 1995). The working principle of convective dryers occurs by heating the air or gas stream over the SS.

Indirect dryers allow the recovery of energy in the form of heat, which makes it an interesting option when selecting the drying mechanism. Direct dryers have been very effective in drying SS cake containing 25%$_{db}$ up to 85-95%$_{db}$ (Lowe, 1995).
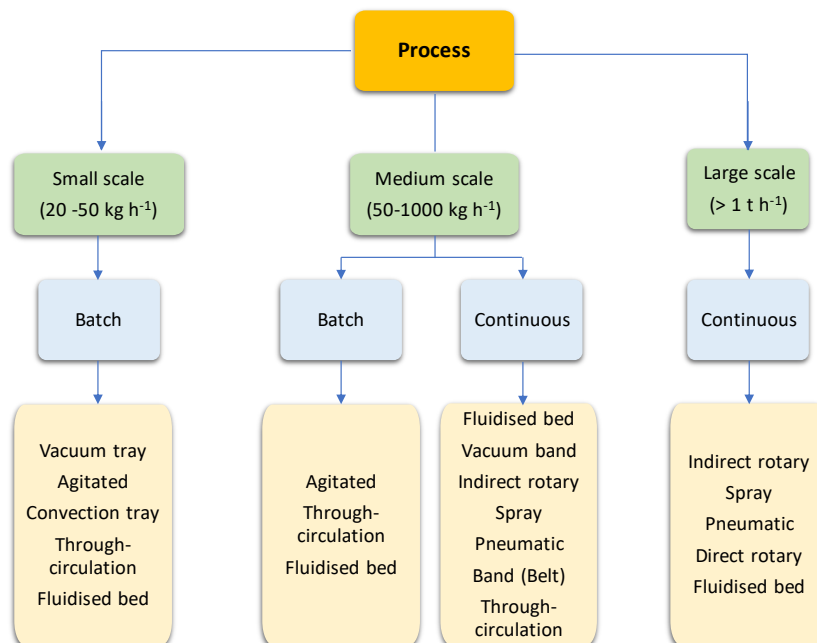
Figure 2.12 - Classification of dryers by scale of production (Nonhebel et al., 1971).

Mujumdar (2014) highlights three important factors that may support the classification of dryers: (i) the way that heat is supplied to the material, (ii) temperature (low, medium or high) and pressure (atmospheric or vacuum) for operation and (iii) the way as the material is handled inside the dryer.

In Europe, the countries that most use thermal drying for SS are Germany (~ 50%), followed by Italy, the United Kingdom and France, each with approximately 10% of the total. Among the commonly used drying systems is the rotary drum dryer, followed by bed dryers and belt dryers (Kelessidis and Stasinakis, 2012). Drum dryers generally operate with inlet temperatures above 400 °C and are more economic when designed with direct heat (Tuncal and Uslu, 2014).

Table 2.5 describes the relevant criteria frequently used for the selection of a dryer (Mujumdar, 2001).

Table 2.5 - Relevant factors to select a dryer.

Criterion	Alternatives
Operation mode	Batch
	Continuous [1]
Heat input-type	Convection [1], conduction, radiation, electromagnetic fields, combination of heat transfer modes
	Intermittent or continuous [1]
	Adiabatic or non- adiabatic
State of material in the dryer	Stationary
	Moving, agitated dispersed
Operating pressure	Vacuum [1]
	Atmospheric
Drying medium (convection)	Air [1]
	Superheated steam
	Flue gases
Drying temperature	Below boiling temperature [1]
	Above boiling temperature
	Below freezing point
Relative motion between drying medium and drying solids	Co-current
	Counter-current
	Mixed flow
Number of stages	Single [1]
	Multi-stage
Residence time	Short (< 1 min)
	Medium (1-60 min)
	Long (> 60 min)

[1] *Commonly used*.

Table 2.6 presents the relevant criteria that may assist in the selection of a convective or conductive dryer for large-scale production (Domínguez, 2011; Mujumdar, 2014)

Regarding Table 2.6, almost all types of dryers are applied to samples from centrifugal systems, filtration, and those in granular or high fibre form. Generally, these samples present about 75% moisture, which allows for greater versatility in the dryer type.

Table 2.6 - Classification of dryers according to feedstock type.

Feeding System Dryers	Liquids			Cakes		Free-flowing solids					Formed solids
	Solution	Slurry	Pastes	Centrifuge	Filter	Powder	Granule	Crystal	Pellet	Fibre	
Convection											
Belt conveyor							×	×	×	×	×
Flash				×	×	×	×			×	
Fluid bed	×	×		×	×	×	×			×	
Rotary				×	×	×	×		×	×	
Spray	×	×	×								
Tray (batch)				×	×	×	×	×	×	×	×
Tray (continuous)				×	×	×	×	×	×	×	
Conduction											
Drum	×	×	×								
Steam jacket rotary				×	×	×	×		×	×	
Steam tube rotary				×	×	×	×		×	×	
Tray (batch)				×	×	×	×	×	×	×	×
Tray (continuous)				×	×	×	×	×	×	×	

2.6.2   Convective dryers

As mentioned in previous sections, convective dryers are very efficient for sludge containing 25% to 85-95%$_{db}$ moisture content. Notable systems include (i) flash dryer, (ii) rotary drum dryer, (iii) belt dryer, and (iv) fluidized bed dryers (Lowe, 1995; Tsotsas and Mujumdar, 2014; WEF et al., 2010).

- **Flash dryers**

Also known as pneumatic dryers or convection dryers, this type of dryer acts more efficiently to remove free surface moisture (Figure 2.13).
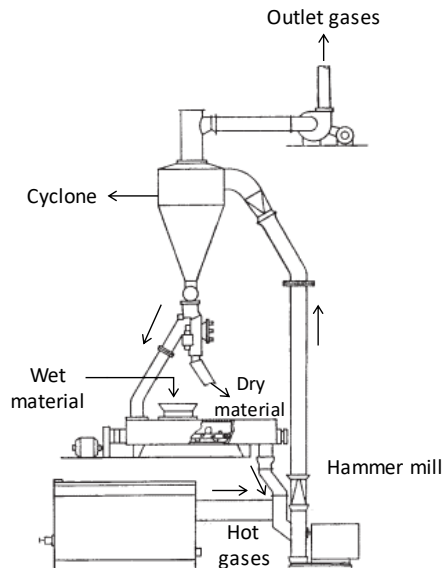
Figure 2.13 - Flash dryer illustration for sludge drying (Adapted from James et al., 2010).

Flash dryers work with temperatures between 100 and 600 ℃ and the drying process takes place in a matter of seconds (0.5-10 s). The wet material is dispersed in a stream of heated gas (usually air),

which moves it upwards through a drying duct. Frequently, a venturi section is used to finely pulverised the solid. The gases and water are then expelled into the atmosphere through a scrubber or an outlet bed. Another water-laden air can be recycled to recover some of the waste heat and maintain a low oxygen atmosphere throughout the system.

This allows preventing dust explosions due to fine particles and high gas flow temperature. Among the main disadvantages of direct dryers are the inconvenience of dust and volatile gas compounds produced during drying and the need for recirculation of dry sludge to mix with influent sludge of varying moisture content. However, many of the largest dryers in the world are flash type dryers.

- **Rotary or drum dryers**

This type of dryer is widespread for drying sludge or biosolids. It is generally used to dry primary sludge, activated sludge and digested biosolids. The rotary dryer consists of a slowly rotating cylinder (usually equipped with internal flights or lifts) through which material and heated gas pass during the drying process (Figure 2.14). The rotation system can range from 200 to 400 rpm.

Generally, it operates with an inlet temperature above 400 °C and is more economical to purchase if designed with direct heat. The velocity of the pipe drying gas is selected considering the possible solids entrainment.

The moisture content of the feed material of 65% allows drying without sticking to the dryer walls. At the end, the dried material contains around 90-95% solids, which are ground and screened. In most systems, about 80% of the furnace gases are recycled, which reduces gas exhaustion.

The temperature of the exhaust gases at the dryer outlet ranges from 60-105 °C. Oil, biogas flaring, or natural gas can be used as fuel, as well as exhaust gases from a power plant. The quality of the final content is excellent, which allows it to be marketable.
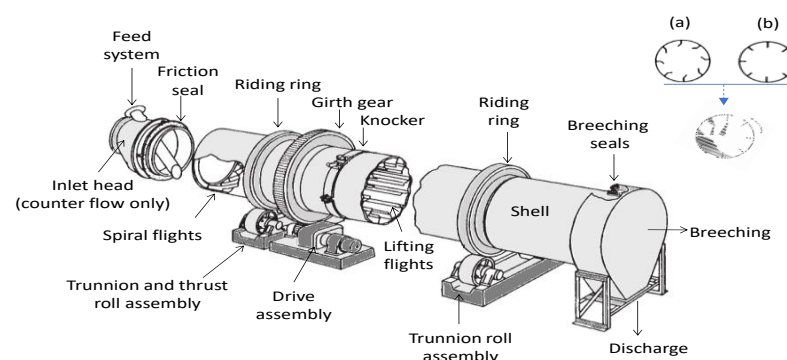
Figure 2.14 - Illustration of a rotary dryer. (a) flights in cascading the drying material inclined 45°, and (b) radial dispositive (Adapted from James et al., 2010).

- **Belt dryers**

Figure 2.15 shows a typical compact belt dyer. Belt dryers may have various configurations e.g., open, semi-open and closed loop. The wet material is deposited on a conveyor belt that receives hot air introduced through a porous bed (Figure 2.15). The operating temperature range from 100 - 180 °C and can operate continuously from efficiently free surface moisture removal to bound water. The system requires maximum moisture of 70% and higher efficiency is achieved when the material is introduced in cylindrical form, which allows a larger exposure area for transferring moisture from wet particles to hot air.
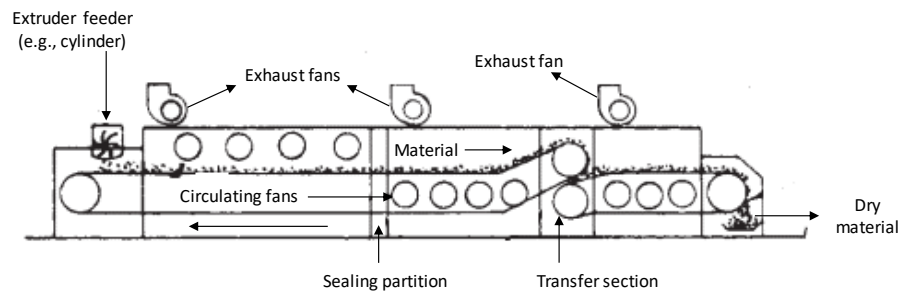
Figure 2.15 - Belt dryer with two-stages straight-through conveyor (Adapted from James et al., 2010).

The material becomes progressively dry as it crosses the length of the belt dryer. This type of dryer is generally suitable for granular, fibre-rich, preformed or extruded wet materials. Uniform drying capacity, low energy demand and high thermal efficiency are the strengths of this type of dryer. In the wet zone, airflow is usually upwards, whereas in the dryer and cooling zones it is downwards to minimize dusting.

The depth of the material on the belt is 1 to 20 cm. Steam gas speeds around 1.5 m s^{-1} are generally used.

- **Fluidized bed dryers**

Figure 2.16 shows a basic type of fluidized bed dryer. This type of dryer has an indirect heating system and operates in a closed inert gas circuit. The method of operation varies by manufacturer. This dryer consists of a vertical chamber divided into three zones (gas chamber, fluidization, and exhaustion). Dry and wet materials can be mixed as a granulation strategy to equalize the drying operation. Granules of material, e.g., sludge, are distributed from the top, held in suspension and intensely mixed by the gas stream passing through the layer of material to be dried.
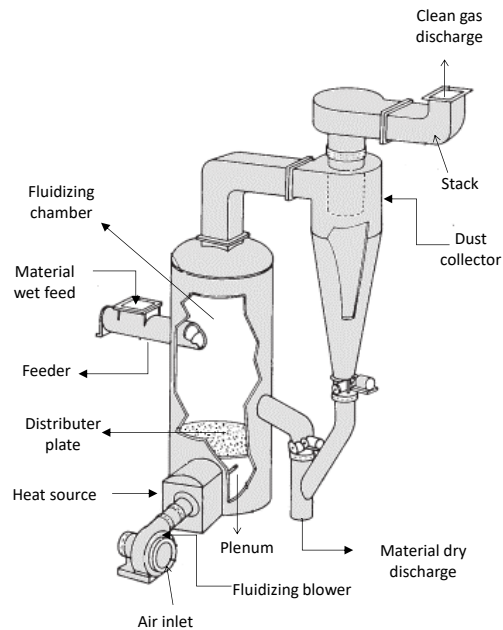
Figure 2.16 - Illustration of a fluidized bed dryer (Adapted from James et al., 2010).

A temperature between 85 to 120 °C is maintained in the bed to promote drying. Due to the cohesive forces exerted by the wetted surfaces, only the upper layer of the solids bed is a fluidized bed. As with rotary dryers, this type of dryer allows the moisture content to be reduced to less than 10%. The lower layers can remain stationary during the initial drying stage when solids are very wet. The low temperatures of this dryer are ideal for waste heat recovery. The gases extracted from the drying zone pass in a cyclone for particle cleaning before discharge.

2.6.3 Conductive dryers

Conduction drying can also be called indirect drying, where the heating medium (e.g., steam, hot gas, thermal fluids) does not contact with the material. Heat for water evaporation is supplied through heated surfaces (stationary or moving), as shown in Figure 2.5 d.

Medium and small companies have commonly employed the conduction drying system to reduce solids content to 10-50% (Chen et al., 2002; Tsotsas and Mujumdar, 2014). Conduction drying is best suited for very damp solids or fine products.

Indirect dryers (e.g., paddle dryer, hollow flight dryer, disc dryer, tray and pressure filter/vacuum dryer) are also applied to SS. However, the main disadvantage is that they are less economical than direct dryers. Details of these dryers will be presented below (Arlabosse et al., 2004; Chen et al., 2002; Metcalf and Eddy, 2014; Tsotsas and Mujumdar, 2014; WEF et al., 2010):

- **Paddle and hollow-flight dryers**

There are three types of dryers in this category: paddle, disc, and rotary chamber. All of them can be fed continuously or in batch. These systems are based on agitation, which is responsible for the continuous renewal of contact between the heated walls and the sludge, and allows a high heat transfer coefficient. SS enters from one end of the dryer and exits at the other. The stirring system is composed of paddles generally accommodated by two stirrers that promote the revolving of the material. Dry steam is entrained and collected in the central part of the dryer. The slope of 1-5° allows the material to flow by gravity during the drying process (Figure 2.17).

The operating temperature is typically 150 - 205 °C (thermal oil or steam is used as circulating hot fluid). The drying time with agitation is in the range of 30 to 180 min. Zhang and co-workers studied bench-scale SS drying using a 3 m² Paddle drying at a temperature of 120 to 208 ℃ based on thermal oil circulation. The authors added rice husk to SS (85% SS+15% RH wt%), and the evaporated moisture improved by 17% (Zhang et al., 2013).
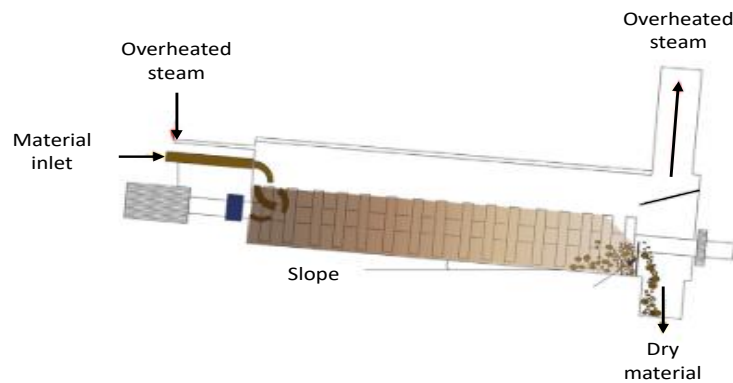
Figure 2.17 - Illustration of a continuous paddle dryer (Adapted from Charlou et al., 2015).

- **Rotary tray dryer**

Indirect drying with simultaneous sludge granulation has emerged in the last decade in Europe as a result of environmental concerns and energy conservation. The dryer has a rotary tray centre shaft where SS is spread uniformly on the heated surface, with controlled layer thickness (20-30 mm) (Figure 2.18). A zigzag moving operation promotes granule formation. At the end, the granules are cooled to 30 °C and stored. The final moisture content is less than 10%.
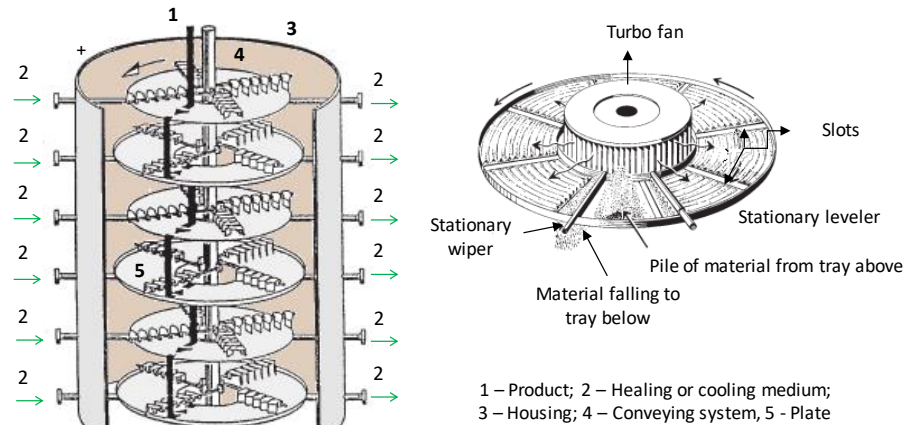
Figure 2.18 - Illustration of an indirect-heated continuous tray dryer (Adapted from James et al., 2010).

- **Pressure filter/vacuum dryer**

Vacuum drying (Figure 2.19) is one of the most expensive methods, being comparable to freezing.
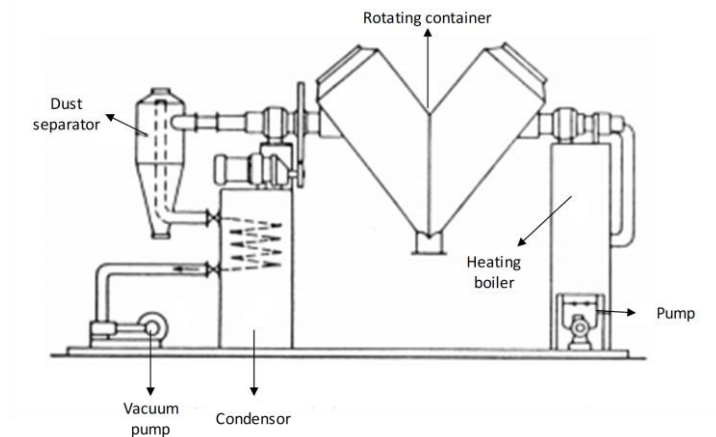
Figure 2.19 - Illustration of a vacuum dryer (Adapted from Tsotsas et al., 2000).

This type of dryer is a variation of a pressure filter that combines dehydration and drying in the same process. Initially, the material is conditioned with lime (CaO) or ferric chloride (FeCl₃) and subsequently submitted to the mechanical pressure cycle. The temperature of hot air used for drying is about 80 °C. The process takes place in batch mode, under agitation or in continuous flow.

This drying system is recommended for materials with temperature below 30 °C. It may be with or without a tray system and may require pre-treatment to maintain uniformity of material. This type of dryer is ideally used to prevent the release of dust and toxic gases during the process. The main advantages of this equipment are the drying capacity (typically 500 kg h^{-1}) and technical aspects regarding.

Finally, there are also other alternatives named "emergent technologies", that are not commercialised on a large scale, namely the solar dryer (Metcalf and Eddy, 2014; Bennamoun 2012; WEF et al., 2010):

- **Solar drying**

This technology can be used to increase the solids content to a range typically between 70 and 80%. It can be open, covered, or combined with a heated floor. The system comprises a rectangular base (translucent chamber) and a ventilation system to ensure convective drying conditions (Figure 2.20). This method is limited to thermal drying for small to medium-sized WWTP, serving an equivalent of 2,000 to 50,000 inhabitants. At the end of the process, the material can be unstable and pathogenic microorganisms may subsist (Bennamoun, 2012; Tuncal and Uslu, 2014). Bennamoun (2012) highlighted the performance of a solar drying system in the sanitation of SS and found that, after 45 days, radiation reduced pathogens from 1×10^7 to less than 2×10^6 CFU g^{-1}.
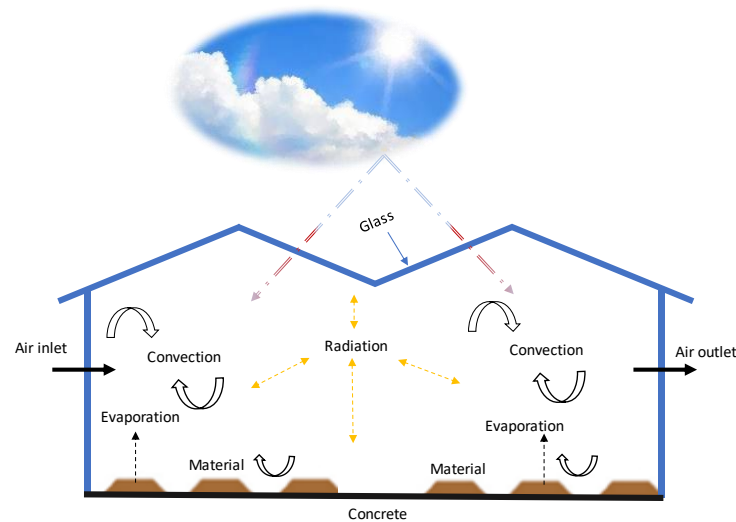
Figure 2.20 - Typical phenomena in a solar drying system (Adapted from Bennamoun 2012).

Another drying technology based on solar radiation is the drying beds. In many hot climate regions, sludge drying beds have become a choice due to economic and operational aspects, e.g., low investment capital and ease of operation, in addition to the high solids content in the dry material. On the other hand, the possibility of attracting insects, the interference of weather conditions and odour generation are the reasons that deserve attention when selecting this alternative (Metcalf and Eddy, 2014).

2.6.4   *Industrial dryers applied to SS*

The belt, rotary, and fluidized bed dryer are among the most commonly used convective dryers for SS from WWTP (Nonhebel et al., 1971; Tsotsas et al., 2000; van't Land, 2011). Table 2.7 shows the main characteristics of the described dryers.

Table 2.7 – Main characteristics of dryers commonly used for SS.

Dryer	Main characteristics	Ref.
Belt	Compact construction and simple design	[1,2]
	Lower drying temperature (100 – 200 ºC)	
	Conveyor velocity (0.1 – 2 cm·s^{-1})	
	Specific energy consumption 700 to 1140 kW h^{-1} t^{-1}	
Rotary	Drying along with disintegration	[1,2,3]
	Internal heating with coils	
	No fire hazards	
	Able to remove 1 - 15 t h^{-1} of water by evaporation	
	Specific energy consumption 900 to 1100 kW h^{-1} t^{-1}	
	Partial drying and possibility of direct heating	
	Hot water from the process as an additional source for heating	
	High maintenance	
	Lost of heat when the temperature of exhaust gases is > 400 °C	
Fluidized bed	Simple, flexibility and intensive drying due to good mixing	[1,2,4]
	Able to remove 1 - 20 t h^{-1} of water by evaporation	
	Suitable, in a small region, for low organic and the high fibre content of SS	
	High-pressure drops	
	No possibility of direct heating, and no hot steam from the process due to low temperatures (~150 ºC)	
	Sensitive to big particles and dust content generation	

Refs.: [1]- (Dobersek et al., 2012); [2]- (Bennamoun et al., 2013a); [3]- (van't Land, 2011); [4]- (Tsotsas et al., 2000)

Therefore, the selection of a suitable dryer must be a compromise between the operating mode (e.g., feeding material flexibility and load variation), the final quality of the dried material, safety aspects (collection of gases generated), and ease of installation and maintenance.

Typically, the required energy to remove water for sludge drying is 2,595 kJ kg^{-1} water evaporated (Kurt et al., 2015). However, according to several other research studies the thermal energy required for sludge drying is significantly higher and depends on the initial moisture content (Table 2.8) and type of dryer (Table 2.9). Another important point is the purchase cost of the different dryers (Figure 2.21).

Table 2.8 - Theoretical energy required for drying SS with different moisture content (Dhir et al., 2001).

Dewatered SS (%$_{db}$)	40	40	25	25	20	20
Dried SS (%$_{db}$)	90	80	90	80	90	80
Energy required (MJ t^{-1}$_{db}$)	4,363	3,928	8,965	8,513	12,034	11,567

Table 2.8 shows that the required energy depends strongly on the initial water content in dewatered SS and to a lesser extent on the final water content in the dried sludge.
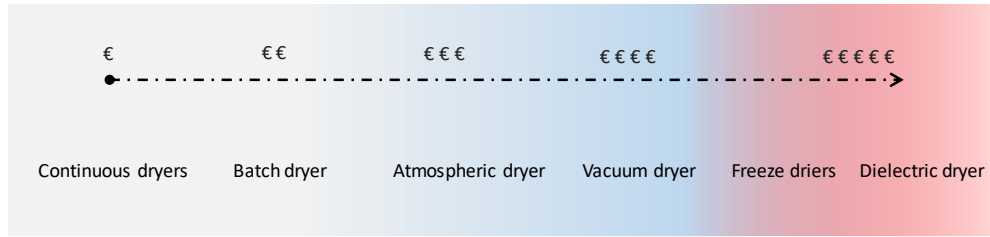
Figure 2.21 - Comparison of the costs for different dryers (James et al., 2010).

Table 2.9 - Capacity and energy consumption for different dryers (Adapted from Mujumdar, 2014).

Dryer Type	Typical evaporation capacity		Typical energy consumption kJ kg^{-1}$_{water\ removed}$
	kg$_{water}$ h^{-1} m^{-2}	kg$_{water}$ h^{-1} m^{-3}	
Rotary dryer		30-80	4,600-9,200
Fluid bed dryer	ni	ni	4,000-6,000
Flash dryer		5-100; depends on particle size	4,500-9,000
Drum dryer	6-20; for pastes		3,200-6,500
Spry dryer		1-30	4,500-11,500

ni –not informed.

It is important to note that biogas from AD treatment in WWTP can be employed as fuel to produce heat and/or electricity (Stürmer et al., 2020). Biogas presents a high heating value (mainly CH_4 and CO_2) of about 21.5 MJ m^{-3} (Syed-Hassan et al., 2017), and is a renewable fuel that can be used to dry SS in the WWTP avoiding the transportation costs. Indeed, Flaga (2005) showed that the estimated cost to dry 1 m^3 of sludge until 25%$_{db}$ is approximately 13-15 € t^{-1}$_{db}$ using biogas, while 21-26 € t^{-1}$_{db}$ is required when fuel oil is used.

For WWTP with large sludge production (usually > 1 t h^{-1}), continuous dryers are less expensive than batch units. Moreover, atmospheric pressure dryers cost about 1/3 less than vacuum dryers. Dryers able to promote gas recirculation can have lower operation cost but could be 50% more expensive when compared to simpler dryers. Rotary, fluidised bed, and pneumatic conveying dryers can provide comparable cost performance in WWTP with annual output in the range of 1-50 Mt (James et al., 2010).

2.7   Adjuvants as drying improvers

2.7.1   General aspects

Industrial activities produce waste with characteristics and quantities that require proper management to protect the environment and human health. The industry has many strategies available to manage waste, such as cleaner production, 3 Rs policy (reduce, reuse, recycle), and waste management plans.

Figure 2.22 shows the generic flows for industrial processes with the generation of products, by-products, and waste. From a circular economy perspective, waste can be incorporated into other

production processes to reduce the use of raw materials and other inputs and for the generation of new products, goods and services.
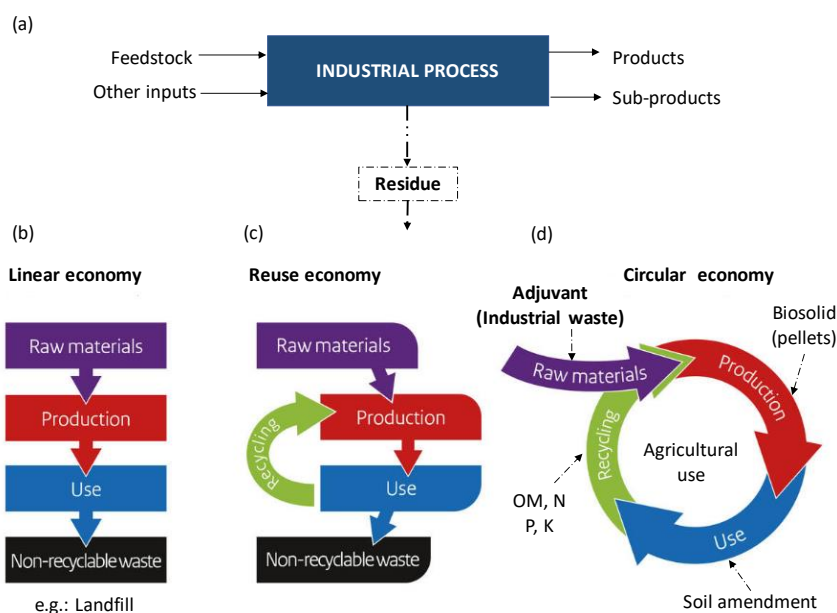
Figure 2.22 - (a) Flows of industrial processes and waste recovery routes according to a (b) Linear economy; (c) Reuse economy; (d) Circular economy.

Waste produced by industry may be used, for example, for soil application, civil construction, landfill impermeabilization, etc. Some studies have pointed out some waste as sludge drying adjuvants, aiming to improve water removal. Thus, in the context of this thesis, coal fly ash (CFA) from a power plant, green liquor dregs (GLD) from a kraft pulp mill, eggshell (ES) from an egg pasteurization industry, and rice husk (RH) obtained in a rice husking plant were used as SS drying adjuvants. The effect of each adjuvant used in SS drying will be detailed in Chapters 4, 5, 6, and 7.

2.7.2   *Role of drying adjuvants*

Adjuvants are materials that can be added to the SS during the drying process to improve the performance without compromising the final product quality and subsequent application to the soil. The use of waste as an adjuvant shows environmental, technical and economic interest. The Directive 2008/98/EC of the European Parliament and the Council highlights the environmental gains. The technical benefits are related to possible improvements in terms of acid neutralization capacity (ANC), water absorption capacity (WAC), pH adjustment, sanitation, and/or phytotoxicity. In addition, economic gains may also arise from the avoided waste management costs and lower energy consumption during drying. Table 2.10 summarizes the relevant properties of the materials used as adjuvants in this work.

Table 2.10 - Main properties of drying adjuvants tested in this work.

Properties	Adjuvants			
	CFA [1]	GLD [2]	ES [3]	RH [4]
pH	8 – 12.5	10 – 12.5	8.4	ni
Particles size (μm)	< 20	~ 12	6.4	3.5
Surface area (m^2 kg^{-1})	250 – 500	18,000	128,500	205,320 [a]
Porosity (%)	50 – 60	> 70	~52	90 [a]
Bulk density (g cm^{-3})	0.54 – 0.86	0.44 – 0.67	1.65 – 1.77	0.083 - 0.125
WAC (%)	35 – 40	70 - 80	> 10	5 - 16
Hydraulic conductivity (m s^{-1})	< 10^{-9}	10^{-8} - 10^{-9}	ni	ni
CaCO$_3$ (%)	< 12.5 (Class F) > 54% (Class C)	~75	92	> 10
PTM (mg kg^{-1})	Low	Low	Low	Low

Refs.: [1]- (Basu et al., 2009; Shaheen et al., 2014; Yao et al., 2015; Yeheyis et al., 2010); [2]- (Mäkitalo et al., 2014; Simão et al., 2018); [3]- (Buasri et al., 2013; Cunha et al. 2019; Freire et al., 2008; Ok et al., 2011); [4]- (Alyosef et al., 2013; Kuncoro et al., 2014; Phonphuak and Chindaprasirt, 2015; Yao et al., 2016); [a] – at silica (ash form); ni – not informed.

A good adjuvant aids the material drying by creating a porous structure (act as a skeleton builder) that facilitates water migration (Zhang et al., 2019). Moreover, the SS drying adjuvants can be selected to improve soil properties if the final product is used in agriculture applications. For instance, an adjuvant containing calcium carbonate (CaCO$_3$) can neutralise soil acidity, acting as a natural liming agent. Table 2.11 shows an overview of the most recent studies in the context of the convective drying using adjuvants as process improvers. CFA, rice husk, hazelnut shell, sawdust, rice straw, pulverized coal, CaO, NaClO, and NaHCO$_3$ are the main adjuvants tested in previous studies. Moreover, the main operating conditions used and the results are also highlighted.

Table 2.11 - Overview of adjuvants tested and operating conditions for SS water removal.

Mixture	Relevant conditions	Main results and conclusions	Ref.
SS; SS:RH; SS:WS, SS:HR:WS	- M$_o$ SS: 80% - WS and RH sieved at 0.25 mm - Formulations: SS, SS + 20% HR; SS + 20% WS, SS + 10% RH + 10% WS -T: 80-120 ℃	- Best results: SS + 10% RH + 10% WS at 120 ℃ - RH and WS increased the thermal conductivity of the SS and heat transfer capacity - Adjuvants created rigid structures and porosity, facilitating moisture removal	[1]
SS; SD; RHC, and PCA	- M$_o$ SS: 80-85% -Two skeleton builders (CTAB and CPAM) combined with SD; RHC, and PCA - Dosages: CTAM (0, 5, 10, 15, 20 g), and CPAM → 25 g	- SD and RHC promotes the formation of porous channels in the sludge, facilitating the drainage of water - Effect of SD or RHC were much better than that of PCA - SD between 7.5-12.5% showed the largest dehydration - Skeleton building was measured by pore volume, average pore size, surface morphology at low doses	[2]
CFA, LG, QL, PP, D_SS, and FTp	- Initial mass: 10 mg - T: 100-180 ℃ - SS pH: 6.71 - SS with CFA-10%; LG-10%; QL- 10, 20 and 30%; D_SS-10 and 20%, and PP-10% - Freeze-thaw samples → raw SS were frozen for 24 h at -18 ℃ and then thawed for 10 h at room temperature	- SS:10% of adjuvants increased DR to → CFA (3.57%); LG (2.81%) QL (2.65%), D_SS (3.05%) and PP (4.80%) compared to raw SS. - For SS FTp, the DR increase from 1.37–21.04% compared with raw SS. - PP can break the structure of polymers in SS releasing free water - FTp freeze/thaw effect breaks the cell and releases intracellular water	[3]

Table 2.11 (cont.) - Overview of adjuvants tested and operating conditions for SS water removal.

Mixture	Relevant conditions	Main results and conclusions	Ref.
CaO, FSD and CSD	- M_o SS: 78.5% - Non-agitated and agitated drying tests. - Speed of rotation: 20 rpm - T: 180 °C - L: 2cm - SS mass: 30 g - Ø FSD: 50.2 mm - Ø CSD: 10 mm - Adjuvant: SS: 1:100	- 5% sludge$_{wb}$ the adhesion and cohesion ranged from 618 for 6581 Pa and 1626 for 9305 Pa, this represents 58% and 28% relative to the original sludge - Adhesiveness of SS was lowered by sawdust addition. - CaO significantly strengthened the solid bridges, as well as the adhesive stress of sludge	[4]
SS:CaO, SS:NaClO	- M_o SS: 88% - T: 70-100 °C - Time: 0-2000 min - CaO: 0.10 mL g^{-1} SS - NaClO: 100 mg g^{-1} SS	- CaO accelerated drying, not cracking, requires less energy consumption. - Better results at 70 ºC - DR (g min kg) at 100 ºC: SS (~4.3); SS+CaO (~5.3) - SS treated with CaO has nearly 6% less volume compared to untreated and NaClO treated samples	[5]
SS:NaHCO$_3$	- M_o SS: 62.2% - OM: 20%$_{db}$ - Heating value: 9,042 MJ kg^{-1} - Sample thickness: ~ 10 mm - T: 100; 120; 140 and 160 °C - L: 5; 10 and 15 mm - SS:NaHCO$_3$: 0.02, 0.06, and 0.1%	- $D_{eff} = 2.967 \times 10^{-7}$ m^2 min^{-1} - 2% NaHCO$_3$ → maximum DR - Best D_{eff} with 2% blend; at 120°C was 3.0654×10^{-7} (m^2 min^{-1}) and 6%, 120 °C 3.006×10^{-7} m^2 min^{-1} - D_{eff} of dried sludge at 100-160°C varied in the range from 2.22×10^{-7} to 6.51×10^{-7} m^2 min^{-1}	[6]
SS:LG	- M_o SS: 82%; M_o SS:LG 60% - T: 80 - 200 °C - Ø Briquette SS:LG: 10×40 mm - Speed of air: 1.5 m s^{-1} - Time: 23,000-24,500 s - OM: 667 g kg^{-1}, N: 56 g kg^{-1} - P: 49 g kg^{-1}, K: 9.8 g kg^{-1} - pH: 6.7	- Lignite created a bridging effect between sludge flakes, promoting permeability and facilitating water drainage. - Best diffusivity with LG and T above 120 °C - D_{eff} for the raw SS in the first falling rate period and the second falling rate period of 3.102×10^{-7} m^2 min^{-1}, and 5.082×10^{-7} m^2 min^{-1}, respectively	[7]
SS:HS	- M_o SS: 79.7% - Sludge mass: 100 g - T: ~ 32 ºC - Mixtures: 20, 40, 60 and 80%	- Best result for SS+20% HS - HS influenced in the porosity and heating value of the material - Best results at 20 % HS+80% SS	[8]
SS:RS	- M_o SS: 87.65% - T: 100, 120, 140, 160 °C - % RS: 0, 1, 2, 3, and 5 - Oven heating power: 3 kW - Air flow rate: 780 m^3 h^{-1}	- raw SS at 100, 120, 140, 160 ºC, the average DR → 0.094, 0.132, 0.174, 0.227 g min^{-1}, respectively - 2% RS was the best results and DR was improved in 14.6, 14.8, 16.0 and 17.6% for 100, 120, 140 and 160 °C, respectively - 5% SS: RS drying rate decrease	[9]
SS:SD	- M_o SS: 85.5% - T: 50-200 °C - Speed air: 2 m s^{-1} - Circular dies of 12 mm - Mass of SS: 500 g	- D_{eff} changed from 4.662×10^{-7} m² min^{-1} (SS) to 4.206×10^{-7} m² min^{-1} with blend 66%SD as adjuvant - Mass transfer changed from 3.49×10^{-4} m min^{-1} (SS) to 4.002×10^{-6} m min^{-1} (SS:SD) and then increased to 7.254×10^{-6} m min^{-1} for SS:SD at 66% - Final volume reduction was between 20-50% - Neglecting the shrinkage phenomenon resulted in an overestimation of the internal diffusion coefficient	[10]
SS	- M_o SS: 67% - T: 50-200 °C - Speed air: 1-3 m s^{-1} - Moisture of the air (0.005-0.5 kg$_{water}$ = kg$_{dry\ air}$) - Mass of SS: 2.5 g - Cylinder Ø: 15 mm - Models tested: Page model, logarithmic model, and the fourth-degree polynomial model	- T: 80ºC; at 130 min, a reduction of 45% was observed. - T: 140ºC; at 50 min, a reduction of 40% and 30% of shrinkage at the application of 200 ºC - Kinetics revealed an adaptation and constant drying periods, and a long falling drying rate. - Krisher curve fits the kinetics of drying in the different phases of the process - The fourth-degree polynomial model presented better results with a correlation coefficient approaching unity	[11]

Table 2.11 (cont.) - Overview of adjuvants tested and operating conditions for SS water removal.

Mixture	Relevant conditions	Main results and conclusions	Ref.
CaO:DSS	- M_o SS: 82% - SS mass used: 200 g - T: 160 °C - Ø CaO: 50 μm - CaO:DSS: 0, 1:200, 1:00, 1:20 and 1:10	- The drying rate increased from 1.8 to 4.7 kg.H_2O kg$^{-1}_{db}$, the drying rate of DSS increased markedly with increasing CaO/DSS value - CaO was more effective in drying rate than DSS	[12]
PC	- M_o SS: 82% - T: 160°C - Ø: 0.401 mm - PC/DSS used: 0, 1:100 and 1:20	- DR: 1.0 - 2.8 kg H_2O kg$^{-1}_{db}$	
HO	- M_o SS: 82% -HO obtained from the pyrolysis of tires at 600 °C - Moisture: 0.9 of total weight (%) - Density: 955 kg.m^{-3} - HO/DSS: 0, 1:20 and 1:100	- HO:DSS fractions of 0 and 1:20, there was a slight increase in the drying rate (2.0-4.0 kg H_2O kg$^{-1}_{db}$)	
SS	- M_o SS: 72.5% - T: 80, 90, 100, and 112 °C - Air speed: 0.43 - 0.65 m s^{-1}	- The integration of Fick's second law with the modified quasi-stationary method can describe the drying drop rates - Best temperature: 112 °C - Relatively long constant drying period and two falling rate periods	[13]
SS, WS, RH	- M_o SS: 81% - T: 80 – 120 °C - Adjuvants as powder sieved at 0.25 mm SS (100%) SS (100%) + RH (20%), SS (100%) + WS (20%), SS (100%) + RH (10%) + WS (10%)	- Drying time: SS (100%) → 170 min; best condition: 120 °C with WS (10%) and RH (10%) → 140 min - SS-RH-WS mixture confers higher thermal conductivity - WS and RH transform SS into a rigid, porous structure that provides well-defined passages for the steam to escape	[14]

Refs.: [1]- (Wang et al., 2019); [2]- (Zhang et al., 2019); [3]- (Zhang et al., 2017); [4]- Deng, et al., (2017); [5]- Danish et al., (2016); [6]- Zhou et al., (2016); [7]- Zhang et al., (2016); [8]- Pehlivan et al., (2016); [9]- Cai et al., (2015); [10]- Li et al., (2014); [11]- Bennamoun et al., (2014); [12]- Deng, et al., (2014); [13]- Reyes et al., (2004); [14]- (Wang et al., 2019). Initial moisture (M_o); Sewage sludge (SS); Rice husk (RH); Wood sawdust (WS); Sawdust (SD); Rice husk char (RHC); Powdered coal ash (PCA); Drying rate (DR); Coal fly ash (CFA); Quick lime (QL); Potassium permanganate (PP); Dry sewage sludge (D_SS); Freeze–thaw pre-treatment (FTp); Lignite (LG); Rice straw (RS); Hazelnut shell (HS); Heavy Oil (HO); Pulverized coal (PC); Fine sawdust (FSD); Coarse sawdust (CSD); Dehydrated sewage sludge (DSS).

The selection of adjuvants depends on costs, ease to use, the possibility of controlling the odour generation during the drying process, etc. In particular, the choice of an adjuvant for SS drying should consider any risks to human health, environmental impacts, occupational and food safety, as well as legislation restrictions. It is also important to consider the positive effect on soil adjuvant, i.e., soil texture improvement, pH correction capacity, soil water retention, impact on agricultural productivity.

The drying process can be improved with adjuvants that can create binding mechanisms between the solid structure of the sludge, favouring the water migration to the surrounding environment. Aiming at contributing to the circular economy, it is important that the adjuvant can be used in agriculture, thus avoiding landfill disposal routes.

Zhang et al., (2016) highlight the effect of lignite to create bridges between the SS structure and the adjuvant, increasing the porosity and facilitating the intracellular water migration. Moreover, it is highlighted the effect of sawdust and rice husk as materials that increase porosity, as well as the heating value of SS (Wang et al., 2019). Another study showed that potassium permanganate (PP) improves oxidation conditions of SS polymers and consequently water is removed more efficiently during the drying process (faster and with energy savings) (Zhang et al., 2017).

2.8   Sewage sludge applications

According to literature, the main SS destinations are agriculture, composting, incineration, and as least preferred environmental option the landfill. Considering the European Sludge Management Policy (Directive 86/278/EEC), this work will focus on the application of SS in the soil. Table 2.12 shows the average costs for different SS applications in European Countries (Kacprzak et al., 2017).

Table 2.12 - Average costs according to different SS management strategies.

SS methods utilization	Cost (€ t^{-1}_{db})
Agriculture	
Dewatered SS (15-25%$_{db}$)	160
Dry SS	210
Composting	310
Incineration	315
Landfill	255

Figure 2.23 depicts the waste management hierarchy stated by European guidelines, which aims to avoid the negative impacts due to the generation and management of waste, as well as to enhance resource efficiency. This hierarchy must be applied not only to SS but also to other industrial waste. Restrictions on current disposal methods (e.g., landfill) and sustainability challenges are driving research for new alternatives for SS management.
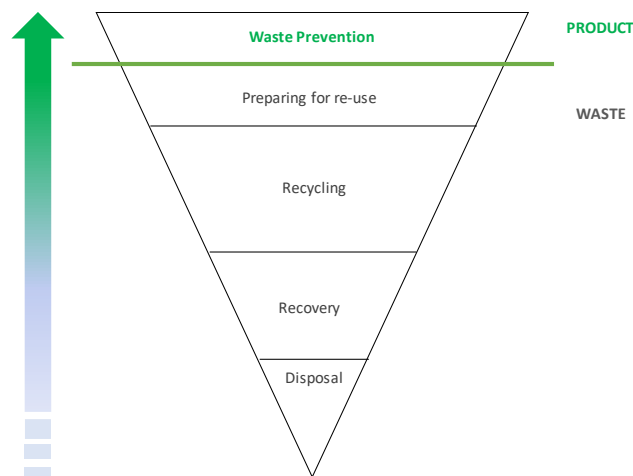
Figure 2.23 - Waste management hierarchy adopted by the EU Member States (from the worst - *Disposal* to the best - *Prevention*).

2.8.1   Agricultural use

Depending on the country or region, the utilization of SS as a soil amendment may or may not be accepted (e.g., Belgium, namely in the cities of Brussels and Flanders; Switzerland and Romania). In Europe, the application of SS or biosolids is regulated by EU Directive 86/278/EEC (EEC, 1986) and in the USA by 40 CFR Part 503 (US EPA, 1993) (Healy et al., 2016). Both legislations describe quantitative standards, management practices, operational standards, monitoring, record keeping requirements, and reports for the use and disposal of biosolids (Lu et al., 2012). Biosolids may be treated

by physical, chemical, and/or biological methods to reduce pathogen levels. Regarding the content in macro-and micronutrients, the application on agricultural soil can be highly beneficial (Urra et al., 2019). The 40 CFR Part 503 legislation classifies biosolids into two Classes "A and B." Class A biosolids can be applied unrestrictedly to the soil. Due to the strict quality control, they do not contain detectable levels of pathogens and PTM must be in reduced concentrations. This type of biosolid is treated by one or more processes such as composting, pasteurization, drying or heat treatment, or advanced alkaline treatment (Oun et al., 2014). For application in public places or some food crops, SS of Class A must be subject to the rigorous treatment referred to above. Class B restricts human exposure to pathogens by delaying application after harvest and prohibits its use in food crops consumed directly without processing. Class B can be applied to grain and fodder crops and pastures. However, in California, due to public concern about potential hazards, the application of Class B biosolids has been prohibited in some areas. (Lu et al., 2012; Oun et al., 2014).

The use of SS as a soil amendment requires discussion by the scientific community and society as it also involves aspects such as economic (technology status, affordability), environmental, and cultural (Slepetiene et al., 2020).

Regarding nutrients content for soil (N, P, K), the production of fertilizers requires raw materials and energy. Moreover, the extraction of phosphate rocks is usually contaminated with Cd, which is then released into the environment (Liu et al. 2016; Smil, 2006). SS has approximately 35 kg N and 20 kg P t^{-1} in dry base, and thus can be of interest to promote sustainable agriculture (Stresa, 2000). Table 2.13 presents a comparison of nutrient levels in commercial fertilizer and in SS (Mendes, 2014).

Table 2.13 - Comparison of nutrients content in commercial fertilizers and in SS.

Material	Nutrients (%)		
	N	P	K
Commercial fertilizer	5.0	10.0	10.0
Typical SS values	3.3	2.3	0.3

SS is one of the most important renewable sources of nutrients. In particular, ash from the incineration of SS is strongly P rich (Fijalkowski et al., 2017). Phosphorus is a limiting element for soil and aquatic ecosystems. According to Gustafsson et al., (2013), most of the nutrients are available for plants within a pH range of 6.5-7.5. Furthermore, SS can be potentially beneficial to the soil due to the presence of carbonates, along with macronutrients (P, K, Ca, Mg) and micronutrients (Fe and Zn) (Almeida et al., 2007, Zambrano et al., 2010).

Although the difficulties pointed out by Fytili and Zabaniotou (2008), related to technical and social obstacles, several authors stressed advantages from the nutrients content (Alvarenga et al., 2015, Kelessidis and Stasinakis, 2012; Leblanc et al., 2008; Mahmoud et al., 2016; Stefanakis and Tsihrintzis, 2011). Furthermore, stabilised alkaline biosolids can be used as a liming material (Lu et al., 2012). Also, the benefits of OM to reduce the leaching of pollutants should also be considered (LeBlanc et al., 2008).

It is important to highlight that after the application of SS to the soil, the aggregate stability, density, porosity, and WAC should be monitored. These effects are evaluated by the ion exchange capacity, the electrical conductivity (EC) increase, and the humic substances. In Portugal, Alvarenga et al., (2015) characterized two SS samples (SS1 and SS2, in db) from distinct WWTP. The results are summarized in Table 2.14.

Table 2.14 - Characterization of two SS samples from Portuguese WWTP (Alvarenga et al., 2015).

Variables	SS1 [1]	SS2 [2]
Moisture (%)	83.9 ± 0	84.6 ± 01
pH	7.1 ± 0	7.4 ± 0.1
OM (%)	67.5 ± 0.06	74.3 ± 0.1
$N_{Kjeldahl}$ (%)	6.2 ± 0.5	6.2 ± 0.3
C/N	5.4 ± 0.5	5.9 ± 0.3
P_{total} (% P_2O_5)	13.5 ± 0.4	6.9 ± 0.08
K (g K_2O kg^{-1})	7.1 ± 0.03	14.5 ± 0.3
Na (g kg^{-1})	2.4 ± 0.16	1.6 ± 0.02
Ca (g kg^{-1})	12.0 ± 0.1	27.6 ± 1.1
Mg (g kg^{-1})	4.6 ± 0.5	7.9 ± 0.7
$N_{organic}$ (%)	4.4 ± 0.5	4.2 ± 0.3
Cd (mg kg^{-1})	1.0 ± 0.1	< 0.3
Cr (mg kg^{-1})	< 5.6	< 5.6
Cu (mg kg^{-1})	140.8 ± 0.1	155.8 ± 3.9
Hg (mg kg^{-1})	< 1.3	< 1.2
Ni (mg kg^{-1})	22.6 ± 0.9	22.5 ± 1.0
Pb (mg kg^{-1})	< 5.6	< 5.6
Zn (mg kg^{-1})	757.2 ± 12.4	581.1 ± 15.2
Escherichia coli (CFU g^{-1})	8.9×10^2	4.3×10^4
Salmonella spp. (Present/Absent 50 g^{-1})	Absent	Present

[1] SS1 - from a big city (134000 inhabitants); and [2] SS2 small village (6000 inhabitants). Mean value $\pm$ standard deviation.

Table 2.14 shows that the presence of pathogenic microorganisms can be a barrier to the direct application of SS to the soil. SS2 did not meet the recommendation of *Decreto Lei Nº*. 276/2009 in terms of pathogenic microorganisms, since *E. coli* is higher than 1000 cells g^{-1} dry matter and *Salmonella* ssp. is present in 50 g of original material.

Usually, SS contains traces of PTM, while in large urban and industrial centres, SS may have higher levels. In the case of PTM, there is a risk of accumulation in the soil and food chain, causing eco-phytotoxic effects on humans and the environment. During the wastewater treatment process, PTM tends to be adsorbed on the OM and/or absorbed by microorganisms. After the application of SS to the soil, PTM can be released, especially Cu, Pb and Cd (Cerne et al., 2019).

A study from Healy and co-workers showed that the application of SS at rates of 10-40 t ha^{-1} increased rice grain yield by up to 40% and the nutrient content available in the soil compared to equivalent doses of fertilizers. However, the Cd and Zn content in plants also increased compared to conventional fertilizers (Healy et al., 2016). Another issue of concern is the solubilisation of metals into

groundwater (Oun et al., 2014; Wen et al., 2014). Mobility, bioavailability and eco-toxicity of metals in plants depend on the chemical speciation. Typical PTM concentrations in different biosolids are shown in Table 2.15.

Table 2.15 - Concentrations of PTM in biosolids from different countries (Adam et al., 2009; Sharma et al., 2017).

PTM (mg kg^{-1})	Countries		
	Australia	China	India
Cd	0.70-13.6	2.23-7.61	32.3-144.5
Cr	308.0	52.8-288	35.5-60.0
Cu	92-1996	0.27-975	186-330.0
Hg	Ni	ni	ni
Ni	166.0	52.5-202	47.17-60.0
Pb	323.0	49.1-186	28.5-240.0
Zn	210-3060	0.21-1350	161-2050

ni –not informed

As aforementioned, SS can contain pathogenic microorganisms causing urinary tract infections (*Escherichia coli*), pneumonia (*Klebsiella* and *Enterobacter*), blood infections (*Enterobacteriaceae*), and gastrointestinal infections (*Escherichia coli* and *Salmonella* ssp.) (Rorat et al., 2019).

Lime stabilization and thermal drying are efficient systems for the inactivation of pathogenic microorganisms (about 99.99%) (Martín et al., 2018). According to Romdhana et al., (2009) *Escherichia coli.* and *Salmonella* ssp. may be present in raw sludge ranging from 6×10^3 to 4×10^5 CFU/g (SS after centrifugation) and 8×10^3 CFU/100 mL (raw SS), respectively. Similar values for *E. coli* have been reported for SS samples in Portugal (Alvarenga et al., 2015). The presence of eggs of Helminths, *Giardia Lamblia* and *Ascaris* were not detected after SS drying. The highly acidic or alkaline environment can also create conditions for the destruction of pathogenic organisms. This decay is probably related to the cellular lysis and inactivation of the microorganisms. Other factors such as temperature, moisture and residence time are parameters affecting the inactivation of pathogens (Tsotsas and Mujumdar, 2014). For complete inactivation of pathogenic organisms, SS must be dried to 90% solids and the wet-bulb temperature must exceed 80 °C. For example, at 50 °C, it is possible to reduce the *Salmonella* ssp. in 30 min and all other pathogens contained in the SS within a shorter period of 10 min at 91 °C (Romdhana et al., 2009; Singh and Agrawal, 2008). However, due to the presence of residual antibiotics in wastewater and consequently in SS as well, other risks are present (Rorat et al., 2019).

Sludge stabilization with lime is often used due to the low costs involved, mainly using commercial calcium oxide (CaO) or hydrated lime Ca(OH)$_2$ (Hung et al., 2007; Singh and Agrawal, 2008). Effectiveness of lime stabilization for pathogen inactivation requires that the pH of the sludge be increased to 12 and a minimum contact time of 2 h (Healy et al., 2016; Hung et al., 2007; Rorat et al., 2019).

Another positive effect of lime is the ability to control bad odours due to nitrogen and sulfur compounds formed during the anaerobic decomposition of OM. Since 1954, the utilization of lime to control odours has been established. Generally, 6-16% of hydrated lime on the dry solids mass is enough to show a positive effect. However, the addition of more than 1% lime can be phytotoxic (e.g., affect watercress seed germination) (Wong and Selvam, 2006). Table 2.16 presents the lime requirements for achieving pH 12.0 in 30 min, for pathogenic microorganism removal (Hung et al., 2007).

Table 2.16 - Lime requirements to obtain pH 12.0 after 30 min.

SS type	Solids (%)		Lime dosage (kg $Ca(OH)_2$ kg^{-1} SS_{db})		pH (Average)	
	Range	*Average*	*Range*	*Average*	*Initial*	*Final*
Primary SS [1]	3-6	4.3	0.06-0.17	0.12	6.7	12.7
Activated SS	1-1.5	1.3	0.21-0.43	0.30	7.1	12.6
AD	6-7	5.5	0.14-0.25	0.19	7.2	12.4
Septage	1-4.5	2.7	0.09-0.51	0.20	7.3	12.7

[1] Includes some portion of waste-activated sludge

Another important aspect of using lime stabilization in SS is the ability to reduce nitrogen when pH is around 12.0, because ammonium (NH_4^+) is transformed into ammonia (NH_3) which is released into the atmosphere (Hung et al., 2007). Thus, ammonia creates adverse conditions for pathogenic microorganisms, reducing the presence of thermotolerant bacteria in 2 to 7 orders of magnitude (Arthurson, 2008).

(i)   Studies on the application of SS in the soil

Table 2.17 summarizes some studies related to the application of different types of sludge and the main effects observed.

Hamdi and co-workers evaluated soil properties over three years on 4 m^2 of uncultivated plots, using SS rates of 0, 40, 80, and 120 t ha^{-1} $year^{-1}$ for sandy loam soil, and sandy soil. The addition of sludge at 120 t ha^{-1} $year^{-1}$ resulted in a significant increase in total organic carbon content to 2.92% in sandy loam soil and 2.64% in sandy soil. The control area at the end of the experiment reached only 1.91% and 1.3% for both types of soil. A considerable increase in microbial and enzymatic activity, particularly at higher applied doses (80, and 120 t ha^{-1} $year^{-1}$) was observed. The pH remained within the neutral to an alkaline range (7.76-8.63), and PTM (Cu, Zn, Ni, and Pb), soil salinity, and faecal coliforms were all below the legal limits for contaminated soils (Hamdi et al., 2019).

Mohamed et al. (2018) used sunflower cultivation with SS rates ranging from 15, 30, 60, and 120 t ha^{-1}_{db} and two further controls (blank and soil enriched with NPK fertilizer) (Table 2.17). The authors concluded that the addition of more than 15 t ha^{-1} promotes better soil performance (ion exchange, nutrient availability) and harvest performance (grain yield and biomass) compared to recommended mineral fertilization regulated (synthetic NPK).

In general, the results in Table 2.17 demonstrate the feasibility of using different types of SS for soil application after the appropriate treatment. The state of the art also reflects the potential of soil amendment with SS for a wide variety of cultivars.

Table 2.17 - Different types of sewage sludge applied to soils and the effects observed.

SS type	Experimental conditions	Main results	Ref.
AD SS	- Soil: loam and sandy soil - Experiment: lots of 4 m^2 - Treatments: control soil (C); 40 t ha^{-1} year^{-1} of SS (SS-40); 80 t ha^{-1} year^{-1} SS (SS-80) and 120 t ha^{-1} year^{-1} SS (SS-120) - SS application: 10-15 cm depth - Monitoring: 3 soil samples per year	- SS improved TOC, N, P, and K content at all application rates. - Positive results in microbial biomass and soil enzymatic activities - Soil loam presented higher retention capacity - Three repeated high doses per year can be applied without causing soil degradation (e.g., 120 t ha^{-1} year^{-1}) - pH in both soils remained between 7.76-8.63 - Cu, Zn, Ni and Pb, soil salinity and faecal coliforms were all below the limit values for contaminated soils	[1]
AD SS	- Culture: *Helianthus annuus L.* - Soil: clay, collected at 0-30 cm - Pots: 27 cm high with base Ø of 21.5 and top Ø 26 cm. - 1 kg gravel + 8.5 kg dry soil + 1 kg soil - Seeds: 3 in each pot, and then reduced to 1 healthy plant per pot. - Irrigation: distilled H$_2$O in 70% of the area, 3 times a week, or 2 times a day on hot days. - Treatments: control (soil); soil + NKP; soil + SS (15, 30, 60, and 120 t ha^{-1}) - Monitoring: height, stem diameter and number of leaves measured every 10 days.	- Soil pH was significantly affected by SS (control pH = 8.4 and SS:120 t ha^{-1} pH = 7.6) - Significant enrichment in N (36, 123, 168 and 248% for the control, SS15, SS:30, SS:60, and SS:120, respectively. - At rates of 60 and 120 t ha^{-1}, P increased 2.5 and 6 times. - Stem length for the control was 24.5 cm while for SS:15, SS:30, SS:60, and SS:120 it was 130, 146, 167 and 172 cm - SS at 15 t ha^{-1} presented similar values of the production compared to chemical fertilizers	[2]
AD SS	- Culture: *E. globulus Labill* - Soil: sandy, collected at 20 cm - Blend: SS + Corn Straw (1:3) - Luminosity: lamp 400 E m^{-2} s^{-1}; 400-700 nm - Cycle: 16/8h - T: 25-19 °C with 50% relative moisture - Transplant after germination - Pots: 10 cm height × 8 of diameter; 1:4 (v:v) sand+soil - *t*: 16 weeks	- After 6 weeks, the soil pH changed from 5.35 (control) to 5.43 (wheat straw), 6.16 (SS) and 6.63 (mixed soil residue) - The application of Al-rich SS, wheat straw or the mixture of both in soil did not increase Eucalyptus *globulus Labill* growth unless inoculated with saprobe and arbuscular fungi	[3]

Refs.: [1]- (Hamdi et al., 2019); [2]- (Mohamed et al., 2018); [3]- (Arriagada et al., 2014).

Table 2.17 (cont.) - Different types of sewage sludge applied to soils and the effects observed.

SS type	Experimental conditions	Main results	Ref.
SS	- Culture: *Sunflower (H. annuus)* - Soil: sandy-loam collected at 30 cm - Treatment: seeds sterilized with 0.001 M $HgCl_2$ - Germination: on paper at 25 °C, dark for one week - Pots: 10 (30 x 30 depth x diameter) - Treatments: control (soil); soil+ SS (2.5, 5, 7.5%) - Planting: pots filled up to 26 cm and after 5 days, 3 germinated seeds were added. - Cycles: 12/12 h - Photosynthetic flux: 300 µmol m^2 s^{-1} - T: 24-18 °C (day-night) - Relative humidity: 60-70% - Harvest: vegetative phase (i.e., 50 days after cultivation)	- SS increase Pb, Ni, Cu, Cr and Zn concentrations in soil - Soil pH decreased (control = 7.86, while SS: 7.5% pH 6.66) - EC increased (0.40, 0.89, and 1.89 mS cm^{-1} for control, SS:5%, and SS:7.5%) - Equal increase for OM (0.67, 2.81 and 3.88%), N-total (0.04, 0.3 and 0.36%), available P (0.5, 20.67, and 30.76 mg kg^{-1}) for control, SS:5% and SS:7.5% - Metal concentration was higher in plant tissues grown in muddy soils. The ranking of metal accumulation in shoots was Cr > Ni > Cu > Zn - Higher phytotoxic effect at the rate of SS:7.5%	[4]
AD SS	- Culture: *Larix decidua* - Soil: sandy loam collected at 20 cm, sieved a 1 cm mesh size - Pots area: 0.0225 m^2 - Treatments: 3 control (soil); soil+SS (30-S1 and 60 mg ha^{-1} - S2); 5 replicas of each - Cycle: 14/10h - Photosynthetic flux: 200 µmol m^2 s^{-1} - T: 24-14 °C - Relative humidity: 60% - SS applied volume: 1.06 and 2.12 L for S1 and S2 - *t*: 6 weeks	- Increased N and P content in the topsoil and no changes appeared in the bottom soils. - Despite the increase of N, there was no damage to the seedlings during the test. - The application of SS in the soil did not increase the metal content	[5]
SS Industrial (tanning, electroplating, and glass)	- Culture: *Sorghum bicolour L.* - Soil collected between 0-25 cm - Blend: (1:3 w/w), and other with 5% CaO - two materials (LSW - lime SS; NLSW - non-lime) - Blends were dried for 8 days and sieved through a nylon sieve (75 µm mesh screen) - Pots: 45 x 35 x 35 cm (length × width × height) - Cycle: 15/9 h - T: 40-45 °C and 25-30 °C - Photosynthetic flux: 400-700 nm	- 5% lime increased SS pH from 7.33 to above 9 - LSW raised pH and reduced availability of most elements, except Cd (37%) and Cu (7.1%) which increased mobility - Metal concentration in sorghum grain was within the normal range for herbaceous plants (5 - 20 mg kg^{-1}_{db}) - As, Cr, Ni, Pb, and Zn (mg kg^{-1}) was higher in NLSW treatment compared to LSW - In the NLSW treatment, Cu and Cd were 9.9 and 1.36 mg kg^{-1}_{db}, while 10.1 and 1.42 mg kg^{-1}_{db} in LSW treated sorghum grains. - Research showed that increased soil alkalinity (liming) allows the use of industrial SS even at high PTM concentration.	[6]

Refs.: [4]- (Belhaj et al., 2016); [5]- (Bourioug et al., 2014); [6]- (Jamali et al., 2007).

2.8.2   *Composting use*

Composting is an aerobic process, where biodegradable OM is used by the microorganisms, releasing of heat and thus causing a temperature increase up to 70-75 °C. The temperature rise (e.g., 55

°C) for an extended period between a day to weeks can inactivate pathogenic microorganisms (Lu et al., 2012). The batch process displays a temperature profile that can be divided into three stages (i) mesophilic phase, where the temperatures are lower or equal to 40 ºC; (ii) thermophilic phase, where the temperature is higher than 40 ºC; (iii) maturation phase, where the temperature decreases approaching ambient conditions (Świerczek et al., 2018).

The moisture content present in composting is a critical factor as the bacterial activity is limited to minimum values of 12 to 15%, and above 60% it is difficult to maintain aerobic activity in the system. Thus, conventional WWTP dewatering processes do not allow direct composting due to the high moisture content (~ 80%). Ideal humidity is between 40-50%. The ideal pH range for the growth of most bacteria is between 6-7.5 and for fungi is between 5.5-8.0. Although the C/N ratio around 30 is desirable, ratios around 25 and 35 provide good conditions. At the end of the process, C/N ratio is reduced, favouring nitrogen loss (Hung et al., 2007).

The thermophilic stage is very effective in inactivating pathogenic bacteria. For example, *Salmonella*, *Typhimurium,* and *Mycobacterium paratuberculosis* are inactivated within 24 h under thermophilic conditions, while under mesophilic conditions, the process may take weeks or months for the complete removal of these pathogens. By increasing the temperature to 70 °C for at least 30 min (pasteurization process), it is possible to kill *Salmonella* ssp. (Arthurson, 2008).

Ignatowicz and co-works (2017) considered composting of SS with 30% sawdust for 60 to 70 days. At the end of the experiment, the authors found that dry matter was 41.33% and carbon increased from 450.50 g kg^{-1}$_{db}$ in SS to 490.14 g kg^{-1}$_{db}$ (SS:Sawdust). Ca content decreased with the addition of sawdust (25.30 to 9.5 g kg^{-1}$_{db}$). N and P in the SS to the mature compound was reduced from 40.6 to 11 g kg^{-1}$_{db}$ and from 43 to 41g kg^{-1}$_{db}$, respectively. K was in low concentrations (Ignatowicz, 2017).

Finally, after compost application to soil, permanent monitoring (soil biodiversity and microbial cycles) is required, especially if SS comes from anaerobic digestion systems. Although SS is stabilized in terms of OM, it can still contain a high level of N (Rorat et al., 2019).

2.8.3   Incineration

As mentioned in Chapter 1, SS needs drying treatment before incineration. The typical HHV of SS is 17–18 MJ kg^{-1}$_{db}$ for raw sludge, 14–16 MJ kg^{-1}$_{db}$ for active sludge, and 8–12 MJ kg^{-1}$_{db}$ for AD SS (Đurđević et al., 2019; Payá et al., 2019; Tsotsas and Mujumdar, 2014). Drying plays an essential role in increasing the dry solids content in SS when the objective is thermal recovery. For the incineration of SS with 30% < TS < 45%, it is necessary to supply 3-5 MJ kg^{-1}$_{db}$ (LHV), while for pyrolysis/gasification process about 14 MJ kg^{-1}$_{db}$ is required. Figure 2.24 shows the main thermal technologies for SS management, which include incineration, co-incineration (SS with other materials), and alternative processes (pyrolysis and gasification).

Wet SS
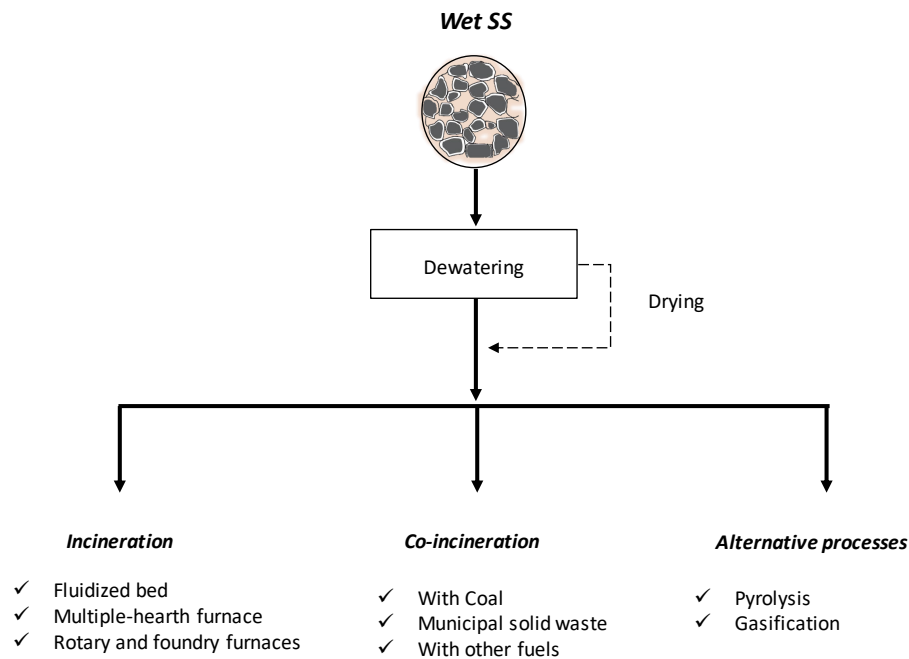
Figure 2.24 - Main thermal technologies for SS management (Adapted from Rorat et al., 2019; Werle and Wilk, 2010).

The differences between these three processes are the operating temperature and the gaseous atmosphere. Among the thermal recovery processes, incineration has been well documented for SS (Syed-Hassan et al., 2017; Tsotsas and Mujumdar, 2014). Figure 2.24, and Table 2.18 shows the main characteristics of SS thermal recovery processes.

Table 2.18 - Main characteristics of thermal processes for SS energy recovery (Adapted from Đurđević et al., 2019; Syed-Hassan et al., 2017; Tsotsas and Mujumdar, 2014).

Technology	T (ºC)	Mains comments
Incineration [1]	About 900	✓ Mechanism: exothermic
		✓ Gaseous atmosphere: air
		✓ Air ratio: about 200%
		✓ Outputs of the process: flue gas and ash
		✓ Autoignition: close to 600 ºC
Pyrolysis	300 - 800	✓ Mechanism: endothermic at 500 ºC and slightly exothermic at a higher temperature
		✓ SS needs to have at least 95%$_{DS}$
		✓ Outputs of the process: combustible gases composed mainly of CH_4, H_2, CO and CO_2, pyrolytic oil (bio-oil), biochar and solids
		✓ Heating values for bio-oil (30-37 MJ kg^{-1}; gas (syngas) 15-20 MJ m^{-3})
		✓ Slow pyrolysis (carbonization): low heating rates with long periods (from hours to days) for biochar production
		✓ Fast pyrolysis: Heating rate occurs at 10–200 ºC s^{-1}, to maximize liquid bio-oil production
		✓ Flash pyrolysis: Occurs at warming rates of 103–104 ºC s^{-1}
		✓ Residence time: Fast pyrolysis is 0.5–10 s (typically < 2), and flash pyrolysis is < 0.5 s

Table 2.18 (cont.) - Main characteristics of thermal processes for SS energy recovery (Adapted from Đurđević et al., 2019; Syed-Hassan et al., 2017; Tsotsas and Mujumdar, 2014).

Technology	T (ºC)	Mains comments
Gasification	800-900	✓ Gasification is an exothermic process to produce gaseous energy composed of H_2, CO, CO_2, and light hydrocarbons, through chemical reactions ✓ Depending on the gasifying medium (air, oxygen, steam or carbon dioxide or mixtures thereof) gases with a heating value from 4-7 MJ Nm^{-3} or 12 to 28 MJ Nm^{-3} (with O_2) can be produced ✓ Gas can be used to generate electricity via combustion in a boiler, engine and gas turbine, or via a fuel cell application

[1] This alternative is mainly used for management purposes, e.g., volume reduction and destruction of harmful substances.

SS incineration occurs at elevated temperatures in an environment with excess oxygen. The process occurs in six steps: drying, devolatilization + self-gasification, volatile combustion, ash fusion, coal combustion, and agglomeration of ash. The main by-products of incineration are CO_2 and H_2O, while the process releases large amounts of heat and other traces of gases. Co-incineration eliminates the need for large capital investments since existing facilities can be used to process SS without major modifications. Co-incineration may occur with coal, municipal solid waste, other biomass, or in a cement kiln (Syed-Hassan et al., 2017).

In 2015, incineration in the EU accounted for 19%, and by 2020 at least 30% is expected (Kleemann et al., 2017; Kominko et al., 2019). However, in some countries such as the United Kingdom, incineration is declining due to its high operating costs. Incineration can be adequate when SS does not have characteristics for direct application to the soil. One of the most relevant aspects is the final volume reduction (~ 95%), destruction of pathogens, and the energy recovery (Świerczek et al., 2018). At the end, the remaining ash is rich in silica, alumina, calcium oxide, and iron oxide. In this form, metals are stabilized, reducing the potential risk to the environment (Đurđević et al., 2019; Rorat et al., 2019). Depending on the levels of PTM in the ash, it can be applied to agriculture. However, the recovery of phosphorus from ashes from co-incineration plants is not yet feasible unless they come from mono-incineration systems.

The costs associated with incineration are in the range of 200 and 400 € t^{-1}_{db}, while for co-incineration range from 150 and 300 € t^{-1}_{db}. Incineration of SS is a potential source of harmful substances such as dioxins, furans, and heavy metals in flue gases (Werle and Wilk, 2010). Also, it is essential to emphasize that this alternative is not in line with the circular economy model for OM reuse, nutrients (e.g., N) and CO_2 emission levels (Đurđević et al., 2019; Kominko et al., 2018).

Kleemann and co-workers compared the effect of incineration and pyrolysis (conventional at 550 °C) on SS ash for P recovery. Leaching tests at L/S ratio 10 L kg^{-1}, showed that P extracted from the pyrolysis ash was higher than those found in the incineration ash. Also, tests demonstrated that the PTM content was less soluble due to the metals were strongly embedded in the SS particles and were not volatilized as in incineration (Kleemann et al., 2017). Many studies indicate that SS ash from incineration can be incorporated into construction materials (e.g., mortars or concrete preparations) (Chen and Poon, 2017).

Wang et al., (2019) investigated the use of incineration ash as an adsorbent to remove PTM (Cd (II), Cu (II) and Zn (II)). The adsorption capacity was 0.13, 0.11, and 0.06 mmol g^{-1} for Cd, Cu, and Zn, respectively.

2.9   References

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3. ANALYSIS OF POTENTIALLY TOXIC METALS CONSTRAINTS TO APPLY SEWAGE SLUDGE IN PORTUGUESE AGRICULTURAL SOILS

The application of sewage sludge (SS) in the soil can be a valuable way to increase its content of organic matter. However, the concentration of potentially toxic metal (PTM) in both SS and soil can hinder this route of management. Thus, the main objective of this work was to evaluate the compliance with the restrictions related to PTM contained in SS from wastewater treatment plants (WWTP) for agricultural land application. The analysis of the amount of SS produced at the national level, the regulatory constraints associated with SS and soil in respect to PTM (Cd, Cr, Cu, Ni, Pb, and Zn) were analysed. These metals showed a deleterious effect on germination of *Lepidium sativum L.* seeds, and their phytotoxicity may be ranked as Cd > Cu > Cr(VI) > Cr(III) ~ Zn ~ Ni > Pb. Portuguese SS samples from different WWTP, from a national sludge management operator and from the literature were analysed. The results showed that the content of these metals, in general, complies with the regulatory thresholds values. The content of PTM in the soil is not restrictive to receive SS in at least 90% of the national territory. The assessment of ecological risk based on the geoaccumulation index (I_{geo}), pollution index (PI) and potential ecological risk index (PERI), showed low risk for all metals. The exception was I_{geo} of Cd, Cu, and Zn, which presented moderate to high level of pollution. According to the state of the art, no significant negative impacts have been detected on human health and the environment due to SS applications in the soil. Thus, in a country with low carbon content in the land and whenever compliance with regulations is achieved, the main route for SS management may be agricultural soil.

Keywords: metals constraints, phytotoxicity, soil amendment, ecological risk, circular economy.

3.1   Introduction

The population growth on Earth and the constant demand for goods and services have boosted an increasing use of natural resources and water. The depuration of domestic wastewater is imperative for ecosystems protection. Wastewater treatment plants (WWTP) based on biological treatment have been widely used, but with the major drawback of creating huge quantities of sewage sludge (SS). The European Union (EU) countries have been struggling to accomplish national legislative requirements and guidelines for SS management, as well as to achieve acceptable indicators of sustainable development (Camargo et al. 2016; Praspaliauskas and Pedišius 2017; Gomes et al. 2018).

In Portugal, 1003 Mm^3 of water were supplied and about 627 Mm^3 of wastewater were treated in 2015 (RARSAP, 2016). The water supply and treatment services cover more than 80% of the population, and the production of sewage sludge (SS) is likely more than 300 kt in dry basis (db) $year^{-1}$ (LeBlanc et al., 2008; RARSAP 2016), which may represent about 30 kg $inhab^{-1}$ $year^{-1}$. The annual per capita generation in the EU countries ranges from 15 to 30 kg_{db} $year^{-1}$ and it is estimated that the annual production of SS in the EU in 2020 will be close to 13×10^3 kt_{db}. This represents a value of around 0.09 kg $inhab^{-1}$ day^{-1} (Fytili and Zabaniotou 2008; Cimochowicz-Rybicka 2013; Mininni et al., 2015; Collard et al., 2017).

Regarding the management of SS produced in WWTP, the main objectives are to reduce the volume, the transport costs, the pathogens and the smell stress in the population (Evans, 2016). To achieve these goals, some intermediate and final technologies are available and applied in developed countries. The intermediate technologies comprise mechanical dewatering, biological treatment (anaerobic digestion and composting), chemical treatment (e.g., lime stabilization) and thermal drying. Final treatments may include valorisation in agriculture, land recuperation, incineration and landfilling. In Europe, the costs of management may represent 30 - 100 € t^{-1}SS (wet basis) (Cimochowicz-Rybicka 2013; Chan and Wang 2016; Healy et al., 2016; Kruger et al., 2014). Each EU country may favour different options to manage SS among the routes allowed: agricultural use (directly or after composting), incineration, landfill or other. For example, Germany tends to favour incineration in mono or co-incineration plants, and this option represents more than 55% (Wiechmann et al., 2013). On the opposite, in Portugal, the main option is the agricultural valorization, which represents more than 50% (APA, 2013; APA, 2017).

Although the land spreading of SS for agriculture purposes is not a consensual option due to technical and social obstacles (Fytili and Zabaniotou 2008; Wiechmann et al., 2013; Evans, 2016), in the present study this will be the route considered. Indeed, several researchers have emphasized that nutrients (e.g., P, N, and K) and organic matter (OM) presented in the SS can improve the physicochemical properties of the soil, with a positive influence in water retention, promotion of cation exchange and improvement of porosity (Alvarenga et al., 2015; Kelessidis and Stasinakis 2012; Kirchmann et al., 2017; LeBlanc et al., 2008; Stefanakis and Tsihrintzis 2012). Another relevant issue is the fact the OM conveyed in SS tends to reduce leaching processes in soil, which reduces the

possibility of contamination of aquatic bodies, and with a positive contribution to soil carbon sequestration (Lal 2003; Fernández et al., 2007; LeBlanc et al., 2008). The main risks of using SS on land applications are associated with several chemicals (including potentially toxic metals) used in households and pathogens (Wiechmann et al., 2013; Evans, 2016). Although some countries are in phase-out of agricultural SS use, there are several (Denmark, France, Ireland, Portugal, Spain, and the UK) where this is the major route (Evans, 2016). The application of SS for soil amendment was regulated by European legislation by the Directive 86/278/EEC, of 12 June 1986, aiming at the environment protection, and in particular the soil, when sewage sludge is used in agriculture. The EU countries transposed it in national law, with the recommended or by setting stricter limits for each limited parameter. In Portugal, this Directive was transposed by *Decreto Lei Nº. 276/2009*, of 2 October 2009, which regulates not only SS from domestic WWTP (code 190805, 200304 and 020199 in the European Waste Catalogue - EWC) but also others with a similar composition (020305, 020403, 020502, 020603, 020705 and 030311). Among the rules established by the *Decreto Lei Nº. 276/2009*, the responsibilities of the SS management operator (SMO) are also indicated. In practice, the application of SS in the soil by SMO must comply with all legislation restrictions, namely the ones associated with the soil, the SS and the rates of application. In particular, the role of the regulatory restriction regarding potentially toxic metals (PTM), such as Cd, Cu, Ni, Pb, Zn, Hg and Cr is of particular importance (Smilde 1981; Kahapanagiotis et al., 1991; Cole et al., 2001; Dimitriou et al., 2006; Healy et al., 2016; Tóth et al., 2016; Duan et al., 2017; Mattsson et al., 2017). These metals are of concern because of their persistence in the environment, bioaccumulation and due to the possibility of its incorporation into the food chain (Kahapanagiotis et al., 1991; Rieuwerts et al., 1998; Cole et al., 2001; Ke et al., 2017; Duan et al. 2017). However, some studies indicate clearly that the amount of those PTM in SS tends to decrease over time (Olofsson et al., 2012; Wiechmann et al., 2013; Evans, 2016; Fijalkowski et al., 2017; Kirchmann et al., 2017), which is a very positive aspect in the case of soil application. Nonetheless, the ecological risk assessment should be addressed to evaluate the real threat to ecosystems (Loska et al., 2004; Fan-Xin et al., 2016; Duan et al., 2017; Ke et al., 2017). In addition, it is important to note that the Directive 86/278/EEC regulates the use of SS in agriculture over more than 30 years, and a draft of a new EU Directive is under discussion for too long (3rd draft version) (ECWD, 2000). Thus, there is an urgent need for a new Directive with updated criteria.

Hence, this study aims to evaluate the constraints associated with toxic metals contained in SS from WWTP for applying to the Portuguese national territory. Constraints imposed on toxic metals in both the soil (depending on their pH) and in the SS will be addressed for Cd, Cr, Cu, Hg, Ni, Pb, and Zn. Phytotoxicity and ecological risk related to those metals will be assessed.

3.2   Materials and methods

3.2.1   Sampling and data collection

Five samples of SS from the Central Region of Portugal were collected (SS1 to SS5), in WWTP with primary and secondary treatments, after mechanical dewatering by filtration or centrifugation. Besides, five samples from a national sludge management operator (SMO) were considered (SMO1-SMO5). In Table S 3.1 of the supplementary information, the main properties of samples SS1-SS5 and SMO1-SMO5 are summarised. In addition, data related to Portuguese SS samples (PT) were collected from the literature (Alvarenga et al., 2015; Bancessi 2009; Lopes 2017; Mendes 2014; Serrão et al., 2007; Sousa 2005). The number of samples for each toxic metal in PT samples from the literature was Cr (n=10); Ni (n=14); Cd (n=15); Pb (n=14); Cu (n=14); and Zn (n=15). The number of samples from Spain (SP), Germany (DE), United Kingdom (UK), Poland (PL), Sweden (SE) and Netherlands (NL) was $n \geq 3$ and the data was obtained from reports and scientific papers (Cole et al., 2001; Di Maria and Micale 2017; Dimitriou et al., 2006; Eriksson 2001; Fijalkowski et al., 2017; Fuentes et al., 2006; González et al., 2017; Herzel et al., 2016; Kahapanagiotis et al., 1991; Kołecka et al., 2017; Mattsson et al., 2017; Milik et al., 2017; Panepinto et al., 2016; Pathak et al., 2009; Rizzardini and Goi 2014; Roig et al., 2012; Kleemanna et al., 2017; Urbaniak et al., 2017; Marchioretto 2003; Smilde 1981; Veeken and Hamelers 1999). As a selection criterion to get data from the literature, only SS samples from urban WWTP with secondary treatment were considered.

Concerning the Portuguese soil, the data was obtained from the literature (Inácio et al., 2008), where 652 sites from the continental area of Portugal were considered, at a density of 1 site per 135 km^2. The samples were representative of "natural soils" and within the upper mineral horizons of the finer fraction soil (FF) < 0.18 mm, coarse fraction soil (CF) < 2 mm, and humic fraction soil (HFF) < 0.18 mm. The number of soil samples for the category HFF were from 195. In addition, thirty soil samples characterized by SMO were also included in this study as representative of agricultural soil receptor (ASR) (Table S 3.2 of the supplementary information).

3.2.2   Analytical procedures

The quantification of metals in SS1 to SS5 samples involved a drying phase at 105 °C for 24 hours. Then, the samples were milled and heated to 550 °C for 2 hours in a muffle furnace to remove the organic matter (USEPA 2001). The remaining inorganic fraction was ground in a mortar to particles with a diameter ≤ 200 mesh. Subsequently, 0.5 g of SS ash were digested with 16 mL of aqua regia, for 4 hours under heating, at a temperature ≤ 97 °C (Saxena and Nielsen 2004). The samples remained overnight in contact with a few milliliters of aqua regia and then were filtered through a 0.45 μm porosity filter. The toxic metals Cd, Cr, Cu, Ni, Pb, and Zn were analyzed by flame atomic absorption spectrometry (FAAS) using a Perkin Elmer 3300 spectrometer.

Moisture and OM were determined by gravimetric method (after achieving constant weight at 105 and 550 ºC, respectively). pH was measured in a 1:10 (mass:volume) suspension (Alvarenga et al., 2016; Oleszczuk and Hollert, 2011). Oxides were analyzed by X-ray fluorescence (XRF) using a Nex CG Rigaku spectrometer (Healy et al., 2016). Statistical analysis (one-way ANOVA p < 0.05) was performed using Microsoft Excel® 2013 to identify the significant differences between samples through the Tukey HSD test (p < 0.05).

3.2.3   Phytotoxicity tests

The phytotoxicity tests involving specific metal solutions were conducted with *Lepidium sativum L.* (garden cress). This plant was used because of its sensitive cultivate, fast growth and low cost (Pavel et al., 2013). Then*,* ten seeds placed on each filter paper, in each Petri dish 90 mm diameter. Afterward, 5 mL of each metal solution was added to the seeds and incubated in an oven at 25±1 ºC for 48 hours, in the dark conditions (Munzuroglu and Geckil 2002; Pinho et al., 2017). A germination rate of over 90% demonstrates the accuracy of this test (Visioli et al., 2013). These tests were done in duplicate and included a control with distilled water (Ozdener and Kutbay 2009; Pinho et al., 2017). Solutions with variable concentrations from 25 to 400 mg L^{-1} (0.2 - 1.9 mM) were tested for each toxic metal. Table 3.1 summarizes the salts used for preparing each stock metal solutions, as well as the corresponding pH and electrical conductivity (EC). A multi-metal solution containing 7.14 mg L^{-1} of each metal was tested. Results were analyzed through one-way ANOVA (p > 0.05) using Microsoft Excel® 2013.

Table 3.1 - Salts used in phytotoxicity tests, pH and EC measured in a stock solution of 50 mg L^{-1}.

Element	Salt - brand	pH	EC (mS cm^{-1})
Cd	Cd (NO$_3$)$_2$ 4H$_2$O – Aldrich®	4.41	0.741
Cr (III)	Cr (NO$_3$)$_2$ H$_2$O – Alfa Aesar®	2.95	0.993
Cr (VI)	K$_2$ Cr$_2$O$_7$ 2H$_2$O – Panreac	3.23	0.435
Cu	CuCl$_2$ 2H$_2$O – Riedel-de Haën	4.83	0.427
Ni	NiSO$_4$ 6H$_2$O – Sigma Aldrich®	3.65	0.413
Pb	Pb (NO$_3$)$_2$ – Alfa Aesar®	3.12	0.387
Zn	ZnSO$_4$ 7H$_2$O – Sigma Aldrich®	5.35	0.391
Multi-metal solution	All above salts	3.31	0.422

EC - Electric conductivity.

The relative seed germination (RSG), the relative root growth (RRG), and the germination index (GI %) were calculated by Eq. (3.1) to Eq. (3.3), respectively.

$$RSG = \frac{\overline{N}}{\overline{N}_{control}} \, 100 \tag{3.1}$$

$$RRG = \frac{\overline{L}}{\overline{L}_{control}} \, 100 \tag{3.2}$$

$$GI = \frac{RSG \times RRG}{100} \tag{3.3}$$

where $\bar{N}$ is the mean of seed germinated and $\bar{L}$ is the mean of root length. The GI results are classified as non-phytotoxic if GI > 80%; mild phytotoxicity 60% < GI < 80%; strong phytotoxicity 40% < GI < 60%; severe phytotoxicity GI < 40% (Pinho et al., 2017).

3.2.4   Ecological risk assessment

The ecological risk assessment was based on the geoaccumulation index (I_{geo}), the pollution index (PI) and the potential ecological risk index (PERI). These parameters were calculated using 25 samples of SS from mainland Portugal.

3.2.5   Geoaccumulation index

The I_{geo} index can be defined as indicated by Eq. (3.4), (Duan et al., 2017; Ke et al., 2017),

$$I_{geo} = log_2 \left(\frac{C_n}{1.5Bn} \right) \tag{3.4}$$

where C_n (mg kg^{-1}) represents the content of a specific metal (n) in SS; B_n (mg kg^{-1}) is the background concentration of the toxic metal (n) in soil; and the constant 1.5 is an adjustment factor to the lithosphere layer to detect very small anthropogenic influences (Loska et al., 2004). The B_n used in the present work refers to the medium values found in the fine fraction (FF) of the Portuguese soil (Inácio et al., 2008): 26 mg of Cr kg^{-1}, 22 mg Ni kg^{-1}; 26 mg Pb kg^{-1}; 21 mg Cu kg^{-1}; and 59 mg Zn kg^{-1}. Regarding Cd, the background concentration used was 0.098 mg Cd kg^{-1}, which corresponds to the average crustal abundance (Taylor and McLennan 1995). The choice of the FF of soil was due to the superficial layer contain the major chemical and biological human activity influence (Ke et al., 2017). The I_{geo} was categorized according to levels shown in Table 3.2 (Duan et al., 2017).

3.2.6   Pollution index

The pollution index (PI) is obtained by Eq. (3.5) (Duan et al., 2017; Fan-xin et al., 2016).

$$PI = (C_i) / (S_i) \tag{3.5}$$

where C_i (mg kg^{-1}) is the concentration of the metal i in SS; and S_i (mg kg^{-1}) is the legal threshold to apply SS to agricultural soil, according to Portuguese law (*Decreto Lei Nº.* 276/2009) for each metal *i*. In Table 2 the levels considered to PI are indicated.

Table 3.2 - Levels and classification associated with I_{geo} and PI indexes.

I_{geo}	Levels	Pollution degree based on I_{geo}	PI	Risk associated with PI
≤ 0	0	Practically unpolluted	≤ 1.0	No contamination
0 - 1	1	Unpolluted to moderately polluted	1.0 - 2.0	Low level of contamination
1 - 2	2	Moderately polluted	2.0 - 3.0	Moderate level of contamination
2 - 3	3	Moderately to heavily polluted	3.0 - 5.0	Strong level of contamination
3 - 4	4	Heavily polluted	> 5.0	Very strong level of contamination
4 - 5	5	Heavily to extremely polluted		
≥ 5	6	Extremely polluted		

3.2.7   *Potential ecological risk index*

The PERI considers the potential ecological risk of toxic metals contained (Ke et al., 2017), by combining the pollution level on SS with the environmental effect. The potential ecological factor in SS, E_r^i, is calculated through Eq. (3.6) and the potential ecological risk index, PERI, can be calculated by Eq. (3.7),

$$E_r^i = T_r^i \,(C_i/C_0) \qquad\qquad\qquad (3.6)$$

$$\text{PERI} = \sum E_r^i \qquad\qquad\qquad (3.7)$$

where C_i is the metal concentration in SS; C_0 is the background concentration in the soil; T_r^i is the biological toxicity factor of each individual toxic metal and takes the value 30 to Cd; 5 to Cu, Pb, Ni; 2 to Cr; 1 to Zn. Thus, the PERI in respect to toxic metals may be classified as summarized in Table 3.3.

Table 3.3 - Classification of potential ecological risk index (PERI).

Assessment criterion	Low	Moderate	Considerable	High	Very high
E_r^i	< 40	$40 - 80$	$80 - 160$	$160 - 320$	≥ 320
PERI	< 150	$150 - 330$	$300 - 600$	> 600	

3.3   Results and discussion

3.3.1   *SS produced in Portugal and in some European countries*

The amount of SS generated in WWTP at a national level has been difficult to determine. Looking through Eurostat databases (http://ec.europa.eu/eurostat/) only 8 out of 28 countries from the EU communicated data for the period of 2004 to 2015 (namely Bulgaria, Czech Republic, Germany, Hungary, Poland, Slovenia, Slovakia, and Sweden). Considering 2012 as a reference year, the specific production of SS, in dry bases, is varied, Figure 3.1 (a). For example, 23.0 kg inhab^{-1}year^{-1} was found for Germany, 21.8 kg inhab^{-1}year^{-1} for Sweden, 18.3 for the UK and 14.0 kg inhab^{-1} year^{-1} for Poland, while 31.9 kg inhab^{-1}year^{-1} was found to Portugal. Indeed, the data available for Portugal is scarce (only three years 2007, 2009 and 2012 were found in Eurostat). From the analysis of the Report COM (2017) of EU for the period 2010 to 2012, some data agree with the Eurostat databases, but in other cases, significant discrepancies are observed. The National Environmental Protection Agency (APA) recently released data for the years from 2010 to 2014, but inconsistent figures are still in these reports (APA, 2013; APA, 2017). Figure 3.1 (b) shows the evolution of the quantity generated for 7 European Countries. Germany shows a dominant position, but the production has been reduced slightly over time from 2261 kt in 2004 to 1821 kt in 2015 (a reduction of 19 %). The profiles of the UK and Spain are uncertain after 2010. The production of Poland seems small compared with the population. The amount produced in Portugal seems in the range of Sweden and the Netherlands, which sounds acceptable since

the population is similar in these countries. According to the analysis of all available data, it seems reasonable that the SS production in Portugal may be 300-350 kt year^{-1}.
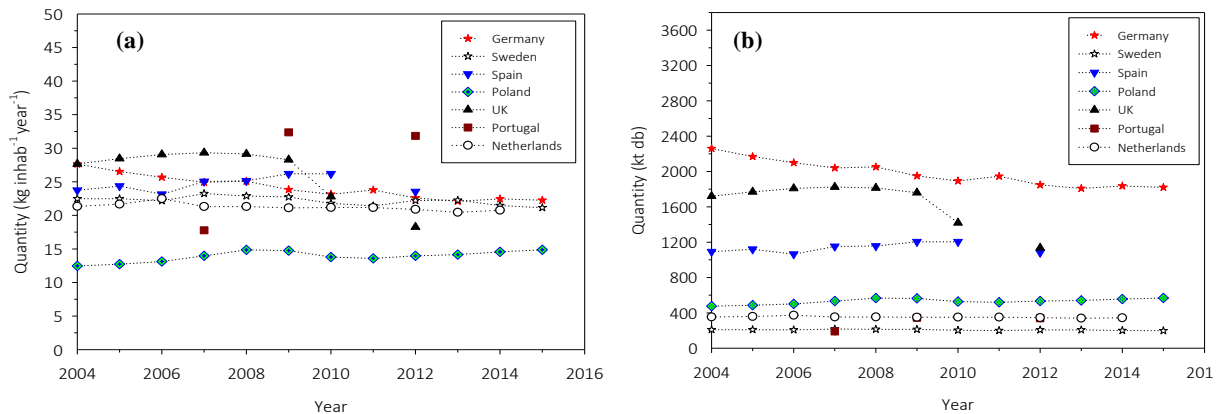
Figure 3.1 - (a) Specific quantity, and (b) Total quantity of SS generated (dry base) in some EU countries from 2004 to 2015 according to Eurostat databases.

3.3.2   *Regulatory limits for applications of SS in agriculture*

The Directive 86/278/EEC established the constraints with respect to soil and SS for agriculture applications in the EU. This directive was transposed into Portuguese law, *Decreto Lei Nº.* 276/2009, imposing limits for specific metals, organic contaminants, and pathogenic microorganisms. Table 3.4 shows the limits of toxic metals in the soil as a function of the pH, which are more restrictive for acidic than for alkaline soils. This is related to the leaching behavior associated with these metals since low pH promotes higher mobilization into the environment. It is important to note that these limits are at least 1.5 times higher than the average crustal abundance (Taylor and Mclennan 1995).

Table 3.4 - Limit concentration for toxic metals content in the soil for receiving SS and average crustal abundance (mg kg^{-1}_db).

Element	Limits in soil [1]			Mean crustal Abundance [2]	Mean content in FF of Portuguese soil [3]
	pH < 5.5	5.5 < pH < 7	pH > 7		
Cd	1	3	4	0.098	NA
Cu	50	100	200	25	21
Ni	30	75	110	20	22
Pb	50	300	450	20	26
Zn	150	300	450	71	59
Hg	1	1.5	2	na	0.056
Cr	50	200	300	35	26

Refs.: [1]- Portuguese law (*Decreto Lei Nº.* 276/2009); [2] - Taylor and Mclennan (1995); [3]- Inácio et al., (2008); na – not available.

Table 3.5 indicates the limits (mg kg^{-1}_db) allowed in SS for use it in agriculture in different EU countries (Portugal, Sweden, Germany, France, Spain, Poland, and the Netherlands), America (Brazil, Canada, the USA), UK and India.

Table 3.5 - Maximum concentration (mg kg^{-1}$_{db}$) of potentially toxic metals in SS for agronomic applications in different countries.

PTM	Portugal [1]	Sweden [2]	Germany [2, 3]	UK [2]	Spain [5]	Poland [2]	Netherlands [2, 4]	Brazil [6]	Canada [7]	USA [8]	India [7]
Cd	20	2	3	Regulated through limits in soil	20	10	1.25	39	3	85	5
Pb	750	100	150		750	500	100	300	150	840	100
Cu	1000	600	800		1000	800	75	1500	100	4300	300
Cr	1000	100	120		1000	500	75	1000	210	3000	50
Hg	16	2.5	2		16	5	0.75	17	0.8	57	0.15
Ni	300	50	100		300	100	30	420	62	420	50
Zn	2500	800	1800		2500	2500	300	2800	500	7500	1000

Refs.: [1]- *Decreto Lei Nº. 276/2009*; [2]- Mininni et al., (2015); [3]- Wiechmann et al., (2013); [4]- Inglezakis et al., (2014); [5]- Mosquera-Losada et al., (2017), Spanish Real *Decreto Nº. 1310/1990*; [6]- (CONAMA 2006); [7]- (Sharma et al., 2017); [8]- (U.S. EPA 1993) Part 503.

The use of SS in the soil may be important mainly in regions where the soil has low agronomic productivity (Mosquera-Losada et al., 2017). The legislation must safeguard the soil quality, and according to Table 3.5, different countries reveal also different criteria. Among European countries, the Netherland and Sweden are the most conservative. In any case, the monitoring of toxic metals in the environment is essential for avoiding their deleterious effect on human health and the environment (Fu and Wang 2011). According to data from the literature, the amount of toxic metals in SS has steadily decreased in developed countries. For example, in Germany Cu decreased from 378 mg kg^{-1}$_{db}$ in 1977 to 300 mg kg^{-1}$_{db}$ in 2006; Zn from 2140 to 714 mg kg^{-1}$_{db}$; Cr from 630 to 37 mg kg^{-1}$_{db}$; Pb from 220 to 37 mg kg^{-1}$_{db}$; and Ni from 131 to 25 mg kg^{-1}$_{db}$ (Wiechmann et al., 2013). Similar trends were reported for Sweden (Kirchmann et al., 2017), while for Portugal no data is available.

3.3.3   *Phytotoxicity of potentially toxic metals*

Lepidium sativum L. was used as test plant and Figure 3.2 (a - c) show the germination index (GI) at different concentrations of Cr(III), Cr(VI), Pb, Ni, Zn, Cu and Cd in the range 0.2 to 1.9 mM (or 25 to 400 mg L^{-1}). Molar instead of mass concentrations are used for comparative purposes. The GI results were obtained in the conditions of pH and EC presented in Table 3.1, which means that all tests were performed in acidic conditions (more relevant for the Portuguese soil).

In general, as the concentration of each metal increase, the root length decreases and consequently the GI of *Lepidium sativum L.* also decreases. All metals tested led not only to strong phytotoxicity (60 < GI < 40%, marked with horizontal red line), but also to severe phytotoxicity (GI < 40%). As an example, Cr(III) originates roots length ranging from 1.09 ± 0.34 cm to 0.25 ± 0.09 cm; whereas Cr(VI) led to roots in the range of 0.54 ± 0.12 cm to 0.21 ± 0.12 cm. The control samples originated an average root length of 1.8 ± 0.60 cm. Figure 3.2 (a) shows that while 0.5 mM of Cr (III) or Pb were not toxic, the same is not true for solutions with 1 mM. The half-maximum effective concentration, EC$_{50,}$ for Cr(VI) is lower than the observed for Cr(III) and Pb. Regarding the results shown in Figure 3.2 (b), Cd reveals the highest phytotoxic effect at 0.2 mM (GI about 26%). Cu also induces severe phytotoxicity at concentrations close to 0.4 mM. Zn and Ni may lead to severe toxicity in the germination, but only for higher concentrations (> 0.8 mM). Similar results of GI were reported by Visioli et al., (2013). In

particular, the effect of the metals in the GI found in the present study for Cd, Cu and Cr were similar to those obtained by other researchers (Pavel et al., 2013).
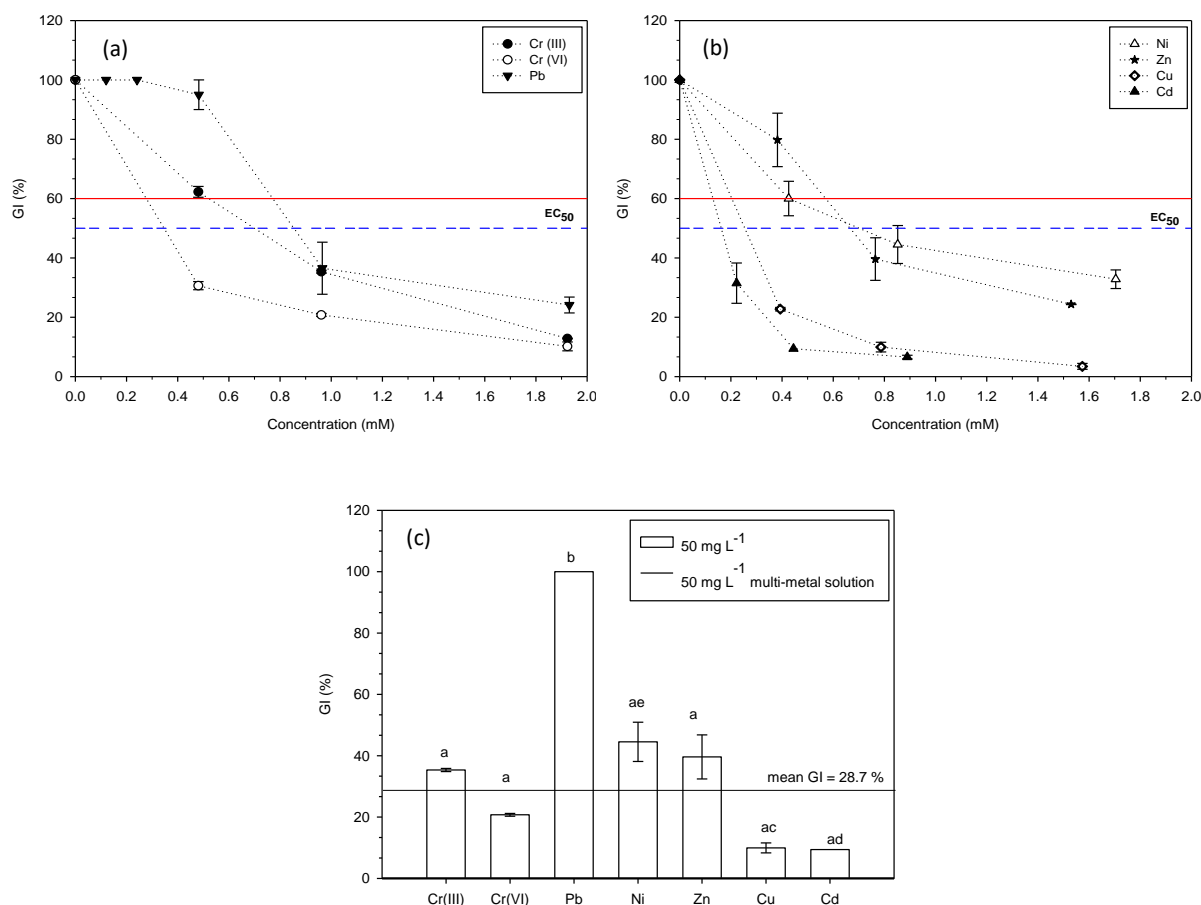
Figure 3.2 - GI of *Lepidium sativum L.* at different concentrations of (a) Cr (III), Cr (VI) and Pb; (b) Ni, Zn, Cu, and Cd; (c) in a solution of 50 mg L^{-1} for each element and for a multi-metal solution. (Results are represented as mean ± sd; the same letter means similar results, Tukey HSD test (p > 0.05).

According to EC$_{50}$, the rank of phytotoxicity for *Lepidium sativum L.* is Cd > Cu > Cr(VI) > Cr(III) ~ Zn ~ Ni > Pb. Figure 3.2 (c) shows the effect of a multi-metal solution (total concentration of 50 mg L^{-1}) on GI, which mean value was 28.7% (marked by the horizontal solid line). This means a severe toxicity, while 50 mg L^{-1} of Cd (or Cu or Cr(VI)) lead to an even higher detrimental effect. The opposite is true for Cr(III), Ni, Zn, and Pb. The effect of interactions between metals has been discussed in the literature (Das et al., 1998). The phytotoxicity is dependent on the chemical speciation of metals (Shahid et al., 2017) but in the present study, free metal ions were tested, because soluble salts were used to prepare testing solutions. Cd is the most phytotoxic metal, and its negative effect on the plant has been documented (Barcelo and Poschenrieder, 1990; Das et al., 1997 and Jiang et al., 2005). Also, some studies indicated that Cr(VI) may hamper seed germination due to suppression of enzymes which reduces sugar availability to develop the embryo. This metal may hinder root growth due to decrease in

cell division (Shahid et al., 2017). Moreover, it is well known that Cr(VI) can be very detrimental to human health, namely provoking skin irritation and lung carcinoma (Fu and Wand, 2011). Thus, the restrictive criteria indicated in Tables 3.4 and 3.5 aimed to protect human health and the environment.

3.3.4 Analysis of Portuguese soil constraints

The application of SS in the agriculture soil is dependent on the concentration of toxic metals and pH in the receptor soils, as shown in Table 3.4. Indeed, Figure 3.3 (a) reveals the distribution of pH in soil type FF and HFF (Inácio et al., 2008) that represents all continental Portuguese territory and for samples of agricultural soil receptor (ASR) characterized by a national sludge management operator (SMO). The interquartile range (Q25 to Q75) of pH is 4.5 to 5.6 for FF and HFF soil, and 5.1 to 6.8 for ASR samples. The acid nature (pH < 5.5) of the Portuguese soil is also highlighted in the literature (Serrão et al., 2007; Quina et al., 2017). The concentration range of the metals is shown in Figure 3.3 (b-h) for the FF, CF, HFF, and ASR soil samples, where the concentrations marked with x, y, and z correspond to the values indicated in Table 3.4 for pH < 5.5, 5.5 < pH < 7 and pH > 7.
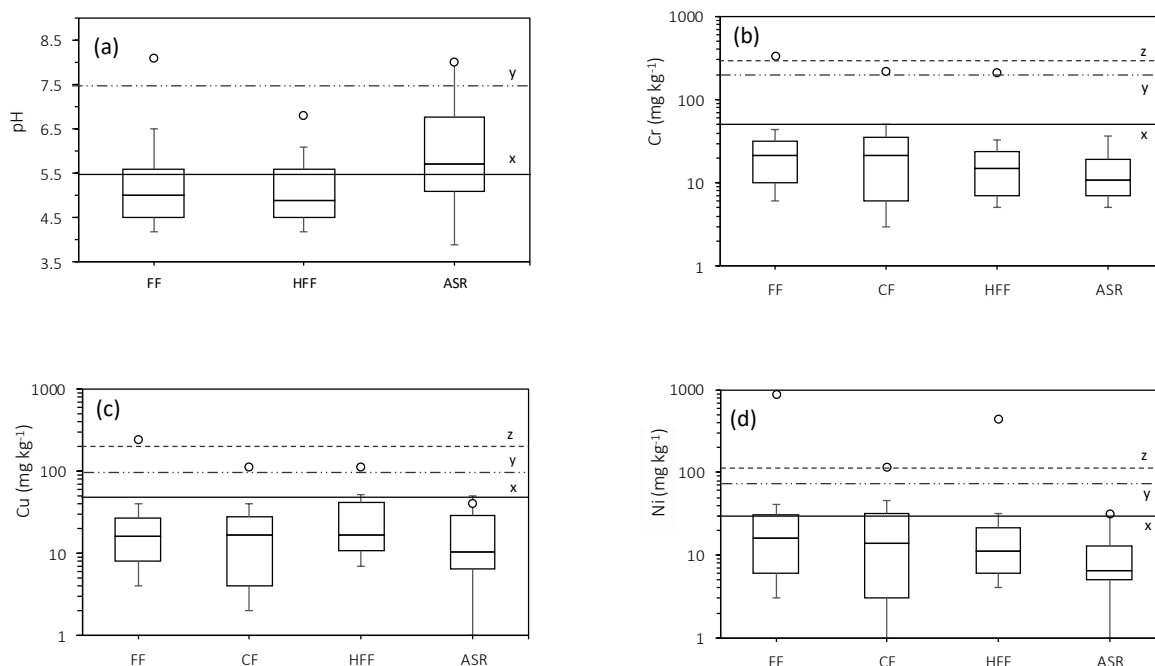
Figure 3.3 – Comparison of properties in Portuguese soil (FF, CF, FSH and ASR) and the limits x, y and z relative to pH ≤ 5.5; 5.5 < pH ≤ 7 and pH > 7, established by *Decreto Lei Nº*. 276/2009 for: (a) pH; (b) Cr; (c) Cu; (d) Ni; (e) Pb; (f) Zn (g) Hg and (h) Cd. (Box plot corresponds to $^{Q10}\!\!\vdash\!\!\boxed{^{Q50}}\!\!\dashv\!\!^{Q90}\circ^{Max}$).
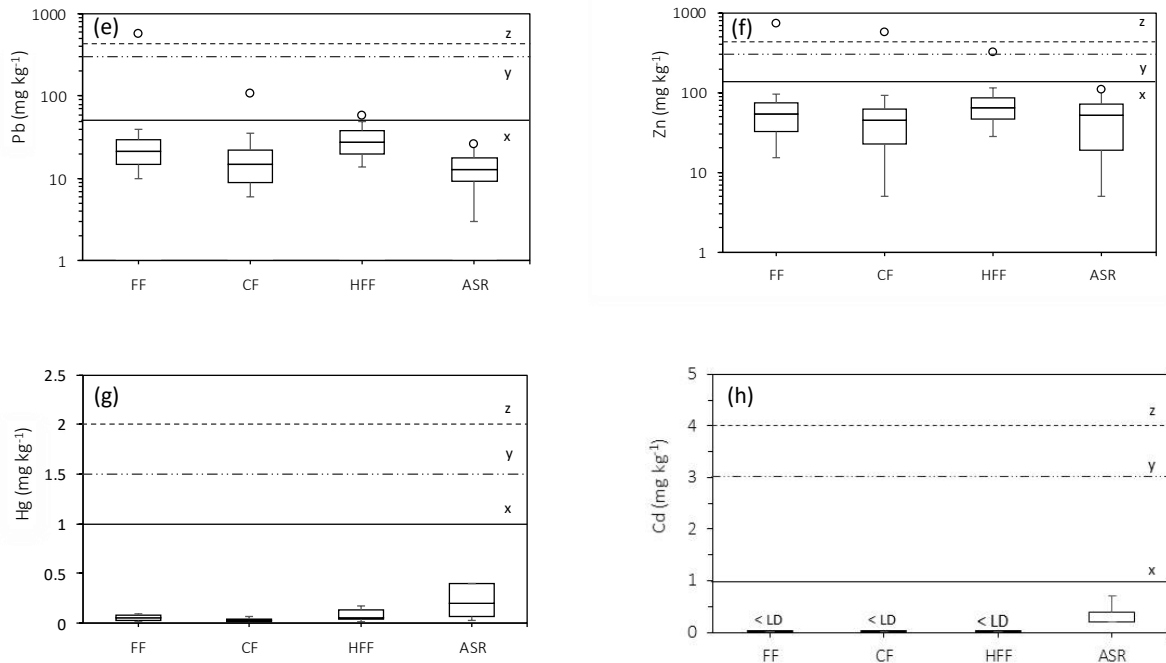
Figure 3.3 (cont.) - Comparison of properties in Portuguese soil (FF, CF, FSH and ASR) and the limits x, y and z relative to pH ≤ 5.5; 5.5 < pH ≤ 7 and pH > 7, established by *Decreto Lei Nº*. 276/2009 for: (a) pH; (b) Cr; (c) Cu; (d) Ni; (e) Pb; (f) Zn (g) Hg and (h) Cd. (Box plot corresponds to Q^{10} ⊢▭▭⊣ Q^{50} Q^{90} ∘ Max)

The interquartile concentration of Cr (Figure 3.3 b) is 10 to 35 mg kg^{-1} for FF, CF and HFF soil, which agrees with Taylor and Mclennan (1995) who indicated an average crustal abundance of 35 mg kg^{-1}. Although the maximum values were 336 mg kg^{-1} (FF); 223 mg kg^{-1} (CF) and 215 mg kg^{-1} (HFF), Q90 were only 44 mg kg^{-1}, 51 mg kg^{-1} and 33 mg kg^{-1}, for FF, CF and HFF, respectively. For the ASR sample, all values are below 50 mg kg^{-1}. Thus, in general, the Portuguese soil complies with the more restrictive Cr limit of 50 mg kg^{-1}.

Similar results are observed for Cu (Figure 3.3 c), since Q90 is 41, 40 and 36 mg kg^{-1} for FF, CF and HFF samples, respectively, and thus always below the limit of 50 mg kg^{-1}. Even the maximum values found were 245, 111 and 114, the limit of 100 mg kg^{-1} was hardly ever surpassed. The ASR samples are characterized by a Q95 of 39 mg kg^{-1}, which means that Cu is not a restrictive metal. The use of pesticides may influence the accumulation of this metal in the soil and in general the agricultural soil of Mediterranean countries are the most affected (Rieuwerts et al., 1998; Tóth et al., 2016).

Regarding Ni, the median values are near to 15 mg kg^{-1} and Q75 are near 30 mg kg^{-1} for FF, CF and HFF samples (Figure 3.3 d). The maximum concentration in samples ASR was 32.3 mg kg^{-1}. Thus, the lower regulatory limit of 30 mg kg^{-1} for pH < 5.5 can be exceeded in a few cases across the national territory. According to Figure 3.4, the most critical regions related to Ni are some areas in Trás-os-Montes, Alentejo, and Algarve. Probably this is due to the soil type (e.g., *leptosols* and *vertisols*), which is formed by metasediments and ultramafic rocks and contains high concentrations of Ni (Inácio et al., 2008).
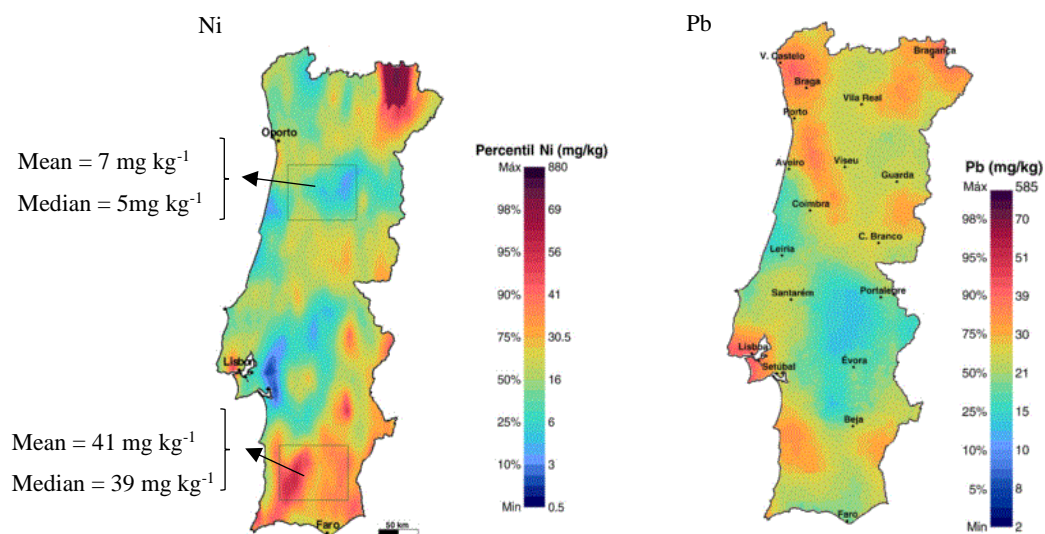
Figure 3.4 - Concentration of Ni and Pb FF and CF Portuguese soil (Adapted from Inácio et al. 2008).

Concerning Pb, Figure 3.3 (e), the Q90 for FF, CF, HFF, and ASR were lower than 50 mg kg^{-1}. The limit 300 mg kg^{-1} was only exceeded for very few samples, as can be observed in Figure 3.4.

Zn concentrations, Figure 3.3 (f), are lower than the value limit of 150 mg kg^{-1} for both Q90 and Q95 (not marked in the graph). So, this is not a restrictive element. Zn is poorly mobilizable in the soil when the pH is greater than 5 (Amaral, 2012). This may explain the accumulation of Zn found by Alvarenga et al., (2016) in the study with Portuguese sludge during sorghum cultivation during two years of monitoring.

Regarding Hg and Cd, Figures 3.3 (g) and 3.3 (h), the contents in soil were lower than the restrictive limit concentrations for deposition of SS in soil (pH≤5.5, Table 3.1). It is likely that these low concentrations are due to the restrictive policies on the use of materials containing Hg and Cd (Kirchmann et al., 2017). Indeed, Cd in European agricultural soil shows very low levels (≤0.15 mg kg^{-1}), and therefore it is not expected that this element will prevent the soil from receiving SS (Tóth et al., 2016).

A recent study involving 2557 samples of soils from Galicia Region in Spain, which is closely located to the border with mainland Portugal, Mosquera-Losada et al., (2017) showed that more than 90% are suitable to receive SS following the current limits (Table 3.5). However, only 28.7% of soil fulfills the criteria of set in ECWD, (2000).

3.3.5   *Restrictions of metal concentration in SS*

Restrictions have been imposed on metal concentration in SS for application in agricultural soil. Figure 3.5 (a) – 3.5 (f) reveal the distribution of Cr, Cu, Ni, Pb, Zn, and Cd for samples studied in "this work", soil analyzed by national sludge management operator (SMO), and data from the literature for PT, SP, DE, UK, PL, SE, and NL. The PT limits and SE limits for SS applications in the agricultural soil are marked by solid and dashed horizontal lines, respectively, in Figure 3.5. As a main result, none toxic metal exceeds the Portuguese limits. However, the same is not true if the most restrictive limits from Sweden were adopted as a reference. The maximum concentration measured in SS produced in Portugal in respect to the legal limit was about 10% for Cr, 30% for Cu, 25% for Ni, 8% for Pb, 40% for Zn and 25% for Cd. Indeed, the concentration of Cr did not exceed 120 mg kg^{-1}; Cu has been below 400 mg kg^{-1}; Ni and Pb tend to be lower than 100 mg kg^{-1}; Zn is mostly lower than 1000 mg kg^{-1}; and Cd is mostly lower than 5 mg kg^{-1}. Toxic metal concentration in SS are usually present in the following sequence: Zn > Cu > Cr > Ni ~ Pb > Cd (Fijalkowski et al., 2017).

As mentioned in the introduction, some studies from the literature show clearly that the concentration of most toxic metals has been decreasing over time (Wiechmann et al., 2013; Evans 2016; Fijalkowski et al., 2017; Kirchmann et al., 2017). In Portugal, no reliable data is available about this aspect. As an example, Kirchmann et al., (2017) referred that the reduction from 250 mg to 22 mg kg^{-1} of Pb in SS may be a result of removing Pb from gasoline and by replacing the composition of the materials in the water distribution network. Data from Germany show that Cd was reduced in SS from 21 mg kg^{-1} in 1977 to 0.96 mg kg^{-1} in 2006; Hg concentration also decreased from 4.8 mg kg^{-1} in 1977 to 0.59 mg kg^{-1} in 2006 (Wiechmann et al., 2013). This reduction is mainly due to the reduction of specific products, better management of dental amalgams as well as the EU policies aiming at reducing Hg use.
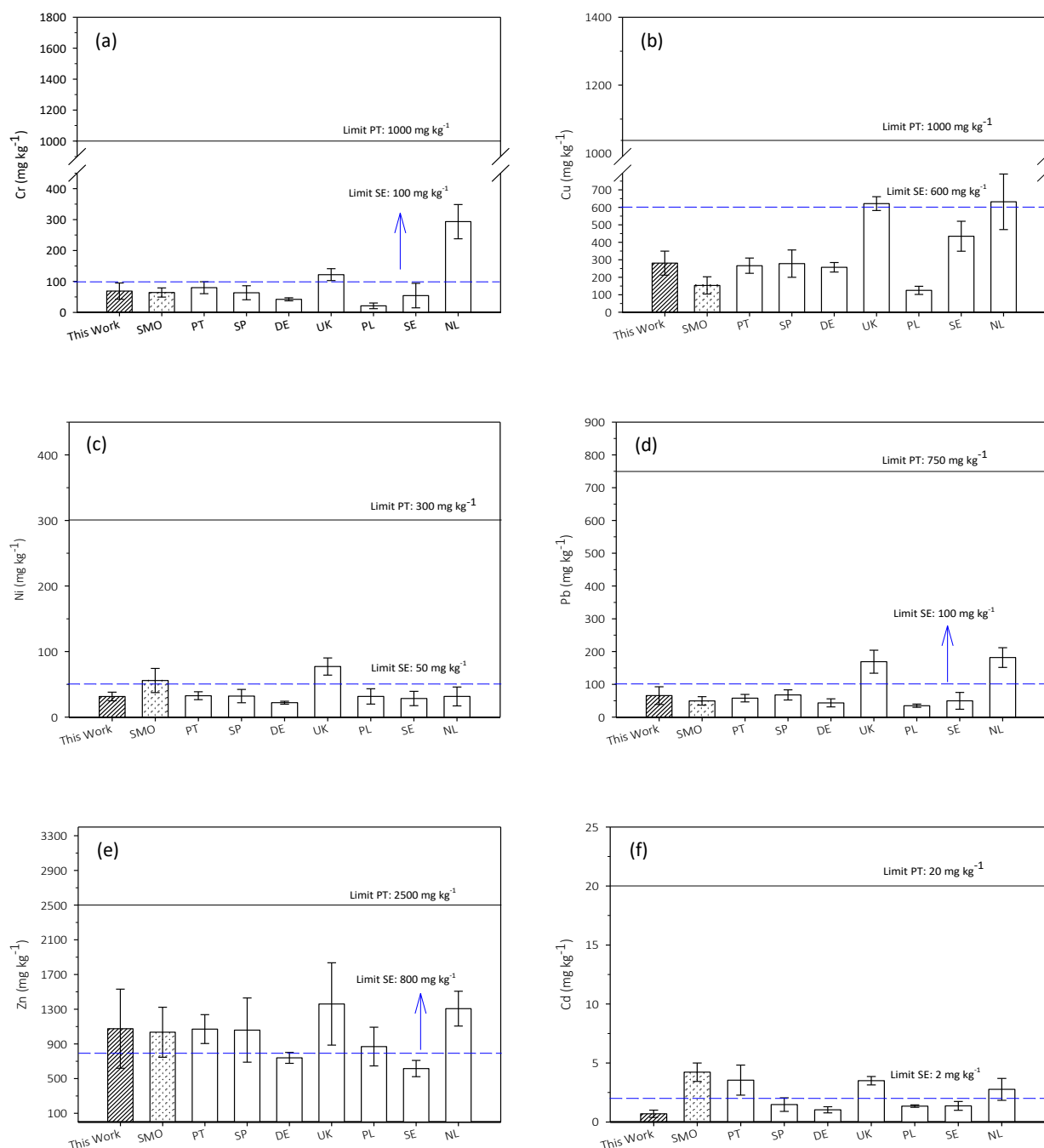
Figure 3.5 - Comparison of potentially toxic metals concentration in the samples analyzed in "this work", SMO and reported in the literature from PT, SP, DE, UK, PL, SE, and NL, (a) Cr; (b) Cu; (c) Ni; (d) Pb; (e) Zn and (f) Cd.

3.3.6 Assessment of ecological risk

Table 3.6 summarizes the mean and the standard deviation (SD) of I_{geo}, PI, E_r^i and PERI calculated for toxic metals in 25 samples of the SS from mainland Portugal. No data was found for Hg and this metal was excluded from the analysis.

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Table 3.6 - Assessment of ecological risk based on I_{geo}, PI and PERI for potentially toxic metals in 25 SS samples.

Index		Cr	Ni	Cd	Pb	Cu	Zn
I_{geo}	Mean	0.02	- 0.34	2.64	- 0.68	2.69	3.27
	SD	1.33	0.71	1.59	1.80	0.96	1.02
	Pollution degree [1]	*(1)*	*(0)*	*(3)*	*(0)*	*(3)*	*(4)*
PI	Mean	0.06	0.10	0.08	0.06	0.25	0.43
	SD	0.04	0.04	0.09	0.05	0.16	0.30
	Risk [1]	*(< 1 to all potentially toxic elements)*					
E_r^i	Mean	0.11	6.62	2.39	0.28	1.26	0.43
	SD	0.08	3.06	2.56	0.25	0.81	0.30
	Level (Pollution degree) [2]	*(< 40 to all potentially toxic elements)*					

PERI $(= \sum E_r^i) = 11.09 < 150$; [1] - Based on Table 3.2; [2] - Based on Table 3.3.

Results indicated in Table 3.6 show that I_{geo} is very low to Ni, Pb, and Cr, and thus the classification is *practically unpolluted* ($I_{geo} < 0$) and *unpolluted to moderately polluted* ($0 < I_{geo} < 1$). However, Cd, Cu, and Zn render a classification *moderately to heavily polluted*. PI for all metals are lower than 1, and thus no contamination is expected considering the current legal thresholds of Portuguese legislation (Table 3.5). Of course, if these limits are decreased PI will increase, thus the risk associated with SS will rise. Even so, the risk may be ranked as Zn > Cu > Ni > Cd > Pb = Cr. Similar results were obtained by Duan et al., (2007), who ordered PI as Zn > Cu > Ni > Cr > Cd > Pb. Regarding the potential ecological risk, E_r^i, the highest indexes were observed for Ni (6.62) and Cd (2.39). Even though, all the results showed low potential ecological risk ($E_r^i < 40$) and PERI=11.09, which is the lowest level of ecological risk (< 150) as reported in Table 3.3. Globally, these results indicate that the ecological risk due to PTM of applying SS to soil is relatively low.

3.3.7 *Way to move forward and the circular economy*

SS is produced in huge quantities in all developed countries and require adequate management (Kelessidis et al., 2012)., Several pros and cons may be associated with the complex matrix of SS, Table 3.7. Indeed, SS may contain measurable quantities of the most chemicals used in modern societies (Olofsson et al., 2012; Evan, 2016). However, depending on the quantity of each contaminant and on the kinetics of degradation (for organics and pathogens) the associated risk for use may be acceptable. Mailler et al., (2017) identified 71 pollutants including pharmaceutical products (PHP), hormones, perfluorinated acids (PFA), linear alkylbenzene sulfonate (LAS), alkylphenol (AP), phthalate (PAE), polycyclic aromatic hydrocarbon (PAH) and polychlorobiphenyl (PCB). However, the concentration varies highly in certain cases, and SS treatment (e.g., centrifugation, digestion, thermal drying, sludge conditioning, press filtration) may increase or decrease its concentration. This means, that further studies are required in this regard.

Table 3.7 - Positive and negative aspects associated with centrifuged SS

Strengths (pros)	Weaknesses (cons)
- High content in water may allow its recovery - Richness in macronutrients (P, N, K) and Ca, Mg, Fe - Organic matter (OM) content - Thermochemical conversion interest - Biological anaerobic conversion interest (AD) - Possible aerobic stabilization to produce compost	- Costs of transportation and difficulties in transport due to water - Low bioavailability of nutrients - Toxic organic pollutants (AOX, DEHP, LAS, PAH, PCB, PCDD/F) - Potentially toxic metals - Pathogen content (viruses, bacteria, etc.) - Bad smell due to OM degradation or volatilization (e.g., ammonia)

AD anaerobic digestion, AOX absorbable organic halogens, PAH polycyclic aromatic, PCB polychlorinated biphenyls, PFC perfluorinated compounds (sum of PFOS and PFOA), LAS linear alkylbenzene sulphonates, DEHP di(2-ethylhexyl) phthalates, PCDD/F polychlorinated dibenzodioxins/furans

At present, no consensual solution is available to protect human health and natural ecosystems, and holistic approaches are required to achieve sustainability and to move toward circular economy (Fytili and Zabaniotou 2008; Spinosa et al., 2011; Kelessidis et al., 2012; Mininni et al., 2015; Mosquera-Losada et al., 2017). Figure 3.6 depicts a simplified overview of the flows associated with SS and highlights the main routes of management: use in agricultural soil/soil amendment, incineration or landfill. Some treatments (e.g., dewatering, AD, composting, liming, drying) may precede these final destinations, aiming at reducing water content (volume) to minimize handling and transport problems, reduce pathogens and prevent bad odours.
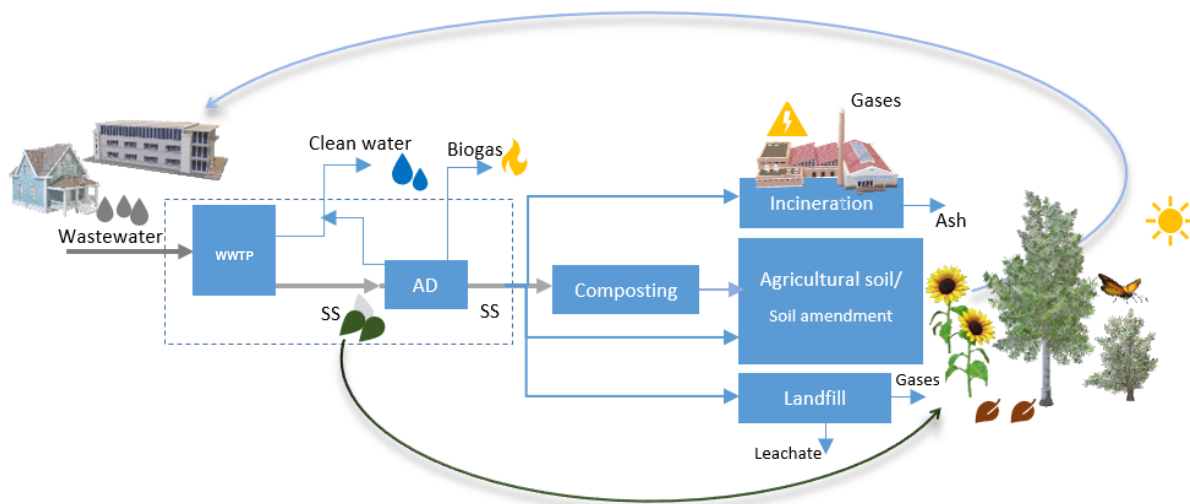
Figure 3.6 - SS possibilities toward a circular economy.

The incineration (mono or co-incineration) has been the main technology to manage SS in Germany, The Netherlands, Belgium and Denmark (Kelessidis et al., 2012; Wiechmann et al., 2013; Panepinto et al., 2016). In this case, dewatering is a key issue to achieve autothermic combustion and flue gas cleaning is compulsory. The remaining ashes may be disposed of in a landfill (or in mine

sealing), used in farming or in asphalt plants (Wiechmann et al., 2013). However, since it has a high content in phosphorous (in forms unavailable to plants), this nutrient may be recovered (Kruger et al., 2014; Herzel et al., 2016). In Germany, there are more than 10 industrial plants in operation or in the pipeline (Wiechmann et al., 2013). Extraction of nutrient from wastes ashes instead of direct organic waste recycling is a possible way to move forward (Kirchmann et al., 2017). Gasification, pyrolysis and supercritical water oxidation may constitute alternatives to incineration in the future (Mininni et al., 2015; Evans, 2016).

Regarding the landfill, besides it is a simple and low-cost route to eliminate SS, this option is in phase-out in the most developed countries, but mainly in Germany and The Netherlands (Kelessidis et al., 2012; Mininni et al., 2015).

The application in agricultural soil or in landscaping (directly or as compost) has been the preferable route in some European countries: Finland, Portugal, France, UK, Ireland, Spain, Denmark, Sweden (Kelessidis et al., 2012). Some studies investigate and encourage this method to manage SS (Cole et al., 2001; Dimitriou et al., 2006; Fernández et al., 2007; Roig et al., 2012; Gustafsson et al., 2012; Rizzardini and Goi, 2014; Duan et al., 2017; Kirchmann et al., 2017; Sharma et al., 2017; Urbaniak et al., 2017). Indeed, SS can supply OM and nutrients (N, P, K) to soil that crops need. Measurements in the present study, in samples SS1 to SS5, showed 55.5-78.5 %TS of OM, 1.2-3.5% of P_2O_5 and 0.2-0.5% of K_2O. In fact, a relevant advantage related to land applications is the possible increase in the carbon of the soil (Bancessi, 2009). Southern EU countries tend to have acidic soil with low organic carbon, with 75% of topsoils containing very low ($\leq 1\%$) to low ($\leq 2\%$) amount of carbon (Quina et al., 2017). Thus, any strategy to increase C-pool is welcome in this region. Some studies indicate that most agricultural soils have lost 50 to 70% of their original OM pool, and the depletion is worsened by further soil degradation and desertification (Lal, 2003). In these conditions, soils are an important carbon sink and may have a positive role in global warming and climate change. Composting SS could be an eco-friendly process to stabilize OM and re-introduce carbon in the soil, as well as to attain the application of end-of-waste criteria (Mininni et al., 2015). Furthermore, in some countries (e.g., Sweden) it has been shown a decrease in toxic metals by 90% since the 1970s, and long-term field experiments demonstrated reduced metal pollution during repeated SS application (Kirchmann et al., 2017).

The way to move forwards in European Countries will depend mainly on the future regulations from the European Commission. The use in agricultural soil is likely an option in the future. Indeed, several member states have paid attention to toxic metals, organic pollutants, and pathogens, but none study has demonstrated negative health and environment impact (Mininni et al., 2015). SS application in soil with well-established criteria constitutes a valuable method toward the circular economy (closing the loop of carbon and nutrients).

3.4 Conclusions

The Portuguese legal constraints associated with potentially toxic metals in soil and in SS from WWTP were analysed, aiming at using this waste in agricultural soil. SS has been produced in high quantities in the European Countries, but databases are incomplete in the last two decades for most countries. Although uncertainties are detected in the literature the production in Portugal is likely to be 300-350 kt_{db} year^{-1}, which means near 30 kg inhab^{-1} year^{-1}. As a Southern European country, the topsoil of Portuguese territory is mostly acidic (pH < 5.5) with low organic carbon, thus the application of SS in the soil is of great interest. Toxic metals may have a detrimental effect on soil capabilities, and *Lepidium sativum L.* seeds germination may be hindered. Ranking of these detrimental metals in root elongation is Cd > Cu > Cr(VI) > C(III) ~ Zn ~ Ni > Pb. In general, the concentration of the metals of the soil complies with the lowest constraint in at least 90% of the territory. This is true also for agriculture soil receptor (ASR). The thresholds imposed for SS in Portuguese legislation were not surpassed for any toxic metals. However, if more restrictive limits were adopted in the future (for example, Swedish limits) in some cases Ni, Zn and Cd may be impeditive to apply SS to the soil. The assessment of the ecological risk showed that the geoaccumulation index to Cd, Cu, and Zn correspond to moderate to high pollution level. However, the PI and PERI reveal that no contamination is expected, and the ecological risk is low.

The analysis of the way to move forward in a circular economy context highlighted that no significant negative impacts have been detected in human health and environment due to SS applications to the soil. Thus, according to the current regulations of Portugal, the Continental National territory could be an important carbon sink (important for global warming issues), improving this way the soil quality in terms of carbon and nutrients.

3.5 References

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3.6 Supplementary information

Table S 3.1 - Physical-chemical characterization of the SS samples.

Parameter	This work					Sludge management operator (SMO)				
	SS_1	SS_2	SS_3	SS_4	SS_5	SMO_1	SMO_2	SMO_3	SMO_4	SMO_5
pH	7.8	7.8	8.0	8.7	nd	6.5	7.5	8.7	6.6	8.6
Moisture (%)	83.1	77.9	91.5	85.4	86.8	82.3	88.0	87.0	64.0	85.0
OM (% TS)	77.3	63.7	78.5	74.7	55.5	84.0	75.0	75.0	93.1	71.0
P_2O_5 (%TS)	2.30	3.50	1.20	2.40	1.30	4.60	3.70	0.60	1.40	3.40
K_2O (%TS)	0.30	0.20	0.20	0.50	0.20	0.40	0.30	0.30	0.20	0.40
CaO (%TS)	2.70	4.70	11.0	3.85	18.2	0.70	4.10	3.10	ni	ni
MgO (%TS)	1.10	0.40	0.2	0.70	0.70	0.40	0.63	0.14	ni	ni
Al_2O_3 (%TS)	1.50	1.80	1.4	1.60	1.80	ni	ni	ni	ni	ni
Fe_2O_3 (%TS)	1.90	10.5	0.1	0.70	0.20	ni	ni	ni	ni	ni
SiO_3 (%TS)	4.10	3.70	1.2	4.60	4.20	ni	ni	ni	ni	ni
Na_2O (%TS)	2.40	nd	nd	nd	nd	ni	ni	ni	ni	ni
Potentially toxic metals (mg kg^{-1})										
Cd	0.07	5.00	0.07	1.31	1.52	5.0	1.10	5.00	5.00	5.00
Cr	51.83	26.06	203.9	39.58	19.43	48.0	35.0	100	38.0	100.0
Cu	172.5	297.8	356.6	634.5	63.48	160.0	180.0	82.0	290.0	71.0
Zn	924.7	331.2	1018	3254	744.0	580.0	1000	283.0	1900	1410
Ni	19.97	62.88	20.72	33.5	10.63	20.0	39.0	100.0	20.0	100.0
Pb	55.50	68.78	80.20	76.70	45.10	28.0	39.0	80.0	20.0	80.0

nd – not determined; ni – not indicated

Table S 3.2 - Characterisation of agricultural soil receptor (ASR) samples.

pH	OM	C_{Total}	C_{Inorg}	$P_{soluble}$	Cd	Cr	Cu	Ni	Pb	Zn
	(%)	(%TS)					mg kg^{-1}			
5.10	3.81	2.43	0.21	117.0	0.40	16.0	1.50	13.4	19.0	74.9
6.20	3.30	1.93	0.02	50.0	0.40	14.2	12.3	13.0	18.8	69.8
6.70	3.88	2.27	0.02	60.0	0.40	15.3	19.7	12.2	19.7	71.4
7.40	5.01	3.29	0.39	71.0	0.20	16.0	12.0	14.0	20.0	80.0
5.70	2.43	3.46	2.05	77.0	0.20	6.00	40.0	3.00	15.0	57.0
7.80	3.14	1.84	0.02	70.0	0.40	28.3	38.2	28.6	24.2	71.8
7.70	3.95	2.39	0.11	76.0	0.40	36.8	32.3	32.3	26.1	88.4
7.80	5.00	3.00	0.10	12.0	0.40	24.3	23.0	20.6	23.0	69.7
7.80	4.27	2.57	0.10	10.0	0.40	11.2	19.4	6.50	8.90	35.8
6.70	4.78	2.87	0.10	10.0	0.40	10.4	18.3	7.40	8.80	28.5
4.10	0.10	1.48	0.01	10.0	0.40	10.7	18.0	6.80	9.20	28.0
4.10	1.00	1.94	0.01	10.0	0.40	10.6	18.4	6.60	10.3	30.9
3.90	2.52	1.93	0.01	10.0	0.70	6.80	11.0	6.70	13.0	18.0
4.00	3.32	1.86	0.01	10.0	0.70	6.90	6.70	6.70	6.80	13.0
4.10	3.31	1.70	0.01	10.0	0.20	0.10	0.10	0.10	4.00	6.00
6.00	3.19	1.32	0.01	10.0	0.20	0.10	1.00	0.10	3.00	19.0
5.80	2.94	1.66		10.0	0.20	0.10	0.10	0.10	3.00	5.00
5.70	2.28			20.0	0.20	0.10	0.10	0.10	5.00	8.00
5.50	2.85			20.0	0.40	8.27	7.70	6.40	13.5	16.4
5.10					0.40	11.9	5.90	7.90	14.5	53.6
5.60					0.40	7.74	9.80	4.60	10.8	18.4

Table S 3.2 (cont.) - Characterisation of agricultural soil receptor (ASR) samples.

	pH	OM	C_{Total}	C_{Inorg}	$P_{soluble}$	Cd	Cr	Cu	Ni	Pb	Zn
		(%)	(%TS)					mg kg^{-1}			
	5.10					0.40	7.40	5.70	5.30	9.40	39.8
	5.50					0.40	4.30	6.90	4.40	10.3	43.0
	8.00					0.40	8.35	6.50	5.60	9.10	57.2
	6.80					0.40	7.25	7.00	5.10	9.60	50.4
	5.20					0.20	19.0	10.0	13.0	14.0	71.0
	5.50					0.20	19.0	10.0	13.0	13.0	110.0
						0.20	19.0	12.0	14.0	14.0	83.00
						0.20	19.0	12.0	14.0	18.0	78.00
						0.20	19.0	11.0	13.0	14.0	76.00
Mean	*5.89*	*3.21*	*2.23*	*0.20*	*34.89*	*0.35*	*12.1*	*12.6*	*9.48*	*12.9*	*49.1*
sd	*1.27*	*1.22*	*0.61*	*0.49*	*32.56*	*0.13*	*8.4*	*10.2*	*7.52*	*6.02*	*28.4*

sd - standard deviation

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4. ISOTHERMAL DRYING KINETICS OF SEWAGE SLUDGE USING WEATHERED COAL FLY ASH AS ADJUVANT FOR AGRONOMIC APPLICATION

This study aims to evaluate the effect of weathered coal fly ash (CFA) as a drying adjuvant of sewage sludge (SS) to produce a soil amendment. The high amount of SS and CFA creates a complex waste management problem in many countries, requiring more research efforts. Towards a circular economy, CFA can be viewed as an anthropogenic inorganic by-product with valuable nutrients (e.g., K), which can be recovered in combination with SS (rich in organic matter, N, and P). Different temperatures (70, 85, 100, 115, and 130 ºC) are tested to dry small SS cylinders, without and with 0.15 g CFA g^{-1} of SS$_{wet\ basis\ (wb)}$. By fitting appropriate models to the experimental drying curves, it is possible to observe an improvement of 1-17% in the diffusion coefficient and 7-19% in the kinetic constants, using CFA. The best drying conditions are achieved with CFA as an adjuvant at 130 ºC, where the drying rate is 31.61 gH$_2$O kg^{-1} SS$_{wb}$ min^{-1}. Phytotoxicity and growth assays are performed to evaluate the effect of the produced materials in the soil. The product with SS and CFA shows the potential to improve soil condition due to (i) the organic matter, N, P, and K content, (ii) the lower phytotoxic effect when compared to raw SS; (iii) the soil pH correction. Thus, not only the addition of weathered CFA facilitates the drying of SS but also the final product has benefits to soil conditions.

Keywords: sewage sludge, coal fly ash, drying kinetics, mathematical modelling, soil amendment

4.1 Introduction

The United Nations set out 17 sustainable development goals in 2015, which will require ambitious government programs and the contribution of each citizen. Namely, the goals "clean water and sanitation", "sustainable cities and communities", "responsible production and consumption", "climate action", and "life on land" are somehow related with this work. A few decades ago, the European Union (EU) regulations recommended to the Member States the environment protection from the adverse effects of the urban wastewater discharges (Directive 91/271/EEC). This Directive indicated that sewage sludge (SS) arising from wastewater treatment plants (WWTP) shall be re-used whenever appropriate. However, the management of SS can be a complex process, mainly due to its high water content and unstable organic matter (OM) (Zhang et al., 2019a). According to the literature, the options for dealing with SS are the direct agricultural use, composting followed by soil application, incineration, landfill or others (Rizzardini and Goi, 2014; Zhang et al., 2016). Countries such as Portugal, with poor soils in OM, prefer the agricultural application of SS, which constitutes a good strategy for the circular economy model and climate change (Arwyn Jones et al., 2010).

In this regard, some studies have shown the benefits of nutrients (such as N and P) and OM present in the SS in the soil properties (Tsadilas et al., 2018, 2014; Alvarenga et al., 2015; Ojeda et al., 2015). The increase of OM in the soil improves the water holding capacity, cation exchange capacity, aeration, drainage, porosity, microbial communities, also contributing to disease suppression, and prevent soil erosion. Furthermore, some studies highlight the valuable contribution of SS to the carbon sink in soil, and thus to the mitigation of greenhouse effect (Cerne et al., 2019; Hamdi et al., 2019; Stockmann et al., 2013). Nevertheless, it is important to control the concentration of some toxic organic compounds, potentially toxic metals (PTM) and pathogens in SS before the application. In addition, care should be taken to avoid the formation of bad odors (Alvarenga et al., 2017).

The SS is commonly mechanically dewatered by filtration and/or centrifugation in the WWTP, but the remaining moisture content is still high (> 80%). The high moisture content creates difficulties in transport, storage, and further management operations. Thermal processes have gained prominence in the last years to remove water from SS and to reduce (or eliminate) the content in pathogens (Collard et al., 2017). Besides a reduction in the volume, drying processes facilitate handling for soil application and reduce odors and transport costs. However, drying SS requires itself a significant amount of energy and any strategy for its reduction is welcome. To enhance the drying process and contribute to the industrial ecology, adjuvants such as hazelnut shell, sawdust, rice straw, lignite, lime and coal fly ash (CFA) have been tested (Cai et al., 2015; Li et al., 2014; Pehlivan et al., 2016; Zhang et al., 2017, 2016). Solid adjuvants may create bridges between the adjuvant and the SS particles with different sizes, which aid the water diffusion process. Also, a rigid skeleton structure is formed, which can be promoted during mixing, extrusion, and drying phases (Deng et al., 2011; Zhang et al., 2017; 2019b). After an initial thermal equilibrium phase, the isothermal drying process exhibits a continuous period of free water loss

(period I). The evaporation occurs at the surface of the wet solid, and the surface temperature is nearly constant (Figueiredo et al., 2015; Srikiatden and Roberts, 2007). This period can be model by Fick's second law. Then, the drying rate decreases and occurs the removal of the bound water (period II). The temperature of the material increases until it reaches the temperature of the drying chamber. This second period corresponds to the removal of water from the solid structure and can be modelled by the thin-layer model (Bennamoun et al., 2013; Danish et al., 2016).

The weathered CFA was not studied yet as an adjuvant of drying. This by-product is formed in high quantities during the coal combustion in several countries in the world and in Portugal as well. Currently, there are two thermoelectric power plants (Sines and Pego) in Portugal, that use mineral coal as a fuel for energy production. In 2014, about 4.4 Mt of coal was imported, which corresponds to a share of 12.7% of total primary energy supply and 23% of electricity generation (IEA, 2017). Recent reviews indicated the main applications of CFA, namely in the construction industry, soil amelioration, ceramic industry, catalysis, separation processes and zeolite synthesis (Yao et al., 2015), geopolymers, aerogels, carbon nanotubes, rare earth elements recovery (Gollakota et al. 2019). However, in Portugal, about 30% of this material is disposed of in landfill because the quality criteria for the cement industry is not fulfilled, which represents a huge environmental problem. CFA is a ferroaluminosilicate fine particulate material and can contain significant amounts of Si, Fe, Ca, K, and Br, and micronutrients (such as Zn, Cu, Mn). The main benefits for soil have been demonstrated, namely for immobilizing PTM present in soil (Kaur and Goyal, 2016; Shaheen et al., 2014; Skousen et al., 2013; Zacco et al., 2014; Zhang et al., 2017). Besides increasing the essential nutrients (e.g., K) for plants, CFA can improve soil structure, aeration, and percolation (Tsadilas et al., 2018). Moreover, CFA may be used for pH adjustment of acidic soils (Basu et al., 2009; Gollakota et al. 2019; Jala and Goyal, 2006; Skousen et al., 2013). Since the Portuguese territory is mainly acidic (Basu et al., 2009; LeBlanc et al., 2008; Quina et al., 2017), the application of CFA as a soil amendment could be of interest. Recently, Zhang et al. (2017) studied five adjuvants of drying (including CFA, but without a weathering period in a landfill) in the range 100-180 °C. In this study, 10 wt% of CFA was added, and the drying rate increased by 3.57% due to the modification into the porous structure and to the increase of the thermal conductivity.

Finally, it is important to note that the controlled utilization of both SS and CFA in the soil is in line with the "4 per 1000" soil carbon initiative launched by the French government at Conference of the Parties in 2015. This program encourages the increase of OM in the soil to improve its fertility and to make it more resistant to climate change (https://www.4p1000.org/).

In this context, this study aims to recycle weathered CFA from landfill as an adjuvant in an SS drying process to obtain an organic-rich material to agriculture applications. Although other wastes have been used as adjuvants to study the drying process, to the best of our knowledge, the present study addresses for the first time the weathered CFA for that purpose. Also, it gives a comprehensive analysis based on not only mathematical modelling but also including insights into the benefit of applying the

product in agricultural. Accordingly, an anthropogenic waste currently in the landfill may be recover as a soil amendment, with a positive contribution to the circular economy.

4.2 Materials and methods

4.2.1 Materials

SS sample (about 5 kg) was collected after mechanical dewatering by centrifugation in a WWTP from the central region of Portugal, which manages SS from primary and secondary treatment by anaerobic digestion. WWTP receives urban effluent and treats about 36,000 $m^3 day^{-1}$. The sample was kept at 4 ºC until use.

A composite sample of weathered CFA (about 5 kg) was obtained by collecting at a depth of 0.5-1 m, 10 subsamples in different locations of a landfill from a coal thermoelectric power plant in the central region of Portugal. The thermoelectric power plant produced in 2017 around 15 kt of CFA, most of it used by the cement industry. In the laboratory, the agglomerates of the sample were disintegrated and sieved through a 425 μm screen.

4.2.2 Physical and chemical characterization of SS and CFA

Moisture and OM are determined by EPA Method 1684. The pH and electrical conductivity (EC) are measured (Consort C1020) in an extract obtained at liquid:solid ratio 10:1 L/kg. To determine the PTM (Cr, Ni, Cu, Zn, Cd, and Pb) and the major-element oxides, SS and CFA samples are dried at 105 °C for 24 h, ground, and sieved through a ~75 μm (200 mesh) screen. Afterward, 4 g of each sample (CFA and SS) are analysed to determine major elements through X-ray fluorescence, Nex CG Rigaku equipment. Acid digestion with aqua-regia followed by quantification with flame atomic absorption spectroscopy (Analytik Jena ContrAA 300 equipment) is used to quantify PTM elements. The Kjeldahl method is employed to measure the nitrogen in SS, through DKL and UDK units from VELP Scientifica. The loss on ignition (LOI) is determined using a muffle at 950 °C for 1 h (NP EN 196-2:2014). Elements in the leaching solution are analyzed by Inductively Coupled Plasma - Optical Emission Spectrometry in an external laboratory, and the preparation of the sample is according to the Portuguese *Decreto Lei Nº.* 183/2009, August 10. Each parameter is measured at least in duplicate.

4.2.3 Drying process procedure

Small cylinders (5 mm diameter and 30 mm length) obtained by extrusion at room temperature, Figure 4.1 (a), are used to study the drying process. A drying screening phase at 100 ºC, supported the selection of the dimensions of the cylinders and the optimal blend of SS and CFA. Cylinders with diverse dimensions (5 mm diameter and 10, 15, 20, 30, and 40 mm length) and formulations (SS plus 0.05, 0.10, and 0.15 g CFA g^{-1} SS_{wb}) are tested. According to the drying moisture profiles (Figure S 4.1 (a)-(b),

supplementary information), no differences are observed for cylinders with lengths equal to 20, 30, and 40 mm. Thus, a 30 mm length guarantees the approximation of an infinite cylinder in the modelling studies. Moreover, the mass of CFA does not significantly influence the moisture profiles over time. Thus, the subsequent tests incorporate 0.15 g CFA g^{-1} SS$_{wb}$.

Formulations of SS and SS plus CFA (SS_CFA) are prepared, ensuring homogeneous composition by mixing both materials for 5 min. Then, 15 cylinders with about 0.7 g each are extruded, placed over an aluminium dish (100 mm diameter), and dried at 70, 85, 100, 115, and 130 ºC in a Moisture Analyzer, *Precisa XM50*. This balance uses a dark radiator heating source, the maximum load is 52 g, readability 0.001 g, and temperature range 30-170 ºC. The weight is recorded once per minute until no variation is detected. To monitoring the temperature inside the pellets, a Pico Technology thermocouple data logger is used (Figure S 4.2, supplementary information).
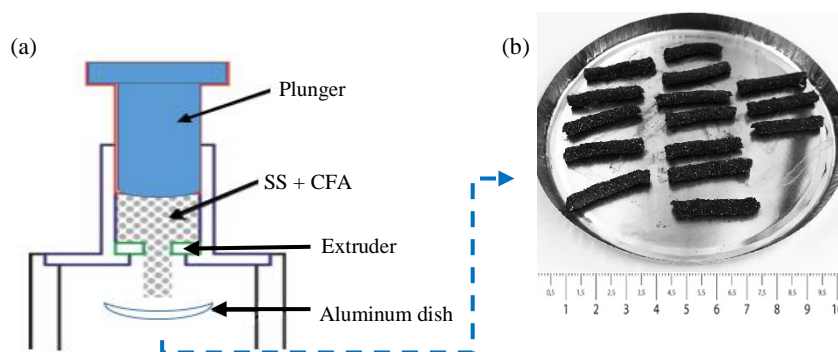
Figure 4.1 - (a) Extrusion system; (b) SS_CFA formulation (0.15 g CFA g^{-1} SS$_{wb}$).

4.2.4   *Phytotoxicity tests*

Lepidium sativum L. (garden cress) is used to evaluate the phytotoxicity of SS, SS_CFA, and CFA. For that purpose, liquid extracts with different liquid to solid (L/S) ratios are obtained based on the standard EN 12457-2:2002. The suspensions are agitated for 2 h in an orbital shaker and filtered with the *Whatman* filter (pore 0.45 µm). pH and EC measured in the leachates are shown in Table S 4.1 (supplementary information). All tests were conducted in triplicate.

Petri dishes (90 mm diameter) with 5 mL of extract and ten seeds are used to perform the phytotoxicity tests. The control test involved distilled water with pH 6.88 and EC 3.23 µS cm^{-1} instead of the extracts. The dishes were kept in an oven at 25 ± 0.1 °C for 48 h, in dark conditions (Santos et al., 2019). For each sample, the germination index (GI) was calculated by combining Eq. (S 4.1), (S 4.2), and (S 4.3) (supplementary information).

4.2.5   Pot experiments

Lepidium sativum L. were grown in pots (90 x 75 mm) in an incubator with white LED light (~ 280 µmol m^{-2} s^{-1}, 400-700 nm, incidence angle of 240°), regulated with a photoperiod of 12 h, temperature 21 ± 0.1 °C and relative humidity 50% (Arriagada et al., 2014; Belhaj et al., 2016). The soil used was collected from a depth of about 20 cm and can be classified as sandy soil. The sample was dried at room temperature and homogenized properly. The characterization reveals a low OM (approximately 2%) and low P content (0.01 wt%). SS was applied to the soil at three different rates, corresponding to 6, 12, and 24 t ha^{-1}. A fourth treatment was performed with SS_CFA (24 t ha^{-1}). The samples were dried at 100 ºC (an intermediate temperature) and sieved through a 1 mm screen. The lower amount of 6 t ha^{-1} rate was chosen based on the recommendation of the Portuguese legislation (*Decreto Lei Nº*. 446/91, November 22). The higher rates were tested for comparison purposes. A control test using only soil was included in the assessment. The pots used (300 cm^3 volume) were filled with gravel in the bottom (about 10 cm^3) and the rest with soil and mixtures thereof (about 290 cm^3). About 17 seeds of garden cress were sown in each pot, and each treatment was conducted in duplicate. After 1 week, a thinning was done, and 10 plants remained in each pot (thinning phase). The experiment lasted 4 weeks. Growth parameters were analyzed with respect to root and shoot lengths, and biomass of the plant. Biomass was determined at 60 ºC in oven-drying until constant weight (Mohamed et al., 2018). The parameters as OM, pH, and EC in the soil were measured at the end of the experimental period.

4.2.6   Drying modelling

As aforementioned, drying curves can be divided into three zones: Period 0 (cylinders temperature increases to wet-bulb temperature); Period I (cylinders temperature remains constant, Figure. S 4.2, supplementary information); and Period II (cylinders temperature increases until equilibrate with the drying temperature). In this work, Period 0 is neglected (almost the first 5 min), Periods I is modelled based on Fick's second law, and Period II through the Thin-layer model. Fick's second law is applied to model Period I because of the constant temperature inside the solid (with null gradients in all directions), considering uniform initial moisture throughout the cylinder, and neglecting shrinkage. In the case of an infinite cylinder, the transient behavior may be modelled along one-dimension of the cylindrical coordinate (radial direction), and the solution of the mass balance is present by Eq. (4.1) (Figueiredo et al., 2015; Srikiatden and Roberts, 2007).

In this study, only the first term of the sum in Eq. (4.1) is considered. The Period II of the drying kinetics is described by the Henderson & Pabis model (or thin-layer model), represented by Eq. (4.2) (Figueiredo et al., 2015).

$$MR = \frac{M(t)-M_e}{M_0-M_e} = \sum_{n=1}^{\infty} \frac{4}{r^2 \alpha_n^2} \, exp(-D_{eff} \, \alpha_n^2 t) \qquad (4.1)$$

$$MR = \frac{M(t)-M_e}{M_0-M_e} = ae^{-kt} \qquad (4.2)$$

where MR is dimensionless moisture ratio, M_0 and $M_{(t)}$ are the moisture content in the cylinder (gH$_2$O g dry solid^{-1}) at t_0 and t time, respectively; M_e is the moisture content in equilibrium (gH$_2$O g dry solid^{-1}); α_n are the roots of the Bessel function of zero-order, J_0, determined by solving the equation $J_0(r\alpha_n) = 0$; r is the radius of the cylinder (m); D_{eff} is the effective diffusion coefficient (m^2 min^{-1}) of water through a solid matrix, a corresponds to a parameter of the thin-layer model, k is the kinetic constant (min^{-1}) and t is the time (min).

The modulus of the drying rate, |DR|, expressed in gH$_2$O min^{-1} kg^{-1} SS$_{wb}$, was calculated by Eq. (4.3), using finite differences, and represents the amount of water leaving cylinders per kg SS$_{wb}$ min^{-1} (wet basis).

$$|DR| = \frac{\partial M(r,t)}{\partial t} \approx \frac{\Delta M}{\Delta t} = \frac{M_i - M_{i-1}}{t_i - t_{i-1}} \tag{4.3}$$

where M is the moisture, t represents the time and i is the record number. To calculate the effect of the adjuvant in the drying process of SS_CFA formulations, the CFA mass was discounted in the calculations.

The relationship between D_{eff} in solids and drying temperature may be obtained through the Arrhenius equation, Eq. (4.4) (Danish et al., 2016; Dissa et al., 2008).

$$ln(D_{eff}) = ln(D_0) - \frac{E_a}{RT} \tag{4.4}$$

where T is the constant drying temperature (K) and R is the universal gas constant (8.314 J K^{-1} mol^{-1}), D_0 is the maximal diffusion coefficient at infinite temperature (m^2 s^{-1}), and E_a is the activation energy for diffusion (kJ mol^{-1}). Both parameters (D_0 and E_a) were obtained through linear regression plotting ln (D_{eff}) versus 1/T.

The energy (kJ kg^{-1} SS$_{wb}$) required for evaporating water to achieve MR = 0.30, $E_{0.30}$, was calculated for the Period I at 70, 100 and 130 ºC, considering the drying rate at any time within this period, Eq. (4.5).

$$E_{0.30} = h \int_{t_0}^{t} |DR(t)| dt \tag{4.5}$$

where h is the latent heat of vaporization (kJ kg^{-1}), t_0 is the time at the beginning of Period I (min), t is the time to achieve MR = 0.30, and DR(t) is the drying rate at time t. The value of h was obtained considering the wet-bulb temperature during the Period I of the drying process (Cengel, 2003).

4.2.7 Statistical analysis

The statistical analysis of data involved mainly mean and standard deviation calculations and one-way ANOVA ($p < 0.05$), using Microsoft Excel® 2013. Moreover, pairwise comparisons were performed to identify the statistically significant differences through the Tukey HSD test (p < 0.05).

Regarding the drying kinetics, the predictive capacity of the mathematical models was evaluated based on the coefficient of determination (R^2) and on the root mean square error (RMSE), calculated by Eq. (4.6) (Bennamoun et al., 2013; Danish et al., 2016; Li et al., 2014)

$$RMSE = \left[\frac{1}{N}\sum_{i=1}^{N}\left(MR_{exp,i} - MR_{pred,i}\right)^2\right]^{1/2}$$

(4.6)

where $MR_{exp,i}$ and $MR_{pred,i}$ are the experimental and predictive calculated value of the dimensionless moisture ratio for observation *i*, respectively, and N is the number of observations.

4.3 Results and discussion

4.3.1 Characterization of the wastes

Table 4.1 shows some properties of SS and CFA, and globally a good agreement with those reported in the literature is observed.

Table 4.1 - Properties of SS and CFA used in this study and from the literature.

Parameter	SS This work [1]	Ref. [1]	Ref. [2]	CFA This work	Ref. [3]	Ref. [4]
pH [b]	6.71	ni	6.5-6.8	8.6	ni	ni
OM (%)	63.7	52.0	72.0	nd	ni	ni
Moisture (%)	78.0	ni	ni	0.07	0.3	ni
EC (mS cm^{-1}) [2]	1.70	ni	0.207	0.49	ni	ni
$N_{Kjeldahl}$ (%)	3.90	ni	7.2	nd	ni	ni
P_2O_5 (%)	3.83	2.00	3.11	0.2	0.3	0.08
K_2O (%)	0.22	0.80	0.16	2.4	1.5	1.64
MgO (%)	0.38	0.84	0.56	1.5	1.1	0.45
CaO (%)	5.50	7.25	3.04	1.4	ni	4.16
BaO (%)	0.02	ni	ni	0.11	ni	0.18
TiO_2 (%)	0.15	0.30	ni	1.1	1.2	1.88
SiO_2 (%)	4.05	7.30	ni	50.8	46	55.07
Al_2O_3 (%)	1.94	2.61	ni	18.1	26	30.07
Fe_2O_3 (%)	nd	2.72	ni	6.5	17	5.44
Na_2O (%)	nd	0.13	0.62	1.3	0.6	0.23
LOI (%)	nd	ni	ni	6.0	2.8[3]	ni

[1] - With the exception of moisture, the % was calculated in dry basis (TS); [2] - Measured at L/S = 10 L kg^{-1}; LOI - Loss on ignition at 950 ºC; [c] at 750 ºC; Refs.: [1]- (Atak et al., 2018), mean of 3 samples, [2]- (Alvarenga et al., 2008); [3]- (Skousen et al., 2013); [4]- (Zhang et al., 2017); nd - not determined; ni - not indicated.

The pH of SS and CFA was 7.7 and 8.6, respectively. In general, the pH of CFA is alkaline due to the presence of some hydroxides and carbonates compounds and CaO (Kaur and Goyal, 2016; Shaheen et al., 2014; Seki et al., 2019). However, the sample in this study revealed pH 8.6 because it was collected in a landfill, and weathering processes (e.g., leaching due to rainfall and carbonation with CO_2 from the atmosphere) occurred. pH is very important for the productivity of the soil, and thus its control is fundamental before wastes were used as soil amendments (Hamdi et al., 2019). The application of these alkaline materials may be valuable, namely to favor the bioavailability of P and other nutrients (Pasquali et al., 2018). SS contains a high amount of OM (~ 64%), and interesting quantities of nutrients

(3.9% of $N_{Kjeldahl}$ and 3.8 % of P_2O_5) and thus it can be beneficial as a soil amendment. Indeed, the topsoil organic carbon content in Portugal is low (less than 2%) in most of the territory (Arwyn Jones et al., 2010; Quina et al., 2017), and agricultural soil contains a mean value of 3.91 mg N kg^{-1} and 20.41 mg P kg^{-1} (Eurostat, 2018).

According to Table 4.1, while SS contains a low concentration of K, weathered CFA contains 2.4% of K_2O. Thus, the mixture of SS with CFA may improve the agronomic quality of the final product due to complementary properties. Indeed, Shaheen et al., (2014) highlighted that mixtures of CFA and SS for land application could prove a beneficial route (instead their disposal), because of their distinct but complementary chemical properties and nutrient contents (e.g., K content readily plant available). Furthermore, Shen et al., (2008) showed that the addition of SS and CFA to the soil can increase the water holding capacity. The main minerals in CFA are SiO_2, Al_2O_3, Fe_2O_3, and CaO (Gollakota et al. 2019), and since the sample sum more than 70% of SiO_2, Al_2O_3, and Fe_2O_3, it corresponds to a "class F" ash (Zacco et al., 2014).

Figure 4.2 (a-f) shows the concentration (mg kg^{-1}) of Cr, Ni, Cu, Zn, Cd, and Pb measured in the CFA and SS. The limits marked with a horizontal solid line correspond to the maximum admissible content in SS to apply it in the soil according to the Portuguese Law (*Decreto Lei Nº. 276/2009*).
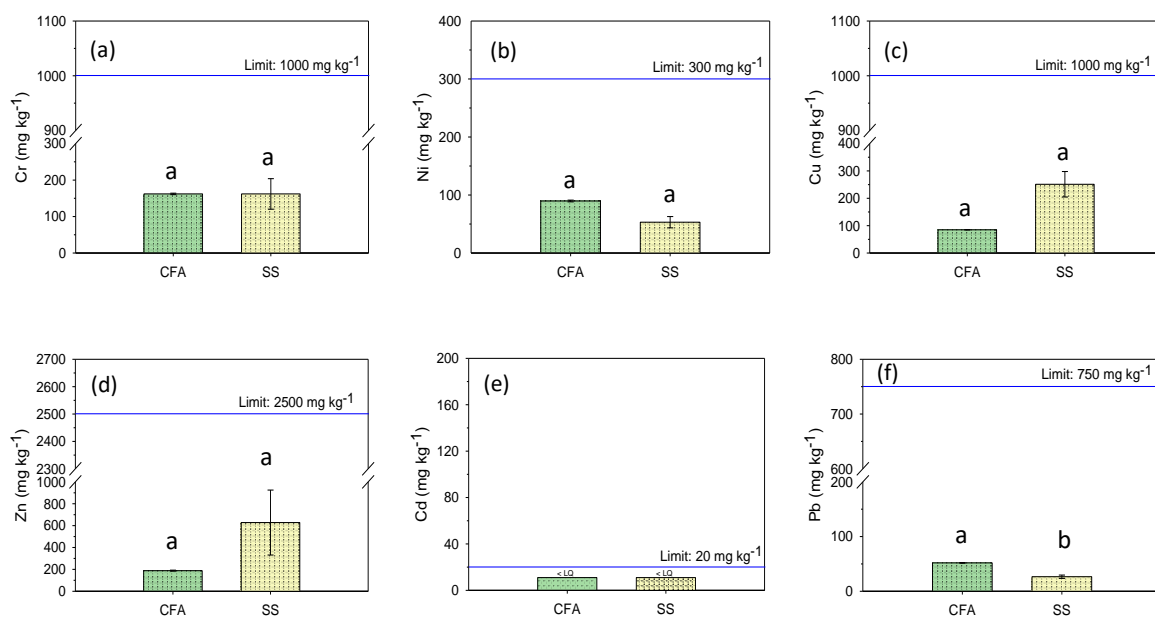
Figure 4.2 - Concentration of PTM in CFA and SS samples: (a) Cr; (b) Ni; (c) Cu; (d) Zn; (e) Cd and (f) Pb. Limit of quantification (LQ) of Cd = 11 mg kg^{-1}. The same letters over each bar means similar statistical results ($p \geq 0.05$).

Both samples (SS and CFA) do not exceed the limits for agricultural application and the results agree with other researches in the literature (Alvarenga et al., 2015; Jala and Goyal, 2006; Ojeda et al., 2015; Pathak et al., 2009; Riehl et al., 2010). In general, CFA seems to have a slightly higher content of Pb in relation to SS (Figure 4.2 f) ($p < 0.05$). In general, the concentrations of PTM in SS and in our study as well may be ordered as Zn > Cu > Cr > Ni ~ Pb > Cd (Fijalkowski et al., 2017).

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It is important to note that the OM content in soil tends to decrease the availability of some metals (Tsadilas et al., 2014; Zacco et al., 2014). In addition, the pH of SS and CFA unlikely increases the risk of leaching PTM in soil. Generally, soil with pH < 7.0 is more prone to the leach metals from the solid phase to the soil solution (Hamdi et al., 2019). The results for the leaching test of the six PTM studied in CFA sample (results not shown) did not exceed in any case the limits for admission to landfills for non-hazardous waste (*Decreto Lei Nº.* 183/2009, August 10), which means very low emissions.

4.3.2   Kinetics of drying

This study is part of a broader project aiming at developing an efficient industrial dryer for facilitating the management of SS, namely the ones formed in big WWTP. The dryer will be designed for dealing with SS after centrifugation and extrusion, in a cylindrical shape, before the drying phase. Thus, the results of the laboratory tests reported will be important to achieve specific deliverables of the project. Figure 4.3 shows an overview of the experimental moisture ratio (MR) as a function of time, measured at 70, 85, 100, 115, and 130 °C, for the SS and SS_CFA formulation as well as the models fitting.

As mentioned in the Introduction (section 4.1), the drying kinetics were divided into three periods and the length of the Period I was determined considering a final MR = 0.30 (Zhang et al., 2016), which corresponds to the constant temperature period (Figure S 4.2, supplementary information). Data visualization in Figure 4.3 reveals that the kinetics are highly dependent on the temperature, while R^2 and RMSE (Table 4.2) indicate that both models described well the experimental data.

As expected, an increase in the temperature led to faster drying. For example, the control sample at 70 °C required around 64 min to reach MR = 0.30, while at 130 °C the same level of dryness was achieved in approximately 17 min. Regarding the average drying rate in the Period I, about 8.32 and 30.73 gH_2O kg^{-1} SS_{wb} min^{-1} were measured at 70 and 130 ºC, respectively, for SS sample. In the case of SS_CFA, the $\overline{DR}$ is within 9.16 and 31.61 gH_2O kg^{-1} SS_{wb} min^{-1} for the same range of drying temperature. Thus, CFA tends to shorten the length of the Period I (t_f in Table 4.2), mainly at lower temperatures. For example, at 70 ºC the difference in t_f is 5 min while at 130 ºC is only 0.6 min.
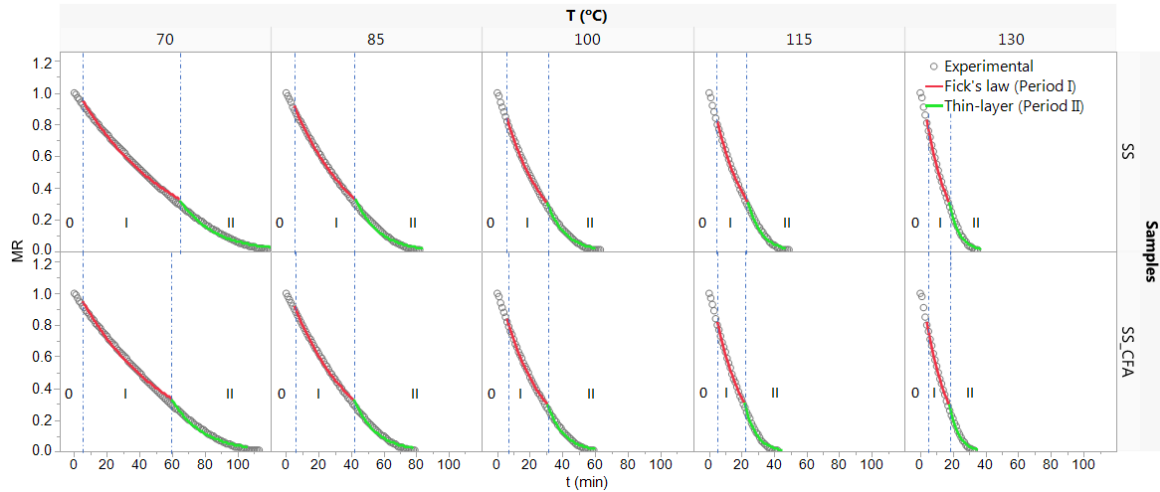
Figure 4.3 - MR evolution and fitting through Fick's law and Thin-layer models as a function of time for control (0%) and SS_CFA (0.15 g CFA g^{-1} SS$_{wb}$) formulation at 70, 85, 100, 115 and 130 °C. [Periods 0, I and II represent the rising rate period, the constant rate period, and falling rate period, respectively; the dash-dot vertical lines separate these periods].

Table 4.2 - Parameters obtained for the different periods of the drying curves at different temperatures.

T (ºC)	Samples	Fick's second law (Period I)					Thin-layer (Period II)			
		D_{eff} (m^2 min^{-1})	t$_f$ (min)	$\overline{DR}$ (gH$_2$O kg^{-1} SS$_{wb}$ min^{-1})	R^2	RMSE	k (min^{-1})	a	R^2	RMSE
70	SS	2.92×10^{-8}	64	8.32	0.993	0.02	0.0468	6.563	0.984	0.01
	SS_CFA	3.12×10^{-8}	59	9.16	0.992	0.02	0.0521	7.366	0.980	0.01
85	SS	4.50×10^{-8}	42	12.62	0.994	0.01	0.0694	6.336	0.983	0.01
	SS_CFA	4.72×10^{-8}	41	13.56	0.994	0.03	0.0725	6.692	0.981	0.01
100	SS	6.92×10^{-8}	30	16.44	0.995	0.01	0.0993	5.236	0.989	0.01
	SS_CFA	7.00×10^{-8}	29	17.72	0.995	0.01	0.0995	6.337	0.990	0.01
115	SS	8.64×10^{-8}	23	22.01	0.995	0.01	0.1196	5.353	0.988	0.01
	SS_CFA	1.01×10^{-7}	21	25.23	0.995	0.01	0.1426	6.886	0.988	0.01
130	SS	1.23×10^{-7}	17.3	30.73	0.995	0.01	0.1630	5.565	0.986	0.01
	SS_CFA	1.27×10^{-7}	16.7	31.61	0.995	0.01	0.1774	6.958	0.985	0.01

t$_f$ – time at the end of Period I; $\overline{DR}$ – average drying rate for Period I.

The diffusion coefficients, D_{eff}, were always higher for SS_CFA sample when compared to SS (Table 4.2). This improvement can be due to the possibility of CFA may act as a skeleton builder inside the pellets (cylinders), with a positive effect for water migration from inside to outside (Zhang et al., 2019b). The highest enhancement with respect to the control occurred at 115 °C, where D_{eff} was nearly 17% higher for the SS_CFA. Zhang et al., (2016) reported D_{eff} in SS from 8.22×10^{-8} to 7.74×10^{-7} m^2 min^{-1} when the temperature varied from 60 to 180 ºC, respectively, while 7.68×10^{-8} m^2 min^{-1} to 1.27×10^{-6} m^2 min^{-1} were achieved when CFA (not from landfill) was added to SS. Li et al., (2014) studied the incorporation of sawdust as an adjuvant on the SS drying, and D_{eff} equal to 8.33×10^{-7} and 7.74×10^{-7} m^2 min^{-1} were reported for SS and SS:sawdust (mass ratio of 9:1), respectively. Regarding the kinetic

constant, k, an increase of 11.3, 4.5, 0.2, 19.2, and 8.8% were observed for SS_CFA, at 70, 85, 100, 115, and 130 ℃, respectively.

The energy required to dry cylinders to MR = 0.30 (end of Period I) is determined by Eq. (4.5) (Fig. S 4.3 (supplementary information). The drying process at 130 ℃ requires less energy compared to the lower temperatures, and CFA promotes a positive effect (a reduction near to 3% on energy consumption, from 886 to 864 kJ kg^{-1} SS$_{wb}$ for SS and SS_CFA, respectively). According to these data, the drying at 130 ℃ with SS_CFA seems to be a good solution, based on the higher D_{eff} and $\overline{DR}$, and lower energy consumption.

The plot ln(D_{eff}) versus 1/T, Figure 4.4 (a-b) allows the determination of activation energy (E$_a$) and the diffusion factor (D$_0$). The magnitude of E$_a$ is similar in both cases (SS and SS_CFA) and within the range reported in the literature (11.83-35.11 kJ mol^{-1}) (Bennamoun et al., 2013; Zhang et al., 2016), while D$_0$ is 17.5% higher for SS_CFA sample.
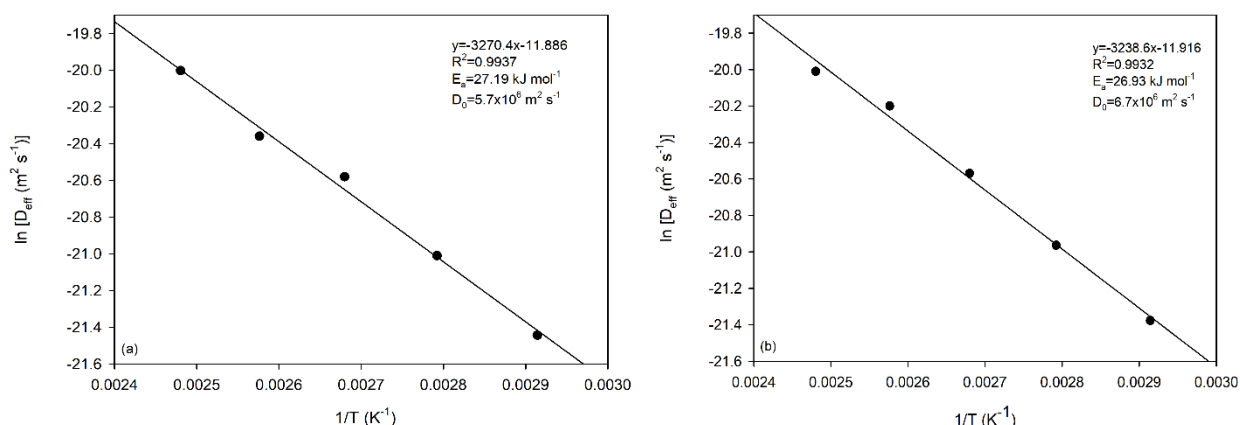
Figure 4.4 - Determination of parameters E$_a$ and D$_0$ for (a) control and (b) SS_CFA.

4.3.3   Phytotoxicity analysis

Figure 4.5 (a) shows the germination index (mean±sd) using *Lepidium sativum L.* in different extracts (Table S 4.1, supplementary information). Results marked with equal letters are statistically similar (Tukey HSD test with p < 0.05).-Several researchers have used this plant (known as garden cress) for this tests due to its rapid growth and since its a good indicator of phytotoxicity (Pavel et al., 2013; Pinho et al., 2017).
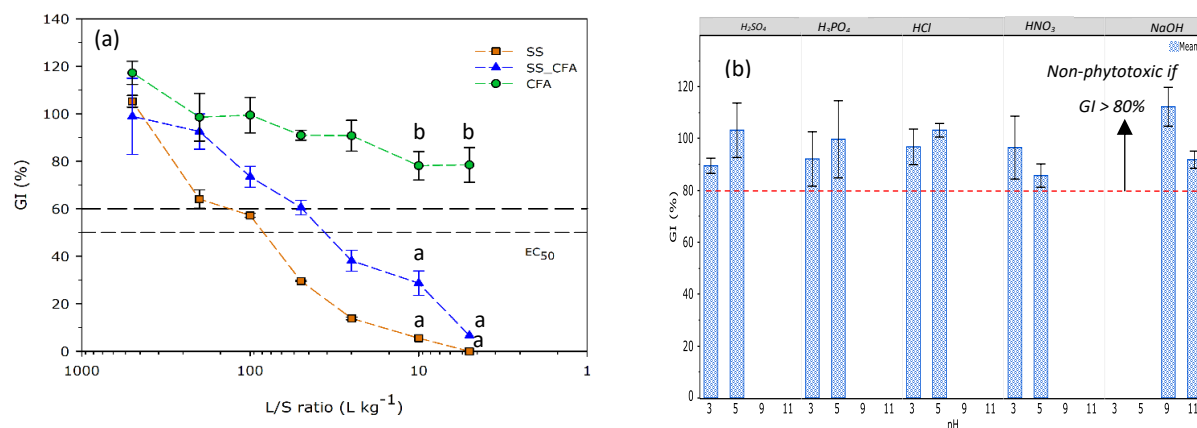
Figure 4.5 - Phytotoxicity test: (a) GI at different L/S ratio (L kg^{-1}) for SS, SS_CFA, and CFA; (b) GI measured in water with pH control using different acids and NaOH.

A reverse logarithmic scale order concerning the L/S ratio (from lower to higher concentration) was selected to represent the phytotoxic profile of each type of extract. The horizontal lines mark GI of 60%, above which mild phytotoxicity occurs, and GI of 50% inhibition (Gomes et al., 2019). Results in Figure 4.5 (a) reveals that the GI of CFA is always superior to 70%, which indicates that the inhibition of seed germination and growth is mild. Also, for 500 L kg^{-1}, the root growth is improved (GI > 100%), which represents a beneficial effect on the extract of CFA when compared to the control. On the contrary, SS eluates show adverse effects on GI, except for L/S 200 and 500 L kg^{-1}. Eluates from SS_CFA tend to improve GI when compared to SS, meaning lower inhibition. Even though, a Tukey HSD test reveals that SS and SS_CFA at 10 L kg^{-1} are statistically equal (p < 0.05), but different from the CFA sample. The EC$_{50}$ (concentration that induces 50% of inhibition) for SS and SS_CFA is 105.4 and 35.4 L kg^{-1}, respectively, corresponding to an enhancement of 66% in the phytotoxic activity of SS by adding the adjuvant. Other studies showed that the GI for different SS in the 10 L kg^{-1} ratio ranged from 41.2-55.2% (Fuentes et al., 2006) and 57.4% (Alvarenga et al., 2015). For lower L/S ratios, the GI values are lower due to the presence of higher concentrations of dissolved salts, as can be concluded by the EC (Table S 4.1, supplementary information). Therefore, in these conditions, the seeds and the radicles are under higher osmotic pressure stress. Furthermore, the SS used in the study comes from a WWTP with anaerobic digestion, so that the presence of ammonia may also interfere with seed germination (Alvarenga et al., 2007). Additionally, a test was conducted with distilled water with pH control in order to evaluate the influence of pH on the GI, Figure 4.5 (b). The results show that the pH has little influence on the GI of the garden cress.

4.3.4   Pot experiments

Figure 4.6 (a) shows that the root length of the *Lepidium sativum L.* is not influenced by the treatments when compared to the control (p < 0.05). In contrast, the amendment with SS, affects the

shoot length, Figure 4.6 (b), except for SS6. In fact, the plants cultivated in soil amended with SS12, SS24, and SS24_CFA reveals an increase of 12.6, 13.4, and 13.4%, respectively, in shoot length compared to control. According to Figure 4.6 (c), SS24_CFA promotes a significant increase in biomass weight ($p < 0.05$), which represents an improvement of 42% compared to the control. The final OM in the soil increases in all treatments when compared to the initial content (1.8%), Figure 4.6 (d), as a result of the OM content in SS applied in the soil in each treatment. Slightly better results may be due to an increase in the soil macronutrients such as N, P, and K (Teglia et al., 2011). Indeed, as shown in Table 4.1, the content of $N_{Kjeldahl}$, P_2O_5, and K_2O in SS is 3.90%, 3.83%, and 0.22%, while CFA contains 2.4% of K_2O. It is important to note that the soil used as control is poor in P (0.01%).
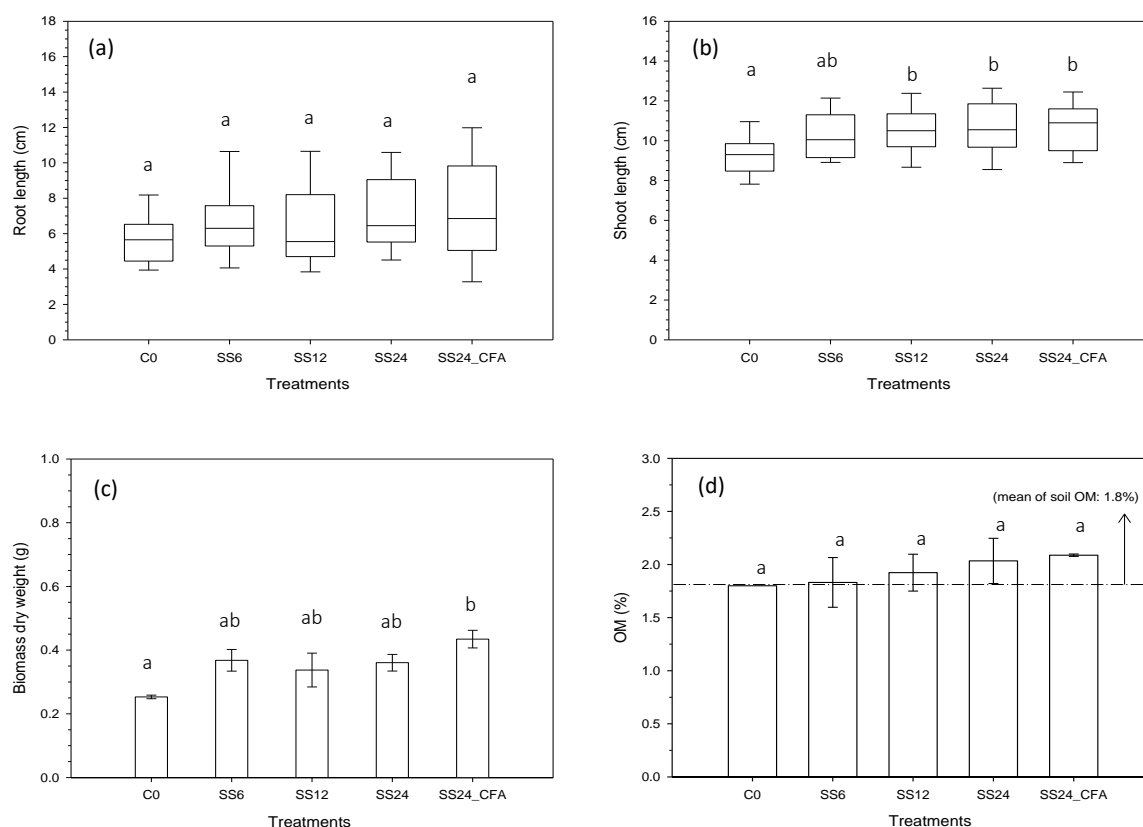
Figure 4.6 - Effect of amendments on (a) root length; (b) shoot length; (c) biomass dry weight and (d) OM on the soil at the end of the experiment.

Moreover, the soil pH increased from 6 to 7 with the SS_CFA treatment, which demonstrates its positive effect for raising soil pH. As aforementioned, the utilization SS_CFA at appropriate rates favors nutrient balance in the soil. The beneficial results obtained in our study from combining SS and weathered CFA as soil amendment are in agreement with the literature (Tsadilas et al., 2014; Shaheen

et al., 2014). Studies are ongoing to perform field studies with some of the final products tested in the laboratory.

4.4   Conclusions

This study shows that the addition of weathered coal fly ash has a positive impact on the drying process of SS. The isothermal drying at 130 ºC of SS_CFA is the best alternative, exhibiting the higher effective diffusion coefficient ($1.27{\times}10^{-7}$ m^2 min^{-1}) and drying rate (31.61 gH$_2$O kg^{-1} SS$_{wb}$ min^{-1}), and the lower energy consumption (864 kJ kg^{-1} SS$_{wb}$). The proposed mathematical modelling approach shows good fitting for both drying periods. Aiming at agronomic applications, the phytotoxicity of SS is reduced using CFA. The pot experiments demonstrate that the amendments boost the growth of plants (e.g., shoot length). Also, SS24_CFA promotes higher biomass of the garden cress and increases the soil pH to 7. The results indicate that the final product after drying has an adequate composition and may be beneficial for agronomic applications. However, more detailed tests should be done to evaluate the impact of this product on the soil. So far, the utilization of weathered CFA as SS drying adjuvant seems a good strategy for valorising both wastes in agronomic applications.

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4.6   Supplementary information

- *Drying process procedure*
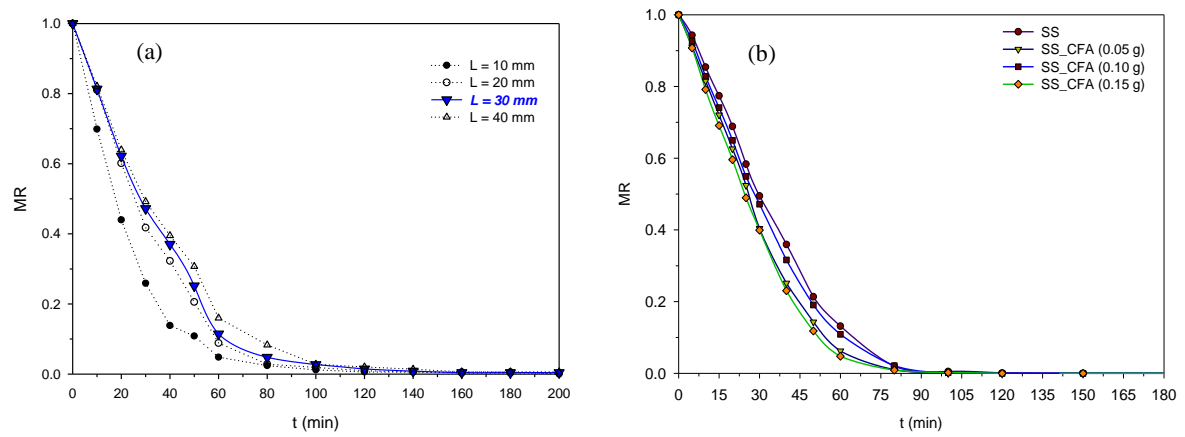
Figure S 4.1 - Drying screening phase to determine the (a) cylinder length, and (b) formulations (SS and SS plus 0.05, 0.10, and 0.15 g CFA g^{-1} SS_{wb}).
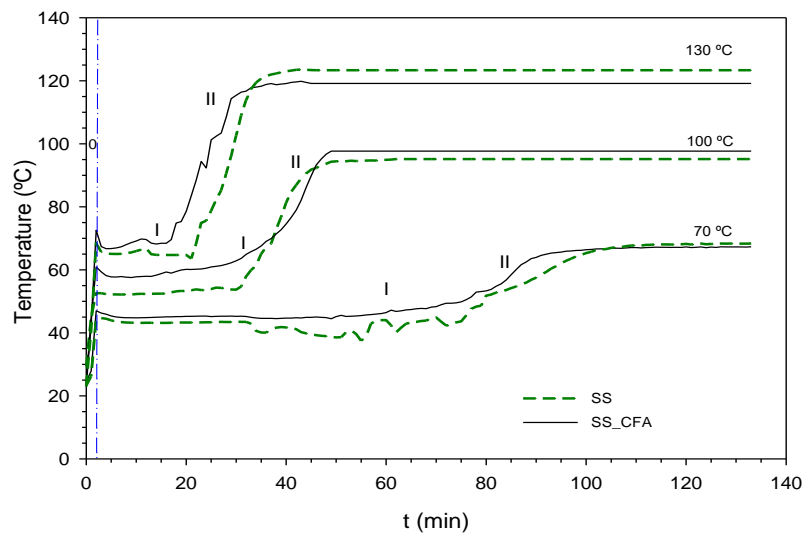
Figure S 4.2 - Temperature evolution inside the cylinder during the drying process at 70, 100 and 130 ºC [Periods 0, I and II represent the rising rate period, the constant rate period, and falling rate period, respectively].

- *Phytotoxicity tests*

Table S 4.1 - pH and EC measured in the extracts used in the phytotoxicity tests.

Samples	Parameter	L/S (L kg^{-1})						
		5	10	25	50	100	200	500
SS	pH	6.44	6.71	6.81	6.81	6.73	6.44	6.13
	EC (mS cm^{-1})	4.48	1.72	1.00	0.59	0.40	0.40	0.19
SS_CFA	pH	6.25	6.73	6.86	6.99	7.07	7.18	7.31
	EC (mS cm^{-1})	4.67	2.63	1.38	0.82	0.45	0.26	0.15
CFA	pH	8.91	8.63	8.52	8.34	7.75	7.97	7.14
	EC (mS cm^{-1})	0.83	0.49	0.24	0.15	0.09	0.08	0.06

- *Germination Index (GI) calculation*

For each sample, the germination index (GI) was calculated by combining Eq. (S 4.1), (S 4.2) and (S 4.3).

$$RSG(\%) = (\bar{N}/\bar{N}_b)100 \tag{S 4.1}$$

$$RRG(\%) = (\bar{L}/\bar{L}_b)100 \tag{S 4.2}$$

$$GI(\%) = (RSG.RRG)/100 \tag{S 4.3}$$

where $\bar{N}$ and $\bar{N}_b$ are the mean number of germination seeds in each sample and in control, respectively; $\bar{L}$ and $\bar{L}_b$ are the mean length of roots in each sample and in control, respectively; RSG is the relative seed germination (%) and RRG (%) is the relative root growth. The GI results were classified as: non-phytotoxic if GI > 80%; mild phytotoxicity 60% < GI < 80%; strong phytotoxicity 40% < GI < 60%; severe phytotoxicity GI < 40% (Gomes et al., 2019; Pinho et al., 2017).

- *Kinetics of drying*
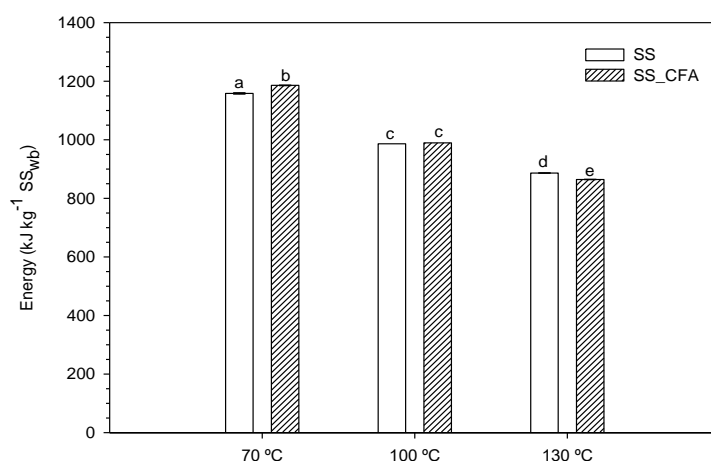
Figure S 4.2 - Energy consumption during Period I at 70, 100 and 130 °C to SS and SS_CFA samples. Results marked with different letters are statistically different through the Tukey HSD test (p < 0.05).

5.   THERMAL DEHYDRATION OF URBAN BIOSOLIDS WITH GREEN LIQUOR DREGS FROM PULP AND PAPER MILL

This study aims to investigate the sewage sludge (SS) drying process by incorporating a by-product formed in the pulp and paper industry (green liquor dregs - GLD) as drying adjuvant. Through an innovative approach, the drying kinetics was modelled, and the final dried product was tested for soil applications. After the characterization phase, small cylinders of SS without and with 0.15 g GLD g^{-1} SS_{wb} (SS_GLD) were dried in isothermal conditions at 70, 100, and 130 °C. The experimental data were fitted by Fick's second law and thin-layer models, and good results were achieved in both cases ($R^2 >$ 0.98 and RMSE < 0.05). Although only a slight improvement was observed, the best conditions for drying were found with the addition of GLD at 130 °C, where the drying rate was 30.88 gH_2O kg^{-1} SS_{wb} min^{-1}. In this condition, a decrease of 8% in the energy required for moisture evaporation was observed. Regarding the phytotoxicity tests with *Lepidium sativum L.* (garden cress), 60% improvement in EC_{50} was noticed for the sample with GLD when compared to the raw SS. The dried product SS_GLD complied with the regulations for soil applications regarding the potentially toxic metals (Cr, Ni, Cu, Pb, Zn, and Cd), and promoted an increase in soil organic matter and pH. However, further and in-depth studies should be conducted to assess the potential of SS_GLD application in agricultural soil.

Keywords: drying, sewage sludge, dregs, soil application, phytotoxicity, kinetic modelling.

5.1 Introduction

Sewage sludge (SS) is a by-product formed in wastewater treatment plants (WWTP) with a high rate of production per inhabitant. The real amount produced in each country is often uncertain because the waste management operators do not communicate reliable data to authorities. According to reports from the European Union (EU), the member states produced around 10.1 Mt of SS on a dry basis (db), in 2008 (Comission, 2008; Kapcprzak et al., 2017; Kelessidis and Stasinakis, 2012). However, by 2020, the expected production of SS exceeds 13 Mt_{db} and the usage in agriculture reaches 4 Mt_{db}. The main option for the SS management within the EU countries is the land application (in more than 50% of the countries), followed by incineration, composting, and landfilling (Hamdi et al., 2019). Globally, the agricultural use of SS represents about 37 wt% in the EU, 44 wt% in China and 65 wt% in the United States (Kelessidis and Stasinakis, 2012; Mohamed et al., 2018; Torkashvand, 2010).

In Portugal, about 80% of SS has been applied to agricultural soils and the rest has been disposed of in landfills and other options (Kelessidis and Stasinakis, 2012; LeBlanc et al., 2008). The application of SS in soil can increase agricultural yield mainly due to its contribution to the carbon pool as well as to the essential nutrients (N, P, and K) (Alvarenga et al., 2015; Hoffmann et al., 2010; Morales et al., 2016; Tervahauta et al., 2014; Vaxelaire et al., 2000). Although some elements such as Zn and Cu have agronomic value, the potentially toxic metals (PTM) and pathogenic microorganisms require control to guarantee the safe application of SS in the soil. Sometimes industrial effluents (e.g., from electroplating and tannery industries) are polished in urban WWTP, which can increase the PTM in SS, hampering its application to soil (Tervahauta et al., 2014).

Challenging issues of SS management are mainly related to transport costs (due to residual moisture content) and emissions of bad odours. Given that the conventional dehydration systems (e.g., mechanical centrifugation and filtration) are limited at best to reach 80% moisture (Shen et al., 2008; Tuncal and Uslu, 2014), the thermal drying process has been referred to as favourable. Moreover, thermal drying may contribute to the inactivation of pathogens, which is a legal restriction to apply SS in agriculture (Bennamoun et al., 2013; Collard et al., 2017). The drying kinetics of the process can be modelled considering three periods. Namely, the initial thermal equilibrium phase or rising period (period 0), the constant rate period (period I), and the falling rate period (period II). In the period I, the moisture evaporation occurs mainly at the surface of the wet solid, which is maintained by the internal movement of moisture to surface. During this period, the surface temperature is almost constant (near the wet-bulb temperature, T_{wb}, of the surrounding air temperature). The transition between the constant and falling periods depends on the layer thickness and the drying conditions (Syed-Hassan et al., 2017). In the falling period, the surface of the material is unsaturated (Srikiatden and Roberts, 2007). To describe the drying process several mathematical models have been used (Bennamoun et al., 2014; Danish et al., 2016; Zhang et al., 2017, 2016). The period I may be modelled by the Fick's second law, while the period II can be described by the thin-layer model.

To improve the drying process of SS, some adjuvants have been tested. The objective is to boost the mass transfer of moisture and thus reduce the drying time. Moreover, specific adjuvants (e.g., coal fly ash) reveal a fungicidal effect when the final product is applied to soil (Basu et al., 2009). Other benefits of the adjuvants may be observed in the soil properties, for example in pH, permeability, nutrient availability, water retention capacity, and soil aeration (Stefaniuk and Oleszczuk, 2016). Recent studies in the literature highlight the effect of sawdust (Deng et al., 2017), rice husk (Wang et al., 2019), and coal fly ash (Zhang et al., 2016) as an adjuvant to the drying process. However, none of these studies combined the drying study with mathematical modelling and the final application of the product in soil.

In this study, the green liquor dregs (GLD) were tested as an adjuvant of the SS drying process. The GLD is formed in the Kraft recovery cycle of pulp and paper mills. This cycle is essential to recovery the chemicals used in the cooking wood phase and comprises the following stages: concentration of the weak black liquor in evaporators; combustion of black liquor in a boiler; conversion of Na_2CO_3 of the smelt into $NaOH$; and regeneration of CaO. GLD is formed after dissolving the molten smelt and the filtration of the green liquor. Thus, it mainly contains sodium, and calcium carbonates, sodium hydroxide, sulfides and small quantities of PTM from the wood. The carbonate content may represent about 70 wt%, and the pH is generally higher than 10 (Faubert et al., 2016; Mäkitalo et al., 2014; Ragnvaldsson et al., 2014). The concentration of GLD in green liquor ranges from 0.6 to 2 g L^{-1}, and the production is 3-4 kg t^{-1} pulp (Golmaei et al., 2017). In Portugal, the biggest company produced about 1.6 Mt of pulp in 2018, and thus more than 6 kt of GLD year^{-1} are produced. Most of this waste has been disposed of industrial landfills (Navigator company, 2017). However, the current social and environmental pressures have been pushing the pulp and paper industry to seek eco-friendly alternatives to landfill, such as agricultural and forestry applications or recovery in products (e.g., components of bio-composites, cement and asphalt, adsorbents, etc.) (Faubert et al., 2016; Mäkelä et al., 2016; Pervaiz and Sain, 2015; Torkashvand, 2010). Other studies reported the influence of GLD in the composting of Kraft mill secondary sludge (Zambrano et al., 2010), and the results showed good performance for pH control. Also, Mäkelä et al (2012; 2016) proposed GLD as a helpful material for acidic soil amendment and for the prevention of the acid rock drainage (due to its high acid neutralization capacity). Thus, the utilization of GLD into the SS drying process may be valuable not only to aid water draining, but also to balance the soil pH in the final application, and to inactivate pathogenic microorganisms in the sludge.

Thus, this research was built based on some considerations: (i) the good properties of GLD to be used as soil improvement agent regarding the final application of the drying product; (ii) the high quantity of GLD discarded in industrial landfills; and (iii) the fact that GLD was not studied before in the literature as drying agent. Also, this investigation explores a different approach to model the kinetic curves and evaluates the performance of the product after drying. In short, this study aims to investigate the drying process under different operational temperature conditions to obtain a product that can be used in soil, recovering both residues (SS and GLD).

5.2 Materials and methods

5.2.1 Materials

A sample of 5 kg of anaerobic digested SS was collected after mechanical dewatering by centrifugation in a WWTP, which treats around 36,000 m^3 day^{-1} of urban effluents. The sample was stored at 4 ºC until further utilization. GLD sample (also about 5 kg) was obtained from a Portuguese Kraft pulp mill. The moisture content of the GLD was 40 wt%, and the sample is representative of one production day of the pulp mill. The sample was dried at room temperature, disintegrated, and sieved through a 425 µm screen. A sandy soil sample (10 kg) was collected in an agricultural field at the central region of Portugal at a depth of about 20 cm. Then, the sample was dried at room temperature and homogenized properly.

5.2.2 Analytical methods for SS and GLD samples characterization

Moisture and organic matter (OM) were determined according to the EPA Method 1684. The pH and electric conductivity (EC) were measured by potentiometry in a liquid to solid ratio (L/S) suspension of 10 L kg^{-1} (Alvarenga et al., 2016; Oleszczuk and Hollert, 2011). The water absorption capacity (WAC) of the samples was determined based on the gravimetric procedure described by Adhikari et al., (2008). Chlorides were quantified by the Mohr method in the liquid extract obtained using an orbital shaker for 24 h at L/S 10 L kg^{-1}. Total dissolved solids (TDS) were determined by evaporating water at 105 ºC of the extract filtered with a 0.45 µm pore filter. The elemental composition (K, Mg, Ca, Si, Al, Na, Fe, Cd, Cr, Cu, Ni, Pb, and Zn) of SS and GLD was determined by X-ray fluorescence (XRF) using Nex CG Rigaku equipment. For that, the samples were dried, grounded and sieved 200 mesh (~75 µm) (Healy et al., 2016). GLD was also characterized by X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer (CuKα-radiation), with a 10-80º 2θ range. The elemental analysis (C, H, N, and S) of SS was performed using an analyzer EA 1108 *Fisons Instruments*. The oxygen content was estimated by difference. The high heating value (HHV) measurement of SS samples was conducted in a Parr 1341 Plain Oxygen Bomb Calorimeter according to Shen et al., (2012), and the lower heating value (LHV) was determined based on Eq. (5.1),

$$LHV = 1.8HHV - 91.23H \tag{5.1}$$

where H is the hydrogen content (%) in the sample, and both HHV and LHV can be expressed in Btu lb^{-1} (2.324 kJ kg^{-1}).

The acid neutralization capacity (ANC) of GLD was determined by suspending 0.75 g of dried solid in several aqueous solutions with increasing quantities of HCl 1 M (increments of 0.5 mL). The total liquid volume (ultrapure water + HCl) was 20 mL in each flask. The samples were kept under

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agitation in an orbital shaker for 24 h to reach the equilibrium. Then, the pH was measured by potentiometry (Mäkitalo et al., 2014). The characterization tests were performed at least in duplicate.

5.2.3 Drying kinetics

Small cylinders of SS without and with 0.15 g GLD g^{-1} SS$_{wb}$ (about 0.7 g, 5 mm diameter, and 30 mm length) were extruded manually using a plastic syringe for determining the kinetics of drying process. Previous studies were performed with cylinders of SS (5 mm diameter and length in a range of 10 to 40 mm, at 100 ℃) to determine the dimension of an "infinite cylinder". Based on the moisture ratio (MR) versus the time it was concluded that a length of 30 mm is appropriated. Thus, SS (control) and SS with GLD (SS_GLD) were prepared to ensure a homogeneous sample. Then, 15 pellets were placed over an aluminum dish (100 mm diameter) and dried at 70, 100, and 130 ℃ in a Moisture Analyzer, *Precisa XM50*. The mass of pellets was continuously recorded with a minute increment until a constant weight was reached. The temperature inside the pellets was measured using thermocouples type K connected to a Pico Technology thermocouple data logger.

Fick's second law was the model used to describe the constant rate period of the drying process (period I). For an "infinite cylinder", the transient behaviour can be modelled along with a one-dimensional layer of the cylindrical coordinate (radial direction). Eq. (5.2) describes the one-dimension solution of the moisture mass balance, considering uniform initial moisture, negligible shrinkage, and null temperature gradient (Figueiredo et al., 2015). In our study, only the first term of the sum in Eq. (5.2) was considered. The Henderson & Pabis model, also known as the Thin-layer model, described by Eq. (5.3), was used to model the second period of the drying kinetics (Figueiredo et al., 2015; Srikiatden and Roberts, 2007),

$$MR = \frac{M(t)-M_e}{M_0-M_e} = \sum_{n=1}^{\infty}\frac{4}{r^2\alpha_n^2}\ exp(-D_{eff}\ \alpha_n^2 t) \tag{5.2}$$

$$MR = \frac{M(t)-M_e}{M_0-M_e} = ae^{-kt} \tag{5.3}$$

where MR is the dimensionless moisture ratio (Danish et al., 2016); M_0 and $M(t)$ are the moisture content in the cylinder (gH_2O g^{-1} dry solid) at t_0 and t time, respectively; M_e is the moisture content in equilibrium (gH_2O g^{-1} dry solid); the roots of the Bessel function of zero-order ($J_o(r\alpha_n) = 0$) allowed to determine α_n parameter; r is the radius of the cylinder (m); D_{eff} is the effective diffusion coefficient (m^2 min^{-1}) of water; *a* is a parameter of the thin-layer model; k is the kinetic constant (min^{-1}) and *t* is the time (min). The length of the period I of the drying kinetics was considered as the period in which the temperature inside the cylinders (T$_{wb}$) is constant, corresponding to MR = 0.30 (constant drying rate). The modulus of drying rate, |DR|, expressed in gH_2O min^{-1} kg^{-1}SS$_{wb}$ was determined by Eq. (5.4),

$$|DR| = \frac{\partial M(r,t)}{\partial t} \approx \frac{\Delta M}{\Delta t} = \frac{M_i-M_{i-1}}{t_i-t_{i-1}} \tag{5.4}$$

where M is the moisture on a wet basis (gH$_2$O kg^{-1} SS$_{wb}$), and t is the time (min).

The relationship between D_{eff} and the temperature was described by the Arrhenius equation (Eq. 5.5),

$$ln(D_{eff}) = \ ln(D_0) - \frac{E_a}{RT} \tag{5.5}$$

where T is the constant drying temperature (K), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), D$_0$ represents the maximal diffusion coefficient at infinite temperature (m^2 s^{-1}) and E$_a$ is the activation energy for diffusion (kJ mol^{-1}). Parameters D$_0$ and E$_a$ were obtained through linear regression plotting ln (D_{eff}) versus 1/T.

The energy (kJ kg^{-1} SS$_{wb}$) required for evaporating the moisture to achieve MR = 0.30 (E$_{0.30}$) was calculated for the period I, considering the drying rate calculated at t time, Eq. (5.6),

$$E_{0.30} = h \int_{t_0}^{t} |DR(t)| dt \tag{5.6}$$

where h is the latent heat of vaporization for wet-bulb temperature (kJ kg^{-1}) (Cengel, 2003); t$_0$ and t (min) correspond to the time after the rising period and to achieve MR = 0.30, respectively; and |DR(t)| is the drying rate at t time (min^{-1}).

5.2.4 Phytotoxicity tests

The phytotoxicity of liquid extracts at different L/S ratios of SS, SS_GLD, and GLD was evaluated with *Lepidium sativum L.* (garden cress) according to the conditions present in Table S 5.1 (supplementary information). The extracts were obtained based on EN 12457-2:2002 by agitating the suspension in an orbital shaker for 2 h. Afterward, the liquid was filtered (*Whatman* filter, 0.45 µm pore). The tests were performed in triplicate along with a control test (Alvarenga et al., 2015; Pinho et al., 2017). About 5 mL of the eluate was poured over a *Whatman* filter paper in a Petri dish (90 mm) with ten seeds. The test lasted 48 h, at 25 ± 0.1 °C, in dark conditions (Santos et al., 2019).

The germination index (GI) was calculated by combining Eq. (5.7), (5.8), and (5.9) (Santos et al., 2019):

$$RSG(\%) = \ (\bar{N}/\bar{N}_b)100 \tag{5.7}$$
$$RRG(\%) = \ (\bar{L}/\bar{L}_b)100 \tag{5.8}$$
$$GI(\%) = \ (RSG.RRG)/100 \tag{5.9}$$

where $\bar{N}$ and $\bar{N}_b$ are the mean number of germination seeds (sample and control, respectively); $\bar{L}$ and $\bar{L}_b$ are the mean length of roots (sample and in control, respectively); RSG and RRG (%) are the relative seed germination and relative root growth, respectively (Oleszczuk and Hollert, 2011). The GI was classified as non-phytotoxic if GI > 80%; mild phytotoxicity 60% < GI < 80%; strong phytotoxicity 40% < GI < 60%; severe phytotoxicity GI < 40% (Pinho et al., 2017; Trautmann and Krasny, 1997).

5.2.5   *Growth tests*

The growth tests with garden cress were performed using pots with a total volume of 300 cm^3. About 290 cm^3 was filled with treated soil and 10 cm^3 of gravel was placed at the bottom of the pot to allow drainage. The soil was treated with different rates of SS equivalent to 6, 12, and 24 t ha^{-1} (SS6, SS12, and SS24, respectively). Furthermore, additional treatment with SS_GLD (in an equivalent rate of 24 t ha^{-1}, denominated by SS24_GLD) was included. The rate of 6 t ha^{-1} was based on the recommendation of the Portuguese legislation (*Decreto Lei N^o*. 446/91). The other rates were tested to evaluate the system in extreme conditions (Alvarenga et al., 2016). A control test (C0) was included in the set of experiments, which were performed in duplicate.

Then, about 17 seeds of garden cress were sown in each pot, incubated in an oven with white LED light (~ 280 µmol m^{-2} s^{-1}, 400-700 nm, incidence angle of 240º), regulated with a photoperiod of 12 h, temperature 21 ± 0.1 °C, and relative humidity 50% (Arriagada et al., 2014). After 1-week germination and growth, 7 plants were carefully removed (thinning phase), and 10 plants remain in each pot. After four weeks of growth, the roots and shoot lengths, and biomass were recorded. The roots were washed, and the biomass was determined at 60 ºC in an oven-drying until constant weight (Mohamed et al., 2018). OM, pH, and EC of the soil were determined at the end of the experiment. Soil characterization was determined in an external laboratory and results are summarized in Table S 5.2 (supplementary information).

5.2.6   *Statistical analysis*

One-way analysis of variance (ANOVA) through the Tukey HSD test ($p < 0.05$) was conducted whenever necessary using Microsoft Excel® 2013. The root mean square error (RMSE), Eq. (5.10), and the coefficient of determination (R^2) were used to evaluate the fitting capacity of the mathematical models used for drying kinetics (Danish et al., 2016).

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^{N} \left(MR_{exp,i} - MR_{pred,i} \right)^2 \right]^{1/2} \tag{5.10}$$

where, $MR_{exp,i}$ and $MR_{pred,i}$ are the experimental and calculated values of the dimensionless moisture ratio for observation *i*, respectively; and N is the number of observations.

5.3   Results and discussion

5.3.1   *Properties of SS and GLD*

Table 5.1 shows some parameters determined in SS and GLD samples, and the overall data agree with those reported in the literature.

While the natural pH of SS is almost neutral (pH = 6.71), the GLD is a strongly alkaline material (pH = 10.3). The WAC of SS is higher than GLD, whereas SS_GLD also exhibited a large value (243 g H$_2$O g^{-1} SS_GLD$_{db}$). This parameter demonstrates the benefits of applying SS_GLD to improve soil water holding levels. Moreover, the EC of GLD (15.6 mS cm^{-1}) indicates a high ionic strength,

corresponding to a TDS nearly 10 g L^{-1} (corresponding to a dissolution of about 10 wt%). This value includes chlorides and other soluble salts (Nurmesniemi et al., 2005). OM and nutrients (N, P, K) are particularly important for valorising wastes in agronomic applications (Collard et al., 2017; Steckenmesser et al., 2017).

Table 5.1 - Properties of SS and GLD used in this study and from the literature.

Parameters [1]	SS		GLD	
	This work	Ref. [1]	This work	Ref. [2]
Moisture (%)	78.0	84.3	20.8	ni
WAC (g H$_2$O 100 g^{-1}$_{db}$)	246	ni	102	ni
pH[b]	6.71	7.30	10.3	12.2
EC (mS cm^{-1}) [2]	1.70	2.40	15.60	ni
TDS (g L^{-1})	nd	ni	9.9	ni
OM (%)	63.7	70.9	9.8	ni
Cl$^-$ (%)	0.13	ni	0.63	ni
N$_{kjeldahl}$ (%)	3.90	6.20	nd	0.07
P$_2$O$_5$ (%)	3.83	10.20	0.15	0.37
K$_2$O (%)	0.22	1.31	0.06	0.37
MgO (%)	0.38	1.04	16.8	5.94
CaO (%)	5.50	2.78	52.9 [3]	62.4 [3]
SiO$_2$ (%)	4.05	ni	2.91	ni
Al$_2$O$_3$ (%)	1.94	ni	1.10	0.47
Na$_2$O (%)	nd	0.27	8.01	9.49
Fe$_2$O$_3$ (%)	nd	ni	0.40	0.59

[1] With the exception of moisture, the % was calculated in dry basis; [2] Measured at L/S 10 L kg^{-1}; [3] these values are reported in CaCO$_3$; Refs.: [1]- (Alvarenga et al., 2015) mean of two samples; [2]- (Cabral et al., 2008); nd - not determined; ni - not informed.

Data in Table 5.1 clearly shows that SS has much better properties in this regard than GLD. The phosphate content in commercial fertilizers is about 5-12 wt% P$_2$O$_5$, and the SS of this work contains 3.83 wt% (Adam et al., 2009). On the contrary, GLD is rich in calcium, magnesium, and sodium.

Table S 5.3 (supplementary information) shows the elemental analysis of SS, which agrees with the literature (Werle and Wilk, 2010; Diaz et al. 2019). C/N ratio is important concerning soil application, and the value found in this work (7.8) is within the typical range reported in the literature (Alvarenga et al., 2016; Díaz et al., 2019; Kätterer et al., 2014). In case the composting was the option to stabilise the SS, a carbon-rich material must be added to raise the C/N to ~30. HHV and LHV reported in Table S 5.3 (supplementary information) show that the dried SS could be an attractive alternative renewable source of energy. The values obtained are similar to other low-rank fuels, such as lignite (11.80-21.90 MJ kg^{-1}$_{db}$) (Syed-Hassan et al., 2017).

Figure 5.1 (a)-(b) show for GLD, the X-ray diffraction spectra and acid neutralization capacity (meqH$^+$ g^{-1}), respectively. According to the XRD diffractogram (Figure 5.1 (a)), the main crystalline phase identified in GLD was CaCO$_3$ in calcite form (about 70 wt%).
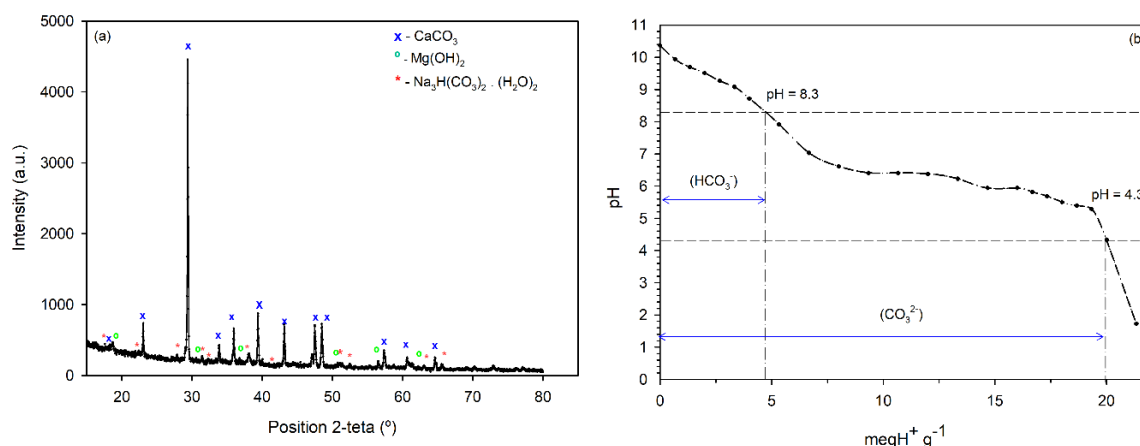
Figure 5.1 - (a) Characterization of crystalline phases of GLD by XRD and (b) Acid neutralization capacity.

In addition, sodium sesquicarbonate ($Na_3H(CO_3)_2$) and magnesium hydroxide ($Mg(OH)_2$), in brucite form, appeared as second-phases, corresponding to 17 and 3 wt% of the sample. Similar results were reported by other researchers (Mäkitalo et al., 2014; Ragnvaldsson et al., 2014). The presence of these phases supports the result of the ANC, Figure 5.1 (b), which corresponds to a high capacity to neutralize acids (Quina et al., 2009). Indeed, ANC to a reference pH 4.3 was about 20 meqH$^+$ g$^{-1}_{db}$, which means about 1 g CaCO$_3$ g^{-1}. This result agrees with Mäkitalo et al. (2014), who demonstrated the ability of GLD to be used as an alkalinizing agent for acidic soils.

Figure 5.2 shows the concentration of PTM of SS and GLD samples on a logarithmic scale.
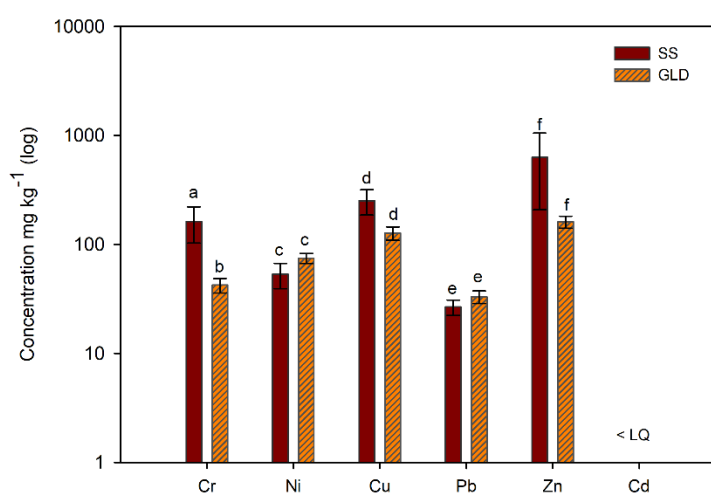
Figure 5.2 - Concentration of PTM (Cr, Ni, Cu, Pb, Zn, and Cd) in SS and GLD samples. [Limit of quantification (LQ) to Cd = 11 mg kg^{-1}]. The same letter means similar statistical results (p < 0.05).

The concentration of PTM in SS is below the maximum limits imposed for application in agricultural soil by Portuguese law (*Decreto Lei Nº*. 276/2009 October 2). Similar results have been indicated in the literature for both wastes (Adam et al., 2009; Alvarenga et al., 2016; Nurmesniemi et al., 2005). Thus, the low PTM concentration in both residues do not compromise the possibility of its reuse in soil.

5.3.2   Kinetics analysis

This research is part of a project aiming at developing an industrial dryer for facilitating the management of SS, namely the ones formed in big WWTP. The dryer will be designed for SS after centrifugation and extrusion in a cylindrical shape before the drying phase.

Figure 5.3 (a) depicts the temperature profiles inside the small cylinders of SS and SS_GLD samples during drying, and Figure 5.3 (b) the relation between the drying temperature, the wet-bulb temperature (T_{wb}), and the air relative humidity. The evaporation rate of moisture from the samples is strongly dependent on-air drying temperature, and thus the temperature inside the cylinders was monitored with high sensitivity thermocouples inserted inside the samples (Liu et al., 2014). As shown in Figure 5.3 (a), a preheating stage occurs in about 5 min for all drying temperatures (70, 100, and 130 ºC). Afterward, a constant period of temperature (period I) is observed and the temperature inside the sample is defined as wet-bulb temperature of drying air. The T_{wb} is always inferior to the surrounding air temperature because the air relative humidity is lower than 100%. For example, at 70 ºC, the T_{wb} is 42 and 43 ºC, corresponding to relative humidity of 20 and 22% for SS and SS_GLD, respectively.
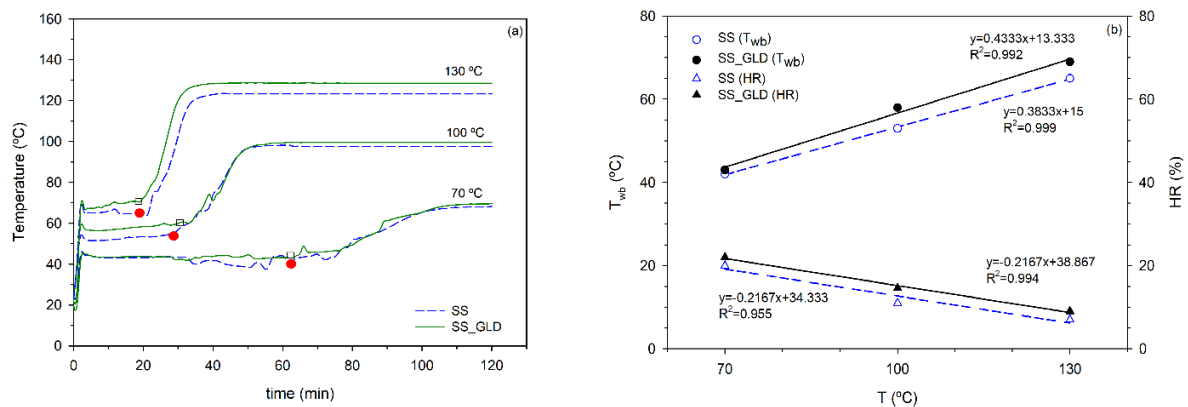
Figure 5.3 - (a) Temperature inside the cylinders during drying process at 70, 100 and 130 ºC; (b) Relation between the drying temperature, wet-bulb temperature and air relative humidity to SS and SS_GLD samples. Symbols ● and □ represent the end of the constant period (period I) for SS and SS_GLD, respectively.

A positive linear correlation between the drying temperature and the wet-bulb temperature was achieved ($R^2 > 0.99$), and consequently the air relative humidity decreases with the drying temperature. It is important to note that the length of the period I is shorter for higher temperatures. At 70 ºC, the period I lasted for about 64 min for both samples (SS and SS_GLD), whereas at 130 ºC it only takes 17 min. At the end of the period I, a secondary heating stage occurs (period II), and the temperature inside the cylinder rises until it reaches the temperature of the surrounding air.

The experimental drying isotherms at 70, 100, and 130 ºC are shown in Figure 5.4, where the three stages (period 0, I, and II) were identified along with the predictions from theoretical models. Figure 5.5 (a-b) show the derivative profiles of the drying rate versus moisture ratio (MR), and the drying rates, respectively, for 70, 100, and 130 ºC.
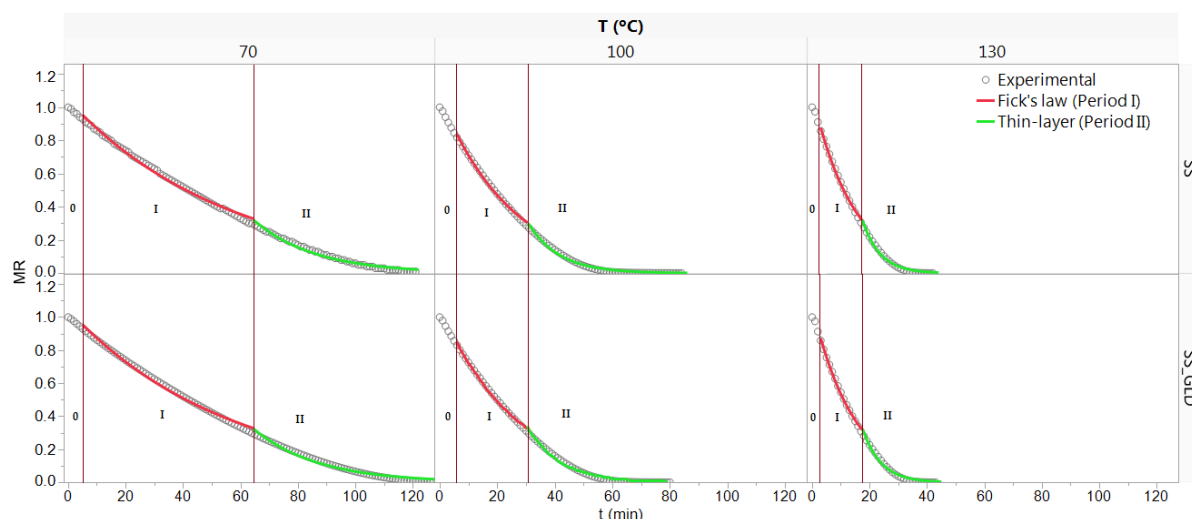
Figure 5.4 - Experimental MR and predictions through Fick's Law model and Thin-layer model as a function of time to SS and SS_GLD at different temperatures (70, 100 and 130 °C). [Periods 0, I and II represent the rising, the constant, and falling rate periods, respectively, separated by solid vertical lines].

According to the results shown in Figure 5.4 and Figure 5.5 (a), it is possible to observe that during the heating period (period 0), the evaporation rate of not bounded water increased significantly (Danish et al., 2016). Subsequently, period I is characterized by different lengths depending on the drying temperature. For example, at 70 ºC, it lasts from 5 to 64 min for both materials (SS and SS_GLD). Thus, the effect of GLD as an adjuvant seems to be limited since the drying time was not reduced. Accordingly, the drying rate was not boosted when GLD was added ($|\overline{DR}|$ are statistically equal for each temperature). For example, $|\overline{DR}|$ at 100 °C were equal to 16.81 and 17.78 gH_2O kg^{-1} SS_{wb} min^{-1} for the SS and SS_GLD, respectively.
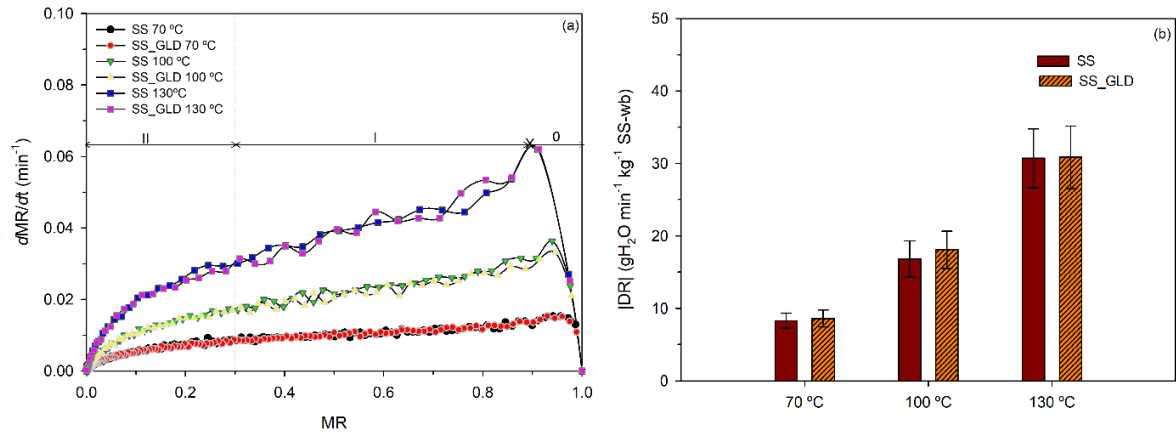
Figure 5.5 - (a) Derivative of drying rate profiles at different temperatures (0 - is the rising rate period; I – the constant rate period and II – bound water); (b) Drying rate, in g H_2O min^{-1} $kg^{-1}SS_{wb}$, for SS and SS_GLD.

Indeed, some properties of GLD may hindered the flow of water *molecules* from inside to outside the material during the drying process, namely the high WAC, the large surface area (around 18 m^2 g^{-1}) (Makitalo et al., 2014), the small particle size (Brebbia and Itoh, 2016), and the low hydraulic conductivity (10^{-8} to 10^{-9} m s^{-1}) (Jia et al., 2013; Makitalo et al., 2014).

Regarding the fitting of the models to the experimental data, Figure 5.4 and Table 5.2 (R^2 and RMSE) show that the Fick's second law and the thin-layer model are suitable to describe periods I and II, respectively. The results of the Tukey HSD test for drying rate (Table 5.2) revealed that SS and SS_GLD are statistically equal for each temperature tested, but different ($p < 0.05$) when the effect of the temperature was considered. Considering the diffusion coefficient, the values are in the range of 2.92×10^{-8} to 1.19×10^{-7} m^2 min^{-1}, increasing with temperature. GLD did not improve D_{eff}, while the values found in this research are within the range indicated by other researchers. Zhang et al., (2016) reported 8.22×10^{-8} to 7.74×10^{-7} m^2 min^{-1} at 60 and 180 °C, respectively. Another study with sawdust as an adjuvant for SS drying indicated 8.33×10^{-7} and 7.74×10^{-7} m^2 min^{-1} for SS and SS:sawdust (9:1), respectively (Li et al., 2014).

Table 5.2 - Parameters obtained for the different periods of the drying curves.

T (ºC)	Samples	Fick's second law (period I)					Thin-layer (period II)			
		D_{eff} (m^2 min^{-1})	t_f [1] (min)	$\overline{\lvert DR \rvert}$ [2] (gH_2O kg^{-1} SS_{wb} min^{-1})	R^2	RMSE	k (min^{-1})	a	R^2	RMSE
70	SS	2.92×10^{-8}	64	8.29 *a*	0.993	0.02	0.0468	6.563	0.984	0.01
	SS_GLD	2.93×10^{-8}	64	8.61 *a*	0.992	0.02	0.0446	5.788	0.978	0.01
100	SS	6.92×10^{-8}	30	16.81 *b*	0.995	0.01	0.0928	5.236	0.989	0.01
	SS_GLD	6.49×10^{-8}	31	17.78 *b*	0.996	0.01	0.0882	4.947	0.989	0.01
130	SS	1.19×10^{-7}	17	30.73 *c*	0.995	0.01	0.1630	5.565	0.988	0.01
	SS_GLD	1.17×10^{-7}	17	30.88 *c*	0.997	0.01	0.1571	5.147	0.985	0.01

[1] - t_f – time at the end of the period I; [2] - $\overline{DR}$ – average drying rate for the period I. $\overline{\lvert DR \rvert}$ – marked with different letters are statistically different (Tukey HSD test, $p < 0.05$).

The effect of GLD as an adjuvant led to E_a in the same order of magnitude as in the case of SS (26.6 and 27.0 kJ mol^{-1}, respectively) (Table S 5.4, supplementary information). Thus, the minimal energy to water diffusion is nearly the same for both materials. Even though, E_a found in this study are close to others reported in the literature (23.42 kJ mol^{-1} was indicated by Zhang et al., 2016). Moreover, the energy consumed to dry the material until MR = 0.30 (end of the constant period) revealed a slight improvement in the case GLD was used. For example, the energy consumption at 130 ºC was 860.7 kJ kg^{-1}wb for SS_GLD while 936.7 kJ kg^{-1}wb, was required for SS (Table S 5.4, supplementary information). It is important to note that, the energy required for drying the material is very dependent on the initial water content and to reduce the energy consumption in a dryer, the solid must be mechanically dewatered as much as possible (moisture ≤ 80%) (Dhir et al., 2001).

5.3.3 *Phytotoxicity assays and growth tests*

For agronomic applications, the phytotoxicity is a major issue. Figure 5.6 reveals GI (mean ± sd) of *Lepidium sativum L.* determined in liquid extracts obtained at different L/S ratios (L kg^{-1}) with samples of SS, SS_GLD, and GLD, which pH and EC are shown in Table S 5.1 (supplementary information). The phytotoxic profile is presented on a logarithmic reverse order scale, with respect to L/S ratio, which means from lower to higher concentration of substances in the extracts. The horizontal lines mark GI = 60%, a value above which mild phytotoxicity is observed (Trautmann and Krasny, 1997) and the GI = 50% of inhibition (to determine EC_{50}).
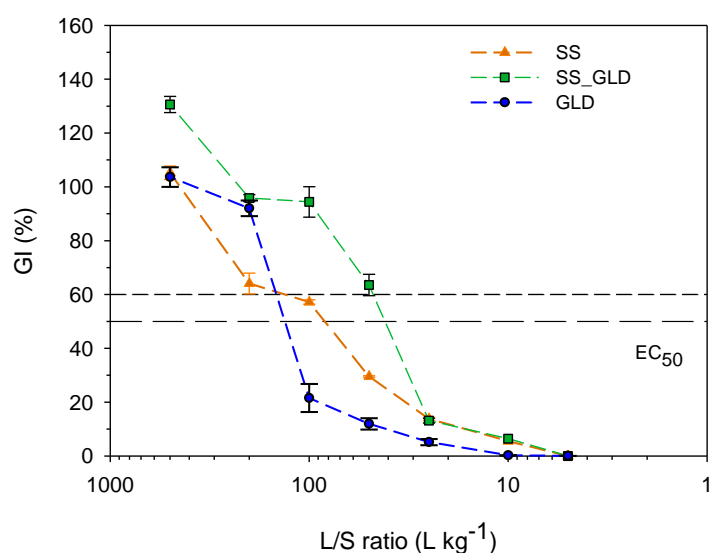
Figure 5.6 - GI (%) at different L/S ratio (L kg^{-1}) for SS, SS_GLD, and GLD (mean ± sd).

Extracts obtained at higher L/S (> 100 L kg^{-1}) led to GI superior to 60% (non-phytotoxic), in agreement with others studies (Alvarenga et al., 2015) for SS samples. EC_{50} was 105.4, 44.7, and 136.1 L kg^{-1} for SS, SS_GLD, and GLD, respectively. Thus, the SS_GLD mixture promoted nearly 60% of reduction in the phytotoxic effect of the SS sample. However, the lowest L/S (5, 10, and 25 L kg^{-1}) were

very aggressive for the germination process in all the cases. Indeed, in this situation, the salinity (EC $\geq$1 mS cm^{-1}), including Cl$^-$, is significant. Barral and Paradelo (2011) indicated that GI is unaffected by a low concentration of PTM, which is the situation in the present study (considering results in Figure 5.2). Furthermore, the low GI for the SS and SS_GLD samples can be attributed to the phytotoxic effect of ammonia, which is a typical compound present in digested SS (Alvarenga et al., 2007; Arthurson, 2008). Based on GI results it is recommended caution in the application of any of the materials (SS, SS_GLD, and GLD) to soil during the seed germination phase.

Regarding the pot experiments, Figure 5.7 shows the effect of the soil treated with SS (6, 12, and 24 t ha^{-1}) and SS_GLD (24 t ha^{-1}) on the growth of *Lepidium sativum L.* These results were compared with the control samples (C0) with only soil. The root length, shoot length, and dried shoot biomass were measured, and the results marked with different letters are statistically different (Tukey HSD test, $p < 0.05$).
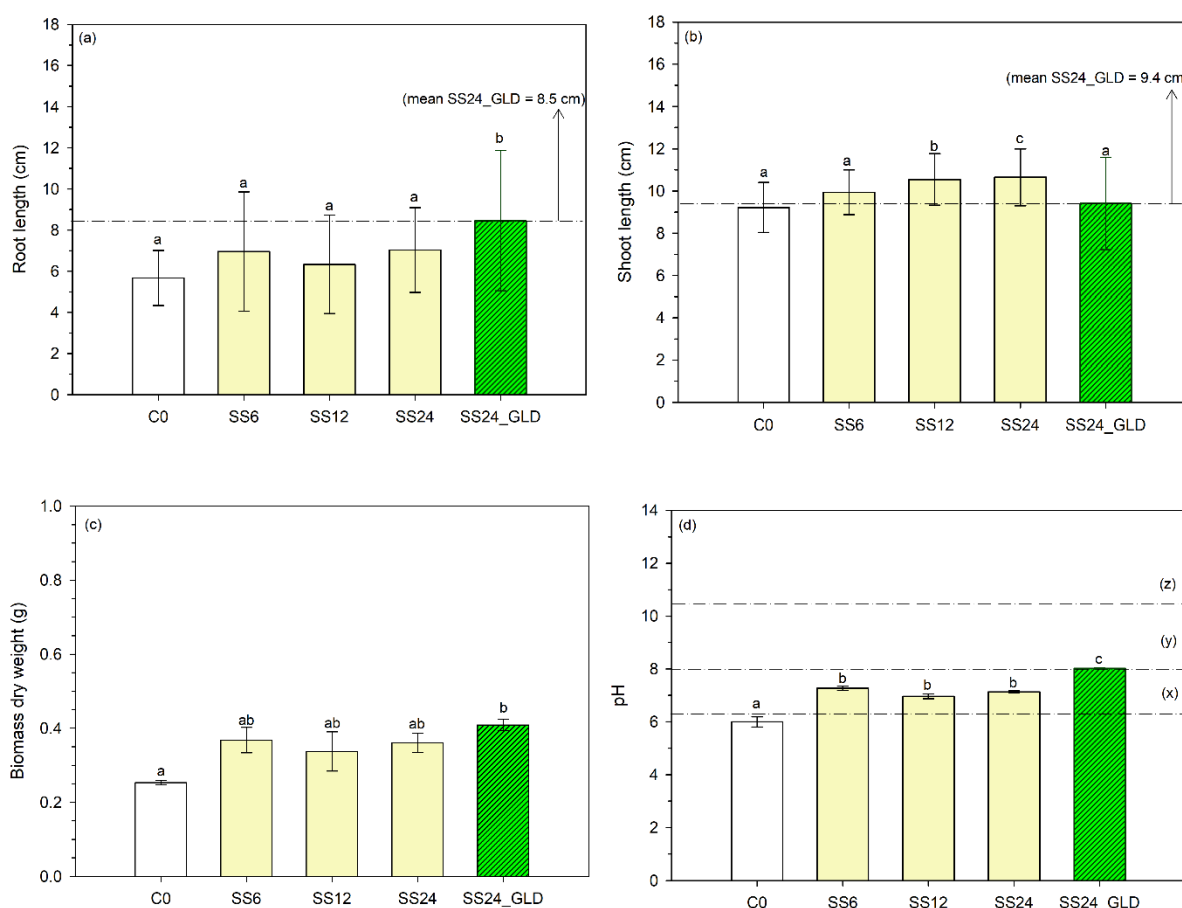
Figure 5.7 - Effect of dried materials on (a) root length; (b) shoot length; (c) biomass dry weight; and (d) pH of soil at the end of the pot experiments. [Horizontal lines marked as x, y, and z refers to the mean pH of the soil, SS and GLD samples, respectively].

The root length was not affected by the incorporation rates in the treatments SS6, SS12, and SS24 when compared to C0 ($p < 0.05$). However, the SS24_GLD showed statistical differences in the root

length (p < 0.05), with a mean value of 8.5 cm, which represents an improvement of 49% compared to C0 sample (Figure 5.7 (a)). Regarding the shoot length, Figure 5.7 (b), C0, SS6, and SS24_GLD had a similar effect, and thus no beneficial effect was observed with GLD. Nevertheless, biomass production was improved by 38% concerning the control sample. At the end of the experiment, the pH of the amended soil was evaluated, and Figure 5.7 (d) depicts a rise in all cases (SS6, SS12, SS24, and SS24_GLD). The highest increase (from 6 to 8) was observed with the addition of GLD. In a study from the literature, the GLD was used as a buffering agent and an increase of the initial pH of the soil from 6.2 to 8.5 was also reported (Torkashvand, 2010). Other researchers stated that the incorporation of GLD in the soil between 10-30% may assist nutrient availability, water retention, and soil pH increase (Zambrano et al., 2010). In addition, ongoing studies show a potential positive effect of GLD as additive to SS, because even at room temperature, a significant reduction in the microbiological contamination (*E. coli*) is observed. These results indicate that the product obtained from sludge drying with GLD may have the potential for agronomic applications. Nevertheless, further testing with more plant types is required, including field tests with various applications over time.

5.4   Conclusions

The characterization of GLD showed that this waste has a very high acid neutralization capacity, and thus potential to be further used as a liming agent to raise soil pH. The concentration of the regulated potential toxic metals (Cr, Ni, Cu, Pb, Zn, and Cd) in GLD is not impeditive for soil applications.

Fick's second law and Thin-layer model described well the isothermal kinetic data of the drying process. However, it was clear that the use of GLD as an adjuvant to the sewage sludge drying process did not boost expressively the mass transfer. Indeed, the drying parameters (D_{eff} and k) at each studied temperature (70, 100, and 130 ℃) were of the same order of magnitude as the control. Even though, the isothermal drying at 130 °C with 0.15 g GLD g^{-1} SS$_{wb}$ showed a slight reduction in energy consumption for moisture evaporation (from 936.7 to 860.7 kJ kg^{-1} SS$_{wb}$). The maximum drying rates achieved were 30.73 and 30.88 gH$_2$O kg^{-1} SS$_{wb}$ min^{-1} for SS and SS_GLD samples, respectively, at 130 °C.

Germination tests revealed that the phytotoxicity of SS could be reduced with the incorporation of GLD, while both materials may be detrimental for the germination process. The growth in pot tests showed that SS6, SS12, SS24, and SS_GLD treatments promoted better conditions for the growth of plants. Moreover, the SS_GLD allowed the soil pH correction from 6 to 8 (as expected). Ongoing studies revealed promising effects of GLD for inactivating pathogens. Despite the incorporation of GLD improved slightly the drying process, the valorisation of both wastes in soil could be still a good strategy. However, additional in-depth tests with plants should be performed to ensure the positive effect of the material produced as soil amendment.

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5.6 Supplementary information

Table S 5.1 - Samples, conditions and L/S ratios used in the phytotoxicity test.

Samples	Parameter	L/S (L kg⁻¹)						
		5	10	25	50	100	200	500
SS	pH	6.44	6.71	6.81	6.81	6.73	6.44	6.13
	EC (mS cm⁻¹)	4.48	1.72	1.00	0.59	0.40	0.40	0.19
SS_GLD	pH	9.98	9.98	10.07	10.16	10.17	10.12	9.98
	EC (mS cm⁻¹)	11.31	3.85	2.48	1.75	0.98	0.56	0.25
GLD	pH	10.18	10.26	10.32	10.32	10.38	10.19	10.10
	EC (mS cm⁻¹)	28.18	15.60	7.52	4.20	2.30	1.28	0.70

Note: the control sample pH = 6.10 and EC = 3.23 µS cm⁻¹

Table S 5.2 - Properties of soil used in the experimental trials.

Parameter	Soil
pH	6.0
EC (mS cm⁻¹)	0.16
OM (%)	1.8
P (wt%)	0.01
ANCpH₄ (meq H⁺ g⁻¹)	0.001
PTM (mg kg⁻¹)	
Pb	< 2.0
Cd	< 0.2
Cr	< 1.0
Cu	7.7
Ni	< 1.0
Zn	6.4

Table S 5.3 - Composition of the SS samples.

Composition (wt%, db)	This work	Literature	
		Ref. [1]	Ref. [2]
C	25.80	28.0 – 45.0	27.86 – 45.06
H	4.48	4.0 – 6.19	3.89 – 6.32
N	3.30	3.0 – 5.0	3.03 – 6.55
O	21.42	2.42 – 43.47	12.51 – 27.16
S	1.70	1.0 – 1.50	1.18 – 4.12
Ash	43.30	ni	16.38 – 50.10
HHV (MJ kg⁻¹db)	10.92	7.56 – 15.10	13.38 – 23.70
LHV (MJ kg⁻¹db)	9.99	ni	2.43 – 4.67

Refs.: [1]- (Werle and Wilk, 2010); [2]- (Díaz et al., 2019).

Table S 5.4 - Activation energy and diffusion factor for SS (0%) and SS_GLD (0.15 g GLD g⁻¹ SS$_{wb}$) and energy required for moisture evaporation (kJ kg⁻¹ SS$_{wb}$) at different temperatures.

Samples	E$_a$ (kJ mol⁻¹)	D$_0$ (m² s⁻¹)	R²	E$_{0.30}$ (kJ kg⁻¹$_{wb}$)		
				70 ºC	100 ºC	130 ºC
SS	27.03	3.93×10⁻⁴	0.993	1154.1 ± 1.7	1003.4 ± 0.0	936.7 ± 0.4
SS_GLD	26.61	3.35×10⁻⁴	0.999	1195.7 ± 0.5	1092.3 ± 0.7	860.7 ± 0.4

6. ISOTHERMAL DRYING OF SEWAGE SLUDGE WITH EGGSHELL FOR SOIL APPLICATIONS

The objective of this work was to analyse the effect of eggshell (ES) as adjuvant of the drying process of sewage sludge (SS) from anaerobic digestion and to evaluate the effect of SS and ES (dry blend) as a soil amendment on certain soil properties and plant growth. Small cylinders were dried in isothermal conditions at 70 and 100 °C, until complete dehydration. Two mathematical models were used to describe the experimental data, and in both cases good fitting was achieved ($R^2 > 0.98$ and RMSE < 0.02). *Lepidium Sativum L.* was used as the test plant, involving both germination and growth tests. The mixture SS:ES equal to 0.15 g ES g^{-1} SS_{wb} revealed a positive effect in the drying rate since the drying time was reduced. When ES was used, the average drying rate observed in the first period at 70 °C was improved by 9.86%, while at 100 °C almost 17% improvement was achieved. The diffusion coefficients (D_{eff}) were also calculated, and the improvements in this parameter were also detect-ed. Indeed, the application of ES as adjuvant increased D_{eff} in 9% and 16.32% at 70 and 100 °C, respectively. Germination studies indicated that SS mixed with ES reduce sewage sludge phytotoxicity, the acidity, and increased the soil organic matter.

Keywords: sewage sludge, eggshell, drying, kinetics modelling, soil amendment, phytotoxicity.

6.1   Introduction

Sewage sludge (SS) is a by-product generated in wastewater treatment plants (WWTP), representing a global problem due to population growth and urbanization. It is estimated that by 2020 the SS production in the European Union (EU) will be about 13 Mt on dry basis (db) (Collard et al., 2017). In Portugal, the annual production of SS is around 300 kt$_{db}$ (LeBlanc et al., 2008). This amount will increase because new WWTP are under construction. Among the main problems associated with SS management, the following aspects stand out: i) high water content, normally above 80%; ii) release of bad odors; iii) presence of pathogenic microorganisms and iv) the possible presence of potentially toxic metals (PTM) above the limits imposed by legislation (Alvarenga et al., 2017). In the EU, the management of SS may involve agriculture applications, incineration, or landfilling. Recently, some studies highlighted the use of SS as an agriculture soil improvement agent. In fact, SS may increase organic carbon storage, promote recycling of the nutrients (e.g., N, P and K), improve water retention capacity, soil aeration and cation (Alvarenga et al., 2017; Ociepa et al., 2017; Syed-Hassan et al., 2017).

Another waste produced in huge quantities in the EU is the eggshell (ES). The consumption of eggs is estimated to be around 10^{12} in worldwide (at home, restaurant, bakehouse, and industry) (Park et al., 2016). Normally, the ES wastes are neglected and discarded in landfills. However, in the last years, some researches have evaluated the potential of recycling this material as a soil amendment, agent of nutrients and PTM adsorbent (Buasri et al., 2013; Quina et al., 2017; Usman et al., 2010). The main constituent of ES is $CaCO_3$, which gives it the capability to be used as a buffering agent. Thus, the application of the SS mixed with ES in the soil has gained importance due to the reduced amount of organic matter (OM) in most of the Portuguese soils (less than 1%), and the acidity (pH < 5.5) in about 83% of the national territory (Inácio et al., 2008; Lopes, 2017).

To mitigate some problems associated with SS, such as high-water content and pathogens, thermal drying can be an efficient method. For reducing cost with energy during drying, the initial moisture content should be near to 80%. Generally, the thermal processes allow achieving final moisture of less than 30%. Several mathematical models based on the general solution of Fick's second law can be used to describe the diffusional process and to optimize the drying process. Moreover, the analysis of the kinetics can be important to obtain the parameters required to design dryer equipment. In the scope of this work and toward the circular economy, the recycling of ES was investigated as an adjuvant of the SS drying process. Thus, this study aims to analyse the drying kinetics of SS mixed with ES and produce a material for agronomic applications.

6.2   Materials and methods

6.2.1   Materials

In this work, two wastes samples with different physicochemical compositions were studied. SS sample was obtained after mechanical dewatering by centrifugation in a WWTP, in the central region of Portugal. The WWTP valorises primary and secondary municipal sludge by anaerobic digestion

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(AD). The operational capacity of the WWTP is 36,000 m^3 day^{-1} of urban effluent. The initial moisture content of SS was around 80% and the sample was kept at 4 ºC until further utilization. ES sample (about 1 kg) was collected in a grocery store. The sample was washed with tap water and distilled water several times, dried at room temperature, milled and sieved through a 425 μm screen. A sandy soil from the central region of Portugal was collected from a depth of about 20 cm, dried at room temperature and then homogenized properly.

6.2.2 *Physical and chemical characterization*

Moisture, total solids (TS) and OM content were determined based on EPA Method 1684. pH and electrical conductivity (EC) were measured in a 1:10 (solid:liquid) suspen-sion (Alvarenga et al., 2016; Oleszczuk & Hollert, 2011). Total nitrogen was determined using the Kjeldahl method. The samples were dried at 105 ºC, ground and sieved through a ~75 μm (200 mesh) screen to determine the major elements (K, P, Ca, Mg, Mn, Si, Ti, Al, and Fe). For this determination, about 4 g of each sample was used in X-ray fluores-cence (XRF) in a Nex CG Rigaku spectrometer. Mineralogical characterization of ES was determined by X-ray diffraction analysis (XRD) using a PANalytical X'Pert PRO diffrac-tometer (CuKα-radiation), with a 10-80º 2θ range. Acid neutralizing capacity (ANC) of the samples was determined following the procedure described by Mäkitalo et al., (2014).

6.2.3 *Drying procedures*

The drying process was investigated using small cylinders (5 mm diameter and 30 mm length) obtained through the extrusion of SS (control) and SS plus 0.15 g ES g^{-1} SS$_{wb}$ (referred as SS_ES). The mass of each cylinder was nearly 0.75 g. The drying tests were conducted placing 15 cylinders in an aluminium dish and dried in an oven with natural convection, at 70 and 100 °C, until constant weight.

6.2.4 *Drying models*

The Fick's second law was used to describe the drying process in the first period, and Eq. (6.1) shows its solution for a cylinder of "infinite length", which allows the analy-sis along one-dimension (radial direction). To solve the Fick's second law a uniform initial moisture distribution was assumed, neglecting shrinkage and temperature gradients (Danish et al., 2016; Figueiredo et al., 2015). In this study, only the first term of the series in Eq. (6.1) was considered. The Henderson & Pabis model (thin-layer model), represent-ed by Eq. (6.2) was used to represent the second period of drying kinetics. The modulus of drying rate |DR|, expressed in gH$_2$O min^{-1} kg^{-1} SS$_{wb}$ (wet basis), represents the amount of water leaving the cylinder per kg SS$_{wb}$ min^{-1}, was determined by Eq. (6.3). To calculate the effect of the adjuvant in the drying process, the ES mass was discounted in the calculations.

$$MR = \frac{M(t) - M_e}{M_0 - M_e} = \sum_{n=1}^{\infty} \frac{4}{r^2 \alpha_n^2} \, exp(- D_{eff} \, \alpha_n^2 t) \tag{6.1}$$

$$MR = \frac{M(t) - M_e}{M_0 - M_e} = ae^{-kt} \tag{6.2}$$

$$|DR| = \frac{\partial M(r,t)}{\partial t} \approx \frac{\Delta M}{\Delta t} = \frac{M_i - M_{i-1}}{t_i - t_{i-1}} \tag{6.3}$$

where MR is the dimensionless moisture ratio; M_i and $M_{(t)}$ are the moisture content in the cylinder (g H_2O g^{-1} dry solid) at t=0 and at any t time, respectively; M_e is the moisture content in equilibrium (g H_2O g^{-1} dry solid); J_0 is the Bessel function of zero order ($J_o(r\alpha_n) = 0$); α_1 is the first root of the Bessel function of zero order; r is the radius of the cylinder (m); D_{eff} is the effective diffusion coefficient (m^2 s^{-1}); *a* represents a parameter of the model (thin-layer model); k is the kinetic constant (min^{-1}) and *t* is the time (min).

6.2.5   Germination assays

The phytotoxicity test was performed with *Lepidium sativum L.* (garden cress). For this purpose, liquid extracts were obtained for the different liquid to solid ratios (L/S), based on the standard EN 12457-2:2002, with some adaptations. The solid samples tested were SS, SS plus 15% (w/w) of ES (hereafter SS_ES), and ES. In each case, 5 mL of ex-tract was added in a Petri dish (90 mm) along with ten seeds, which were placed over the Whatman filter paper. The samples stayed in an oven at 25±0.1 °C for 48 h, in dark conditions (Baderna et al., 2015). The pH and EC measured in the leachates are shown in Table 6.1. Germination Index (GI) was obtained by comparing the percentage of the number of germinated seeds and the percentage of the root lengths of the samples with respect to the control sample (Pinho et al., 2017).

Table 6.1 -pH and EC measured in extracts tested in the phytotoxicity assays.

Samples	Parameters	L/S ratio (L kg^{-1})						
		5	10	25	50	100	200	500
SS	pH	6.44	6.71	6.81	6.81	6.73	6.44	6.13
	EC (mS cm^{-1})	4.48	1.72	1.00	0.59	0.40	0.40	0.19
SS_ES	pH	7.26	7.38	7.53	7.66	7.72	7.86	7.96
	EC (mS cm^{-1})	3.90	2.61	1.29	0.77	0.47	0.27	0.17
ES	pH	8.86	9.10	9.10	9.50	9.41	9.33	9.01
	EC (mS cm^{-1})	0.32	0.21	0.15	0.18	0.10	0.08	0.05

Note: The control sample (distilled water) is characterized by a pH = 6.88 and EC = 3.23 µS cm^{-1}.

6.2.6   Pot experiments

Plants *(Lepidium sativum L.)* in pots were grown in a chamber with light provided by a white LED light (~ 280 µmol m^{-2} s, 400-700 nm, incidence angle of 240º) with a photoperiod of 12 h, temperature control of 21 ± 0.1 °C and relative humidity of 50% (Arriagada et al., 2014; Belhaj et al., 2016). Pots (90x75 mm) were filled uniformly to a total volume of 300 cm^3. The SS was applied to the soil at three different rates, corresponding to 6, 12 and 24 t ha^{-1}. A fourth treatment was performed with SS_ES (24 t ha^{-1} of SS). A control test using only soil was performed. At the bottom of each pot was added gravel to enable drainage of the water. About 17 seeds of garden cress were sown in each pot. Each treatment was conducted in duplicate. After 1 week, plants were harvested, remaining 10 plants in

each pot (thinning phase). The experiment lasted for 4 weeks. Growth parameters were analysed with respect to root and shoot lengths, and biomass of the plant. For deter-mining the biomass, the plants were oven-dried at 60 ℃ until constant weight (Mohamed et al., 2018). The OM, pH, and EC in the soil were measured at the end of the experimental period.

6.2.7 Statistical analysis

The fitting quality of the mathematical models was evaluated based on the root mean square error (RMSE) and on the coefficient of determination (R^2) (Bennamoun et al., 2013; Danish et al., 2016). The length of the Period I of the drying process, where the drying rate is constant, was determined considering MR = 0.30.

6.3 Results and discussion

6.3.1 SS and ES characteristics

Table 6.2 shows the physico-chemical characteristics of the two wastes studied (SS and ES). The results found in this study are consistent with those reported in the literature.

Table 6.2 - Properties of SS and ES used in this study and in the literature.

Parameters	SS			ES		
	This work	Literature Ref. [1]	Ref. [2] [1]	This work	Literature Ref. [3]	Ref. [4]
pH	6.7	5.0 – 8.0	7.3	9.10	ni	8.73
OM (% TS)	63.7	30 – 88.0	70.9	4.30	ni	6.3
Moisture (%)	78	> 95.0	ni	1.10	ni	1.0
EC (mS cm^{-1})	0.17	ni	0.26	0.21	ni	0.45
N $_{Kjeldahl}$ (%)	3.89	ni	6.20	nd	ni	1.0
P_2O_5 (% TS)	3.83	0.8 – 11	10.20	0.29	0.15	ni
K_2O (% TS)	0.22	0.4 – 3.0	1.30	0.10	0.07	ni
MgO (% TS)	0.38	ni	1.04	0.72	0.003	ni
CaO (% TS)	5.30	ni	2.78	86.11[2]	91.99 [2]	88.0 [2]
SiO_2 (% TS)	4.05	10-20	ni	0.19	0.13	ni
Al_2O_3 (% TS)	1.94	ni	ni	0.19	0.14	ni
Fe_2O_3 (% TS)	11.56	ni	ni	nd	0.04	ni
Na_2O (% TS)	nd	ni	0.27	nd	0.51	ni

Refs.: [1]- (Pathak et al., 2009)[1]; [2]- (Alvarenga et al., 2016)[1]; [3]- (Usman et al., 2010), and [4]- (Quina et al., 2017); nd - not determined; ni - not indicated; [1] mean of 2 sewage sludges samples. [2] these values are reported in $CaCO_3$.

The pH found for SS and ES are 6.7 and 9.1, respectively, and agree with the results reported in the literature. Thus, mainly ES waste can present an alternative for the correction of acid soils, such as Portuguese soils (Inácio et al., 2008). The OM and the presence of nutrients, such as N, P and K, are higher in SS comparing to ES. The SS contains some Ca, but the ES may comprise more than 90% of calcium carbonate ($CaCO_3$). The XRD analysis (spectrum not shown in this work) confirmed that ES contains mostly $CaCO_3$ in the calcite form (~ 86%).

The result of the soil ANC was very low (0.001 meq g^{-1}), which indicates a weak buffering capacity against acidification. On the contrary, ES revealed a high ANC (19.7 meq g^{-1}). Thus, the application of SS and SS_ES will be favourable not only as pH correction agents but also as suppliers

of OM and nutrients (high levels in the wastes analysed). Additionally, the application of SS_ES can raise the buffer capacity of the soil. All PTM concentrations measured in the soil, SS and ES are below the limit imposed by the Portuguese legislation (*Decreto Lei Nº*. 276/2009 – October 2). Thus, this soil can be amended not only with SS but also with the mixture of SS and ES for agronomic applications.

6.3.2 Drying kinetics

Figure 6.1 presents the isothermal drying curves that correspond to the moisture ratio (MR) as a function of time, at 70 and 100 ºC for the control (0% of adjuvant) and SS_ES (0.15 g ES g^{-1} SS$_{wb}$). In addition, the experimental data was adjusted through the Fick's second law (Period I) and the thin-layer model (Period II).
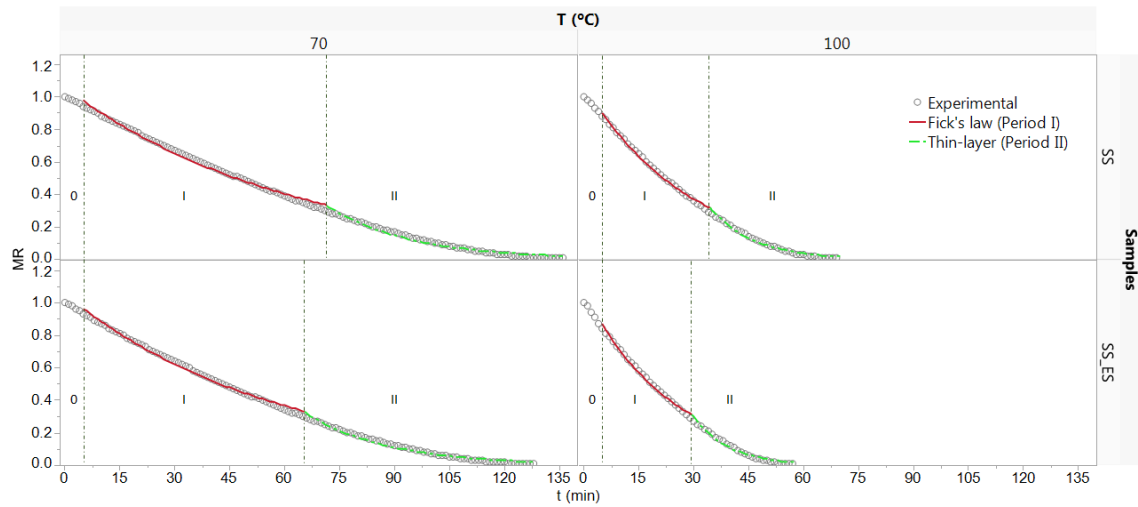
Figure 6.1 - Moisture ratio (MR) as a function of time to Control and SS_ES samples, at 70 and 100 ºC. [Periods 0, I and II correspond to the rising period, the constant rate period, and falling rate period, respectively; Dashed vertical lines separate the drying phases].

Results in Figure 6.1 show that the theoretical models present a very good fit to the experimental data, which is confirmed by the R^2 and RMSE values (Table 6.3). Indeed, the drying curve can be divided into three distinct periods: heating phase (Period 0) where the temperature is rising; the constant rate phase (Period I) where the free water is evaporated; and the decay stage (Period II) where the bounded water is removed. Period 0 was assumed equal to 5 min for all the tests.

Table 6.3 summarizes the principal parameters that describe the drying curves and Figure 6.2 represents the modulus of the drying rate (DR), expressed in gH$_2$O kg SS$_{wb}$ min^{-1} at 70 °C and 100 ºC, respectively.

Table 6.3 - Parameters obtained for the different periods of the drying curves.

T (ºC)	Samples	Fick's second law (Period I)					Thin-layer (Period II)			
		D_{eff} (m² min⁻¹)	t_f (min) [1]	$\overline{\|DR\|}$ [2] (gH$_2$O kg⁻¹ SS$_{wb}$ min⁻¹)	R^2	RMSE	k (min⁻¹)	a	R^2	RMSE
70	SS	2.66×10^{-8}	71	7.63	0.992	0.02	0.0433	7.271	0.981	0.01
	SS_ES	2.89×10^{-8}	65	8.34	0.992	0.02	0.0446	6.054	0.984	0.01
100	SS	6.01×10^{-8}	34	15.98	0.994	0.01	0.0849	5.930	0.986	0.01
	SS_ES	6.99×10^{-8}	29	18.74	0.995	0.01	0.1038	6.686	0.987	0.01

[1] - t_f – time at the end of Period I; [2] - $\overline{DR}$ – average drying rate for Period I.
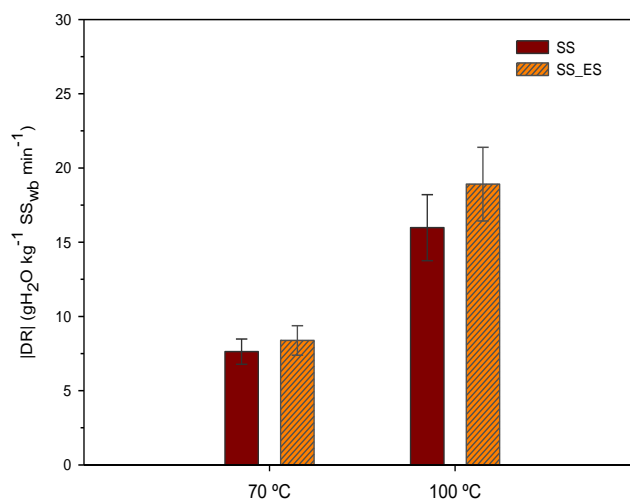
Figure 6.2 - Drying rate |DR| expresses as gH$_2$O kg SS$_{wb}$ min⁻¹ at 70 and 100 ºC to control and SS_ES samples.

Through the drying curves (Figure 6.1), it is possible to notice that the drying profiles are dependent on the temperature. At 70 ºC the decay of MR is slower than at 100 ºC, indicating difficulties to remove both free and bound water. Moreover, it is possible to observe that at 70ºC, the Period I is 9% shorter in the case of SS_ES (t_f = 65 min) than in the control sample (t_f = 71 min). At 100 ºC, the period I ends at 29 min for SS_ES, while 34 min were measured for 0% of adjuvant (Control sample). At 100 ºC, the D_{eff} obtained was 16.32% higher for the drying aided with adjuvant (Table 6.3). Besides, the values founded to D_{eff} are within the range reported in the literature Zhang et al., (2016). In terms of prediction of Period II with the thin-layer model, the kinetic constant (k) of drying at 70 and 100 ºC with adjuvant increased by 3.19 and 22.26%, respectively. The average drying rate at 70 °C with adjuvant, compared to the control, improved the drying process by 10%, while at 100 °C almost 18% of improvement was achieved. As expected, the DR is higher at 100 ºC and it is possible to achieve a maximum of 18.74 gH$_2$O kg⁻¹SS min⁻¹ in the presence of ES (Figure 6.2). On the other hand, only 8.34 gH$_2$O kg⁻¹SS min⁻¹ were removed from the sample at 70 ºC during the Period I.

6.3.3   Germination studies

Germination tests with garden cress seeds were performed to evaluate the phytotoxic activity of aqueous extracts of SS, ES, and SS_ES as shown in Figure 6.3. Additional tests were performed with SS plus 5% and 10% (w/w) of ES (results not shown), but phytotoxic behaviour was similar when compared to SS_ES (0.15 g ES g^{-1} SS_{wb}).
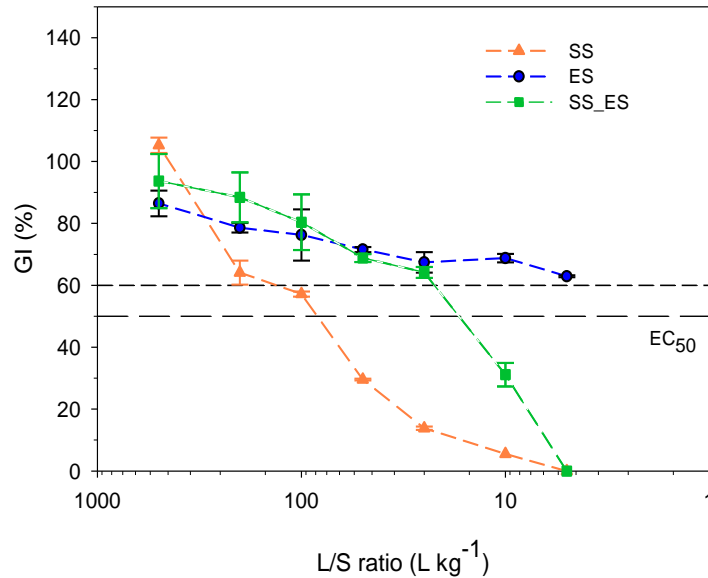
Figure 6.3 - GI (%) at different L/S ratio (L kg^{-1}) for SS, ES and SS_ES after 48 h of incubation.

Results in Figure 6.3 revealed that the GI of ES is always superior to 60%, which indicates that does not exist inhibition of seed germination and growth in the different L/S ratios tested. Contrarily, SS demonstrated high inhibitory potential, except for 200 and 500 L/S ratios. The EC_{50} obtained was 105.4 L/kg, which corresponds to the concentration that induces 50% of inhibition. The SS_ES eluate only shows inhibitory effects for 5 and 10 L/S ratios. Moreover, the EC_{50} for the SS_ES was reduced to 19.2 L/kg, which represents a decrease of approximately 80% compared to the value obtained for the SS eluate. Thus, it is possible to conclude that the blend between SS and ES decreases the phytotoxic activity.

6.3.4   Pot experiments

The pot experiments were realized with a control sample (C0) and four different treatments were implemented in the soil: application of SS at 6, 12 and 24 t ha^{-1} (SS6, SS12, and SS24, respectively) and SS_ES. Figure 6.4 presents the different treatments growths for 4 weeks of the experiment.

Figure 6.4 - Illustration of treatments growth for 4 weeks.

Figure 6.5 (a)-(d) shows the evolution of growth parameters in terms of root length, shoot length and biomass, and organic matter in the soil, respectively. Results marked with the different letters are significantly different according to Turkey's test ($p < 0.05$).
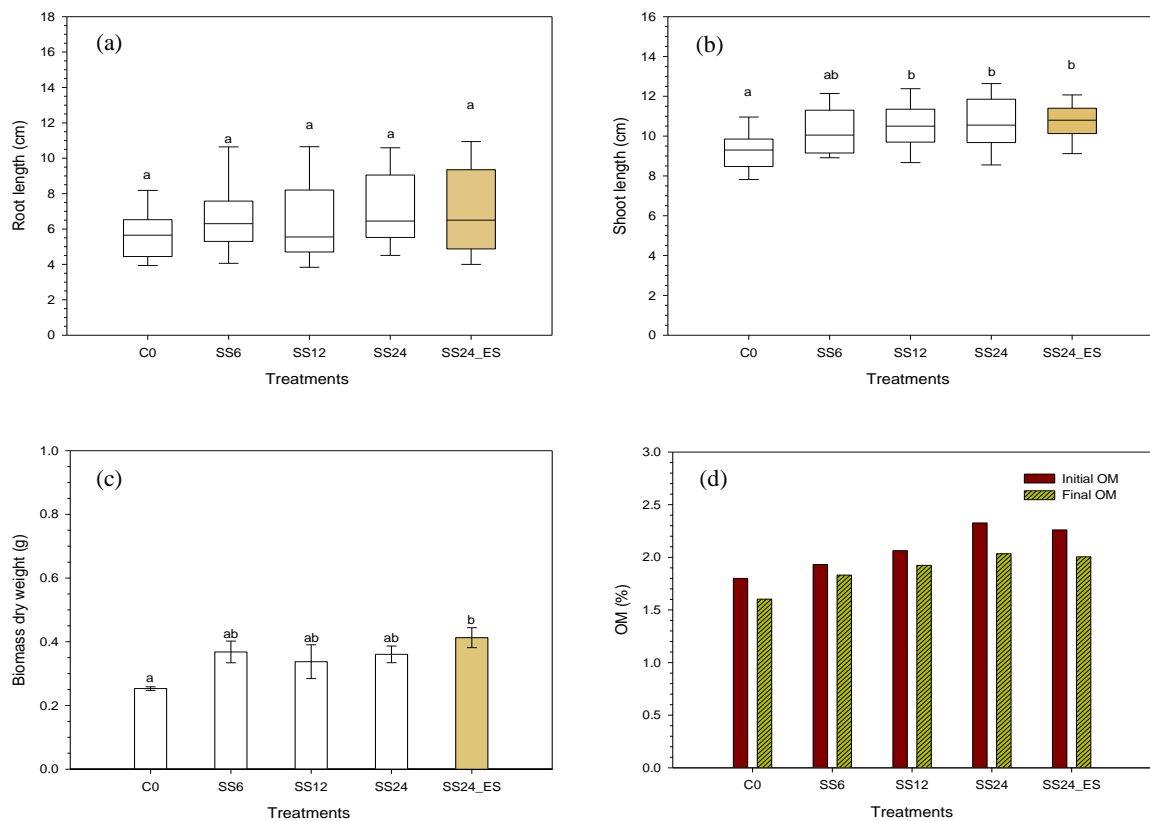
Figure 6.5 - Effect of amendments: (a) root length; (b) shoot length; (c) biomass dry weight and (b) in soil organic matter.

The growth analysis revealed that the root length of the garden cress was not influenced by the treatments when compared to the control ($p < 0.05$). Contrarily, the shoot length was affected when the soil was amended with the wastes. The results show that all the treatments, except SS6, are statistically different in terms of shoot length ($p < 0.05$). In fact, the plants were grown in soil amended with SS12,

SS24 and SS_ES treatments exhibited an increase of 14.4, 15.5 and 16.1%, respectively, in shoot length as compared with control. From Figure 6.5 (c), it is possible to conclude that SS_ES promotes a significant increase in biomass dry weight ($p < 0.05$). Indeed, SS_ES presents a higher biomass value (0.413 g), which represents an improvement of 63% compared to the control sample. The initial OM of the soil in all the treatments increased after amendment with SS or SS_ES. The final OM of the soil decrease in all the treatments due to the growth of the plants. Moreover, after 4 weeks of the experiment, the pH of the soil raised for values higher than 7 for the treatments SS6, SS12, SS24, and SS_ES, with a maximum of 7.80 for SS_ES. Thus, these results revealed the capability of these two wastes to act as pH correction agents.

6.4 Conclusions

According to the results, the use of eggshell as an adjuvant to the SS drying process enhances the performance either at 70 and 100 ºC. In the drying period I, the addition of the adjuvant promoted an improvement in the diffusion coefficients of 9.0 and 16.3% to 70 and 100 ºC, respectively. Besides, the ES increased the drying rate compared to the control sample. The final product (SS mixed with 0.15 g ES g^{-1} SS$_{wb}$) may be valuable for agriculture applications that require extra calcium or in case the soil requires pH correction. The results showed that the phytotoxicity of SS tested in seeds of *Lepidium sativum L.* may be reduced with the addition of a small amount of ES (for example 0.15 g ES g^{-1} SS$_{wb}$). Moreover, SS12, SS24, and SS_ES treatments empower the growth of plants (e.g., shoot length). Besides, SS_ES led to a higher biomass value and corrected the soil pH to 7.80. All the treatments caused an increase in soil organic matter and a better condition for pH. It is important to notice that this study requires further analysis to evaluate other risks (e.g., associated with pathogens) of applying sewage sludge in the agriculture soil. Finally, in the context of the circular economy, it is suggested to test other materials as SS drying agents to produce soil improvement agents with specific properties.

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7. SCREENING OF WASTE MATERIALS AS ADJUVANTS FOR DRYING SEWAGE SLUDGE BASED ON ENVIRONMENTAL, TECHNICAL AND ECONOMIC CRITERIA

Thermal drying allows the reduction of the moisture contained in the sewage sludge (SS) formed in wastewater treatment plants (WWTP) to less than 80%. The management of the dried SS is easier and may have good properties as a soil amendment (carrying organic matter and N, P nutrients). This work aims to select the most appropriate drying adjuvant for application in full-scale and produce a material adequate for agriculture soil applications by applying two multi-criteria decision making (MCDM) methods, the MOORA and TOPSIS. The criteria weights were determined using the CRITIC method. Within the circular economy framework, four industrial wastes were considered as drying adjuvants: weathered coal fly ash (CFA), green liquor dregs (GLD), eggshell (ES), and rice husk (RH). Then, small cylinders of SS were extruded with 0.15 g adjuvant g^{-1} SS_{wb} and dried at a constant temperature of 70 and 130 °C. Eleven criteria were grouped into three areas (environmental, technical, and economic). Both methods MOORA and TOPSIS showed that the use of GLD at 130 ℃ is the best option. Moreover, ES at 130 ℃ and GLD at 70 °C are also good options, and the choice should consider the need for removal of pathogenic contamination. The worst alternatives were CFA and RH at 70 ℃ according to both MCDM methods. The most influential criteria for decision making were the removal efficiency of pathogenic microorganisms, acid neutralization capacity (ANC) and germination index (GI).

7.1   Introduction

Sewage sludge (SS) management is an urban problem that is currently gaining importance since large quantities are generated and landfill disposal has been restricted by the environmental policies of developed countries. In Europe, the SS production is approximately 45-90 g_{db} population equivalent (p.e.)$^{-1}$ day^{-1} (Mininni et al., 2015), while the amount produced on a wet basis is significantly higher since the moisture of SS in wastewater treatment plants (WWTP) is often more than 80%. The main routes for the management of SS have been applications in agricultural soils amended (directly or after composting), land remediation, incineration, and landfilling (Gomes et al., 2019). Despite some controversy (e.g., related to organic pollutants), several countries have favoured the agricultural use because of the beneficial properties to the soil due to the SS content of organic matter, nitrogen (2.8-3.8%), and phosphorus (2-4%) (Turunen et al., 2018).

To mitigate the management problems associated with the high moisture content in SS, the thermal drying process has gained prominence in the last years. Indeed, this study is part of a broader project – Dry2value, which aims to develop an industrial dryer to be used in WWTP, to facilitate the following management phases (transport, storage, soil applications, or incineration). A special focus of the project will be on obtaining a dry SS product (~ 30% of moisture) that can be used in agricultural applications. For this purpose, waste materials as drying adjuvants have been tested in our previous studies (Gomes et al., 2020a; 2020b; 2020c). In this scope, a reliable drying adjuvant for SS should (i) aid the drying process with energy gains; (ii) act as sanitizing agent; (iii) act as a pH buffering agent for soil; and (iv) contain macro and micronutrients. The buffering properties are important for countries like Portugal because the national soil is mostly acidic (average pH 5.1) (Inácio et al., 2008; Quina et al., 2017). This approach contributes positively to the circular economy (CE), which has been promoted by an ambitious action plan adopted by the European Union (EU), fostering sustainable economic growth (COM, 2015). The pressure from government agencies and the need to create competitive markets have changed the focus from the concept of *end of life* to a new approach that encourages recovery. In fact, the CE covers the whole cycle of materials (extraction, production, consumption, waste management, markets for secondary raw materials, etc.). Therefore, the Member States must search for waste management alternatives to reduce landfill disposal, while reuse and recycling must be favoured. According to the former directive launched in 1980 (Directive 86/278/EEC), the use of SS in agriculture applications has been regulated in a clear CE perspective, but preventing harmful effects on soil, plants, animals, and humans. Towards sustainable development, the use of waste as drying adjuvants (e.g., sawdust, coal fly ash, and rice husk) can not only assist the SS drying process but also enable the production of an improved final product for soil applications, avoiding landfill. In this case, wastes can be transformed through innovative processes into new products following the CE perspective. Recent studies showed that some inorganic materials can create bridges (acting as skeleton builders) between the SS flocks, assisting in the water migration during the drying phases (Deng et al., 2017; Wang et al., 2019; Zhang et al., 2016; 2019).

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To the best of our knowledge, the studies reported in the literature are limited to the assessment of the drying kinetics, i.e., determination of the temperature effect or the adjuvant quantity on the removal of residual moisture. However, to maximize the use of waste materials as adjuvants, the analysis of the best material should be done considering technical, environmental, and economic aspects. For this, the use of multi-criteria decision-making methods (MCDM) permits to sort criteria preferences and therefore optimize the choice of materials (An et al., 2018). Multicriteria analysis permits to evaluate other aspects besides moisture removal. It is possible to consider characteristics such as the acid neutralization capacity (ANC), inactivation of pathogenic microorganisms, phytotoxic effect, biomass productivity of the plants, etc. MCDM methods have been applied in a wide range of fields, namely in agriculture, resource management, immigration, education, transportation, investment, environment, defence, health care, etc. (Kumar et al., 2017; Stojčić et al., 2019). Moreover, MCDM has been also employed in a few cases to assist in decision-making in the area of waste management. For example, Pokoo-Aikins et al. (2010) used MCDM to select the best sustainability-focused sewage treatment alternative, whose primary objective was to convert SS to biodiesel. Other studies also report the selection of SS management alternatives, e.g., landfilling, composting, and drying incineration (Ren et al., 2017) and the agricultural use, incineration, wet oxidation, and recovery in cement kiln (Bertanza et al., 2016).

Recently, with the increasing generation of waste resulting from both population and technological growth, the search for alternatives to guide and formulate public policies with relevant information has emerged. Therefore, different types of strategies need to be developed for waste management (Ighravwe and Babatunde, 2019). Bertanza and co-workers emphasize the importance of a systemic analysis that involves environmental, technical, economic, and social criteria in an integrated manner. This type of approach tends to reduce the risk of adopting an inadequate solution to the complex problems faced by the decision-maker (Garrido-Baserba et al., 2014; Bertanza et al., 2016). In the context of SS drying, it is important that the manager considers multiple alternatives for the selection of an adjuvant, that weighs not only the efficiency of the waste in the drying process but also the associated costs for its management, and at the same time has into consideration environmental issues as a way to value the properties of each waste and contribute to the circular economy.

In this context, the current study aims to apply MCDM methods to select the best adjuvant and temperature for the application in full-scale SS drying processes and to produce a soil amendment to be further used for agricultural applications. Four waste materials were selected and tested (weathered coal fly ash - CFA, green liquor dregs - GLD, eggshell - ES and rice husk - RH) as drying adjuvants intending to contribute to the circular economy in the geographic area of the SS generation.

7.2 Materials and methods

7.2.1 Materials

The samples used in this study were obtained in mainland Portugal. The SS was collected after anaerobic digestion in a WWTP with a capacity of 140 000 population equivalents (p.e.). The SS was dehydrated in the plant by centrifugation, and the moisture content was near to 80%. Considering an average production of 18 kg_{db} p.e.$^{-1}$ year $^{-1}$ (Kelessidis and Stasinakis, 2012), the annual production of SS in the selected WWTP is about 12.6 kt_{wb}.

Four waste materials were selected as adjuvants for the SS drying process: CFA, GLD, ES, and RH. These materials were selected base on: (i) the identification of the main industries in central region of Portugal, near the WWTP; (ii) the quantity generated and its availability (e.g., t year^{-1}); (iii) the current management routes and the possibility of creating an alternative to landfill following the circular economy approach; and (iv) the properties of the waste materials to assist in the drying process and improve soil characteristics. A composite sample of weathered CFA was obtained from a landfill that receives approximately 40 kt year^{-1} of this waste from a thermoelectric power plant, which did not comply with the criteria for the cement industry with respect to the carbon content. GLD was obtained from a pulp and paper industry that produces an average of 7.2 kt_{db} year^{-1} of GLD. ES samples were collected from an egg pasteurisation industry that produces 4 kt year^{-1} of this waste. RH was provided by a rice husking factory whose production is around 10 kt year^{-1}. The place where the four adjuvants (CFA, GLD, ES, and RH) were collected is illustrated in Figure S 7.1 (supplementary information) as well as the position of the WWTP. Considering that the SS drying process uses 0.15 g adjuvant g^{-1} SS_{wb}, it will be necessary to collect and transport to the WWTP about 1.9 kt per year.

7.2.2 System boundary and alternatives

As aforementioned, this research is part of a project to develop an industrial-scale dryer for SS. It is considered that the dryer will be placed in a WWTP located in the central region of Portugal, and the distance for the collection of adjuvants is accounted for and shown in Figure S 7.1 (supplementary information).

Figure 7.1 (a) shows the current situation adopted by SS operators. The SS is collected from the WWTP with a moisture ≥ 80% (after centrifugation), transported, stored, and then applied in the soil. In this case, the transport costs are high, and the storage is a problem due to the high quantities generated, the seasonality of the application in agriculture, and the bad odour emission. Figure 7.1 (b) refers to the alternatives assessed in this study, where a drying step and the addition of adjuvants are considered.

(a)

(b)
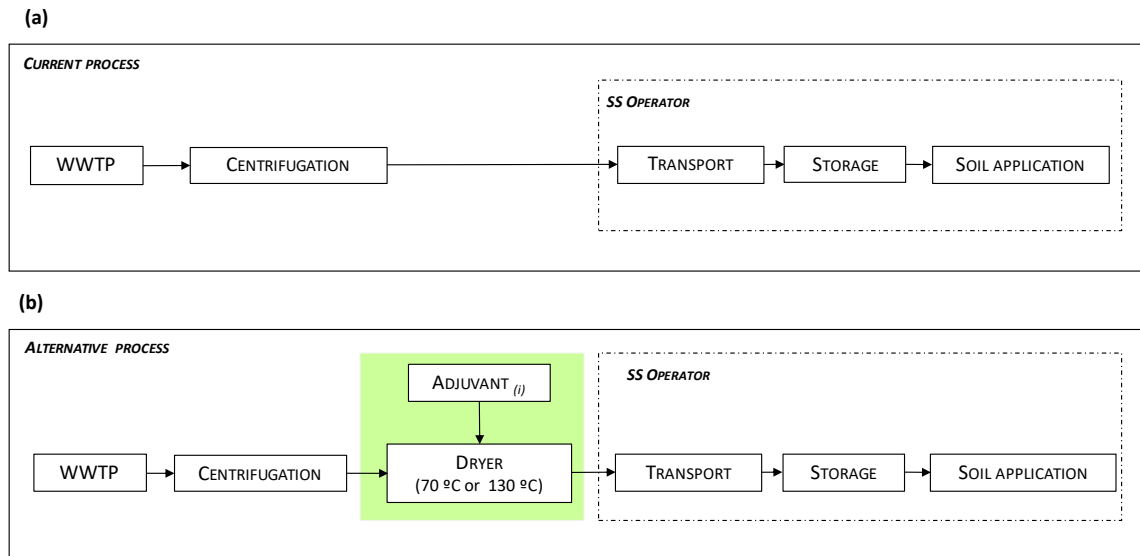
Figure 7.1 - SS management flow for soil amendment (a) current situation, and (b) alternative assessed in this study. (Adjuvant$_{(i)}$ = CFA, GLD, ES, or RH).

In this study, eight alternatives were considered to select the best adjuvant and the drying temperature, as summarized in Table 7.1.

Table 7.1 - Description of the alternatives studied.

Alternatives	Nomenclature	Description
A1	CFA_70	SS plus CFA dried at 70 ºC
A2	CFA_130	SS plus CFA dried at 130 ºC
A3	GLD_70	SS plus GLD dried at 70 ºC
A4	GLD_130	SS plus GLD dried at 130 ºC
A5	ES_70	SS plus ES dried at 70 ºC
A6	ES_130	SS plus ES dried at 130 ºC
A7	RH_70	SS plus RH dried at 70 ºC
A8	RH_130	SS plus RH dried at 130 ºC

7.2.3 Characterization and drying process

The characterization of the samples (SS and SS plus adjuvants) involved the determination of several physicochemical parameters. Moisture and organic matter were determined by gravimetry. The pH and electrical conductivity (EC) were measured in a 1:10 (solid:liquid) suspension. For the determination of six potentially toxic metals (PTM) (Cr, Ni, Cu, Zn, Cd, and Pb) and major oxides, SS and each adjuvant were previously dried at 105 °C for 24 h, ground, and sieved through a ~ 75 μm (200 mesh) screen. Then, the samples were analysed by X-ray fluorescence, using a Nex CG Rigaku equipment. Nitrogen was analysed by the Kjeldahl method. The acid neutralizing capacity (ANC) of the samples was determined following the procedure described by Mäkitalo et al., (2014). The extract used

in the phytotoxicity tests with *Lepidium sativum L.* (garden cress) was obtained according to EN 12457-2:2002 in a 10:1 L/S ratio (L kg^{-1}). The *Lepidium sativum L.* was selected because it is a sensitive and low-cost culture with fast growth potential (Barral and Paradelo, 2011; Pavel et al., 2013). The number of germinated seeds and the length of the radicle were measured, and the results expressed as a germination index (GI) (Gomes et al., 2019). The enumeration of *Escherichia coli* in the biosolid was determined in an external laboratory according to ISO 16649-2:2001. Each parameter was measured at least in duplicate. Properties of SS and adjuvant samples are presented in Table S 7.1 (supplementary information).

At the laboratory scale, the drying process of SS plus adjuvant was studied using small cylinder-shaped samples (0.7 g weight, 5 mm diameter, 30 mm length) obtained by extrusion at room temperature. The drying of the 15 cylinders of each alternative was performed in a Moisture Analyzer, *Precisa XM50*, at 70 and 130 ºC, until a constant weight be reached. The drying kinetics are shown in Figure S 7.2 (supplementary information). From these data, the drying rate (DR), diffusion coefficient (D_{eff}), and kinetic constant (k) were obtained (Gomes et al., 2020a; 2020b; 2020c). The D_{eff} and k were determined by fitting the Fick's second law and the thin-layer model, respectively, to the experimental data (Eqs. S 7.1 and S 7.2 in supplementary information).

7.2.4   Selection criteria

The screening of drying adjuvants for SS in a circular economy perspective was based on eleven criteria grouped into three categories: environmental, technical, and economic.

7.2.5   Environmental

Four environmental criteria were selected: germination index (C1), biomass production (C2), microorganisms removal (C3), and CO_2 emissions (C4).

The germination index (GI) corresponds to the percentage of root growth in an extract solution, which is related to the phytotoxicity of a material in the germination phase (Gomes et al., 2019; Santos et al., 2019).

Biomass production in pot tests corresponds to the quantity of matter (roots, stem, and leaves) that was obtained from the growth in soil and amendments (SS plus adjuvants after drying). This criterion assessed the influence of each alternative as fertilizers. The growth tests were performed in pots (90 x 75 mm) with *Lepidium sativum L.* using sandy soil. An incubator with white LED light (~ 280 µmol m^{-2} s^{-1}, 400-700 nm, incidence angle of 240°) was used to regulate the photoperiod (12 h), the temperature (21 ± 0.1 °C), and the relative moisture (50%) (Arriagada et al., 2014; Belhaj et al., 2016). Figure S 7.3 (supplementary information) shows the setup used in the growth tests.

The pathogenic microorganism removal was selected as an environmental criterion due to its importance to public health. Therefore, the higher the pathogen removal, the better the adjuvant performance. Moreover, the use of SS on agricultural soil is regulated by *Decreto Lei Nº.* 276/2009, and

Escherichia coli is limited to < 1000 cells g^{-1}_{wb}. Although this regulation also imposes limits on the PTM content in SS, the concentrations obtained meet the limits (Table S 7.1, supplementary information). Based on this, PTM concentration was not included as an environmental criterion.

The CO_2 emissions were included because of the concern about global warming, and emissions were evaluated in two stages: i) the drying process; ii) the transportation of the adjuvant from the source to the WWTP. The operation of the dryer releases CO_2 due to the energy consumption, and natural gas was the energy source adopted since it is less expensive (0.0336 € kWh^{-1}) than electricity (0.1381 € kWh^{-1}) (Pordata, 2019). Based on the drying studies at the laboratory scale, it was possible to predict the energy/kg water removed (kJ kg^{-1} SS_{wb}) (Eq. S 7.4, supplementary information). Additionally, an emission factor of 0.231 kg CO_2 kWh^{-1} was considered according to Portuguese *Despacho Nº. 17313/2008*. Regarding the CO_2 emission during transport, it was assumed that the collection and transportation of the adjuvant to the WWTP will be performed in a truck with a capacity of 18 t. To transport the required quantity of adjuvants about 105 loads per year will be necessary. The distance between the location of adjuvant industries and the WWTP is presented in Figure S 7.1 (supplementary information). The emission factor of 50.6 g CO_2 t^{-1} km^{-1} was applied (IPCC, 2006), and the intermediate calculations are present in Table S 7.2 (supplementary information).

7.2.6   Technical

Based on the modelling of the kinetic drying curves determined in the laboratory, three technical criteria were selected: drying rate (C5), diffusion coefficient (C6), and kinetic constant (C7). The determination of these criteria is extensively explained in Section 7.6 (supplementary information). The C5 represents the amount of water removed from the cylinders as a function of drying time, while C6 is associated with the transport of water from the interior to the exterior of the system. The kinetic constant *k* (C7) is a parameter of the mathematical model used to describe the second drying period. These parameters were calculated according to the literature (Danish et al., 2016; Dissa et al., 2008; Figueiredo et al., 2015). Moreover, an additional technical criterion was selected: the acid neutralising capacity (ANC) (C8). This parameter reflects the capability of the final product (SS plus each adjuvant) to neutralise acids, which corresponds to its liming capacity to act as a pH soil amendment.

7.2.7   Economic

Three economic criteria were selected: drying energy cost (C9), transport cost of the adjuvants (C10), and waste management cost (C11). Thus, C9 expresses the cost to dry 1 t of SS_{wb}. As referred in Section 7.2.5, the energy source adopted was natural gas with a cost of 0.0336 € kWh^{-1} (Pordata, 2019). Thus, based on the energy required to evaporate water during drying (kJ kg^{-1} SS_{wb}) determined in the lab, the cost of the energy to dry SS can be obtained considering that the WWTP produced about 12.6 kt SS_{wb} $year^{-1}$. The daily cost of contracted power was not considered. For adjuvant transport cost prediction, a diesel average consumption of a truck with a capacity of 18 t was considered 0.35 L km^{-1}

according to T&E (https://www.transportenvironment.org/). Also, the diesel price was estimated to be 1.36 € L^{-1} (in Portugal in July 2019) (Pordata, 2019). The truck will make 105 trips per year (see intermediate calculation in Table S 7.3, supplementary information). Finally, the waste management cost (C11) represents the landfill adjuvant disposal cost if they were managed as industrial wastes. In this study, these costs were considered a positive externality. Indeed, if the residues are used in the drying process, the industry operators are not required to pay the landfill costs. The discharge costs adopted were equivalent to the Portuguese waste management fee (equal to 9.9 € t^{-1}) (https://www.apambiente.pt/). In the case of the RH, the cost was set to zero because of its use by farmers in the region instead of the landfill. The adjuvant annual production (t $year^{-1}$) according to industry information is 39,210 CFA, 7,200 GLD, 3,300 ES, and 9,900 RH.

Table 7.2 summarizes all the adopted criteria in the environmental, technical and economic categories. The multi-criteria analysis includes general factors (independent on the local issues: C1, C2, C3, C5, C6, C7, C8) and local factors (dependent on the local issues: C4, C9, C10, C11).

Table 7.2 - Description of the criteria used.

Areas		Criteria	Units
Environmental	C1	Germination index (GI)	%
	C2	Biomass production	g
	C3	Microorganisms removal	%
	C4	CO_2 emissions	t CO_2 $year^{-1}$
Technical	C5	Drying rate (DR)	gH_2O min^{-1} kg_{wb}^{-1}
	C6	Diffusion coefficient (D_{eff})	$m^2 s^{-1}$
	C7	Kinetic constant (k)	min^{-1}
	C8	Acid neutralization capacity (ANC)	g $CaCO_3$ g^{-1}
Economic	C9	Drying energy cost	€ $year^{-1}$
	C10	Adjuvant transport costs	€ $year^{-1}$
	C11	Residues management cost	€ $year^{-1}$

7.2.8 *Multi-criteria decision making methods*

Multi-criteria decision making (MCDM) methods were used to rank the alternatives of adjuvants and conditions (A1-A8) to be selected based on the assessment criteria (C1-C11). The framework includes the definition of the problem, followed by five steps, as illustrated in Figure 7.2.
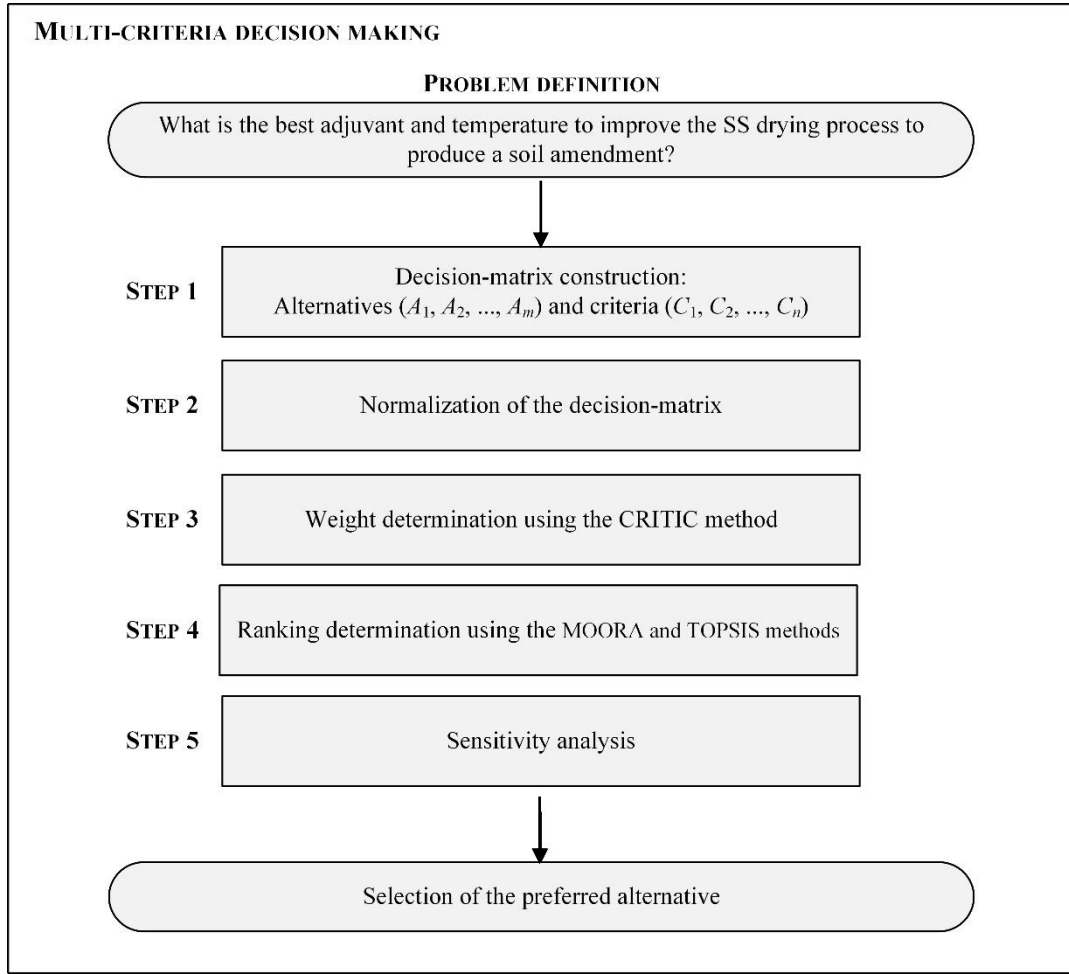
Figure 7.2 - Decision-making framework.

Step 1: Creating the decision-matrix

The decision-matrix (x) considers *m* alternatives (A_1, A_2, ..., A_m) and *n* criteria (C_1, C_2, ..., C_n) for a decision problem, as illustrated in Eq. (7.1) (Adalı and Işık, 2017; Anwar et al., 2019; Lee and Chang, 2018).

$$x_{ij} = \begin{bmatrix} x_{11} & x_{12} & ... & x_{1n} \\ x_{21} & x_{22} & ... & x_{2n} \\ ... & ... & ... & ... \\ x_{m1} & x_{m2} & ... & x_{mn} \end{bmatrix} \tag{7.1}$$

where x_{ij} is the response of alternative $i = 1,2, ..., m$ on the criterion $j = 1,2, ..., n$.

Step 2: Normalization of the decision-matrix

In this step, a normalized decision-matrix is constructed, Eq. (7.2) (Tzeng et al., 2011), to obtain comparable values for the different criteria within the same range (0 and 1).

$$r_{ij} = \frac{x_{ij}}{\sqrt{\sum_{i=1}^{m} x_{ij}^2}} \tag{7.2}$$

where $r_{ij} \in [0, 1]$ is the normalized response of alternative i on criterion j. The normalization adopted does not consider the type of criteria – beneficial or non-beneficial, i.e., if the criterion is to be maximized or minimized.

Step 3: Weight determination using the CRITIC method

The CRITIC (criteria importance through inter-criteria correlation) is an objective weight method that is data dependent. The advantage of this method is that it reduces the subjective impact of decision makers and considers the variability and relevance of criteria. It is based on the analytical testing of the decision-matrix in order to determine the information contained in the criteria by which the alternatives are evaluated (Diakoulaki et al., 1995).

For each criterion, the standard deviation, σ_j, is determined, Eq. (7.3), and the correlation between the jth criterion is calculated against the rest of the criteria k in the decision-matrix by a correlation coefficient r_{jk}, Eq. (4). Hence, the amount of information C_j contained in the criteria j can be determined, Eq. (7.5). Finally, the weight, w_j, is obtained through Eq. (7.6).

$$\sigma_j = \sqrt{\frac{\sum_{i=1}^{m}\left(x_{ij}-\bar{x}_j\right)^2}{m}} \tag{7.3}$$

$$r_{jk} = \frac{\sum_{i=1}^{m}\left(x_{ij}-\bar{x}_j\right)\left(x_{ik}-\bar{x}_k\right)}{\sqrt{\sum_{i=1}^{m}\left(x_{ij}-\bar{x}_j\right)^2 \sum_{i=1}^{m}(x_{ik}-\bar{x}_k)^2}} \tag{7.4}$$

$$C_j = \sigma_j \sum_{j=1}^{n}\left(1-r_{jk}\right) \tag{7.5}$$

$$w_j = \frac{C_j}{\sum_{j=1}^{n} C_j} \tag{7.6}$$

where $\bar{x}$ represents the mean value.

Step 4: Ranking determination

For the determination of the alternative ranking, two MCDM methods were applied – the MOORA and TOPSIS.

MOORA is a simple method where the sums of weighted normalized values for non-beneficial criteria are subtracted from the sums for beneficial criteria, Eq. (7.7). The result is the overall score of each alternative (S_i) (Zopounidis and Pardalos, 2010).

$$S_i = \sum_{j=1}^{g} w_j r_{ij} - \sum_{j=g+1}^{n} w_j r_{ij} \tag{7.7}$$

where g and (n - g) are the number of criteria to be maximized and minimized, respectively, w_j is the weight of the jth criteria which can be determined using several methods such as the CRITIC.

The acceptance of TOPSIS method is increasing among researchers (Lee and Chang, 2018). Similar to the MOORA multi-criteria tool, TOPSIS also uses the normalized dataset, (Eq. 7.2), followed by a calculation of the weighted normalized decision-matrix, (Eq. 7.8). The calculated standard weighted decision-matrix is presented in Table S 7.5 (supplementary information).

$$v_{ij} = x_{ij}\, w_{ij} \tag{7.8}$$

The TOPSIS method (Hwang and Yoon, 1981) is based on the calculation of the ideal and non-ideal distances between each alternative *i* (Eqs. 7.9 and 7.10) (Chen, 2019). The ideal and non-ideal solutions for each criterion corresponds to the best and worst values of criteria in the weighted normalized decision-matrix, which depends on the objective to maximize or minimize a criterion, as shown in Eqs. (7.9) and (7.10). After determining these values, the proximity distance from the ideal (best) solutions is expressed by Eq. (7.11), while the proximity to the non-ideal (worst) solutions is expressed as Eq. (7.12). Based on the distance of ideal and non-ideal alternatives, their closeness coefficients are determined using Eq. (7.13), which assist in the ranking of the alternatives. The higher and lower values of CC_i represent the most and least preferred alternative options, respectively.

$$d_j^+ = \left(\max v_{ij} \in J\right) \text{ and } \left(\min v_{ij} \in J'\right),\ \forall i \tag{7.9}$$

$$d_j^- = \left(\min v_{ij} \in J\right) \text{ and } \left(\max v_{ij} \in J'\right),\ \forall i \tag{7.10}$$

where *J* and *J′* are the benefit and non-benefit criteria, respectively.

$$D_i^+ = \sqrt{\sum_{j=1}^{n} \left(v_{ij} - d_j^+\right)^2} \tag{7.11}$$

$$D_i^- = \sqrt{\sum_{j=1}^{n} \left(v_{ij} - d_j^-\right)^2} \tag{7.12}$$

$$CC_i = \frac{D_i^-}{D_i^+ + D_i^-} \tag{7.13}$$

Step 5: Sensitivity analysis

The sensitivity analysis is important to evaluate to what extent a change in the criteria weight affects the final ranking. This analysis may assist in the successful implementation of the best alternative. Two types of sensitivity analyses were performed in this study. The first evaluated the change in the criteria weight by ±40% from the previously calculated using the CRITIC method. Since the criteria weight must sum 1, the remaining criteria were proportionally adjusted accordingly. In the second methodology, four scenarios were considered to evaluate the effect of the criteria areas selected – environmental, technical, and economic. As shown in Table 7.3, scenario 1 considered the three areas

equally important. The scenarios 2, 3, and 4 attributed 50% of the weight to the environmental, technical, and economic categories, respectively. The residual weight was distributed equally between the remaining areas. The weights for the criteria were obtained by dividing the category weight by the number of criteria within that area.

Table 7.3 - Criteria weights for different scenarios.

Criteria	Scenario 1	Scenario 2	Scenario 3	Scenario 4
Environmental	0.333	0.500	0.250	0.250
Technical	0.333	0.250	0.500	0.250
Economic	0.333	0.250	0.250	0.500

7.3 Results and discussion

7.3.1 Decision-matrix

Table 7.4 presents the decision-matrix obtained for the 8 alternatives (A1 to A8) and 11 criteria (C1 to C11) used for the decision analysis, where the objective of maximizing (Max) or minimizing (Min) each criterion is also shown.

Table 7.4 - Alternatives and evaluation criteria used for the selection of SS drying adjuvants.

Alternative	Environmental				Technical				Economic		
	C1 (%)	C2 (g)	C3 (%)[1]	C4 (t CO$_2$ year^{-1})	C5 (g min^{-1}kg^{-1})	C6 (m^{2}s^{-1})	C7 (min^{-1})	C8 (g CaCO$_3$ g^{-1})	C9 (€ year^{-1})	C10 (€ year^{-1})	C11 (€ year^{-1})
	Max	Max	Max	Min	Max	Max	Max	Max	Min	Min	Max
CFA_70 (A1)	31.9	0.434	0	3291	9.2	3.12×10^{-8}	0.052	0.061	136851	11781	18711
CFA_130 (A2)	45.2	0.435	0	3108	31.6	1.27×10^{-7}	0.177	0.061	110332	11781	18711
GLD_70 (A3)	2.8	0.409	86	2211	8.6	2.93×10^{-8}	0.045	0.380	140505	6243	18711
GLD_130 (A4)	0.5	0.409	86	1941	30.9	1.17×10^{-7}	0.157	0.380	101261	6243	18711
ES_70 (A5)	27.0	0.413	0	1977	8.4	2.89×10^{-8}	0.045	0.533	141556	5035	18711
ES_130 (A6)	29.1	0.413	0	1747	28.1	1.17×10^{-7}	0.157	0.533	107996	5035	18711
RH_70 (A7)	8.3	0.503	0	2244	8.6	2.90×10^{-8}	0.043	0.061	145323	6243	0
RH_130 (A8)	18.9	0.503	0	1974	29.8	1.34×10^{-7}	0.160	0.061	105956	6243	0

[1] - Initial *E. coli* density = 4.8 log CFU g^{-1}; CFU – colony-forming unit.

Regarding the environmental criteria, the germination index (C1) shows that GLD had a higher phytotoxic effect for *Lepidium sativum L.* than the other adjuvants tested (Table 7.4). On the other hand, GLD was the only material that promoted pathogenic microorganism removal (86%) as shown by criterion C3. GLD has a high concentration of chloride (0.63%), dissolved salts (~ 10 g L^{-1}), EC (~ 17 mS cm^{-1}) as well as a highly alkaline pH (greater than 10) (see Table S 7.1 – supplementary information) (Cabral et al., 2008). It is possible that these characteristics are the most relevant to determine the GI and the pathogen microorganism inactivation. Indeed, the literature refers that alkaline pH (for example) is a major adverse factor in the survival of pathogenic microorganisms (Metcalf and Eddy, 2014). Thus, SS_GLD is an alkaline material, which can be able to inactivate faecal coliforms (Hung et al., 2007; Rorat et al., 2019). On the contrary, the pH of other materials is less than 8, and therefore ineffective in

reducing microbiological contamination. Also, increasing the pH to the alkaline region (close to 12) may deprotonate ammonium (NH_4^+) to ammonia gas (NH_3), which creates adverse conditions for pathogens (Arthurson, 2008).

The drying rate (C5) at 130 ºC presented the highest value (31.6 gH_2O kg^{-1} SS$_{wb}$ min^{-1}) for CFA and the lowest for ES (28.1 gH_2O kg^{-1} SS$_{wb}$ min^{-1}). At 70 ºC, the ranking of the highest to the lowest drying rate is CFA > GLD = RH > ES. Recent studies indicated that the use of CFA, wood sawdust and RH tends to act as skeleton builders, facilitating the water flow from the interior to the surrounding environment, thus assisting the drying process (Wang et al., 2019; Zhang et al., 2019).

In terms of the ANC parameter (C8), Table 7.4 shows that ES and GLD have high alkalizing power (0.533 g $CaCO_3$ g^{-1} and 0.380 g $CaCO_3$ g^{-1}, respectively) while the opposite is observed for CFA and RH. Besides the liming effect may be important for the productivity of acidic soil, also a positive effect may be observed in the bioavailability of phosphorus and other nutrients (Pasquali et al., 2018).

7.3.2   Criteria weight determination

Table 7.5 presents the standard deviation, σ_j, the parameter C_j that carries the information contained in each criterion, and the weights, w_j, obtained using the CRITIC method. The normalised decision-matrix calculated using Eq. (7.2) is reported in Table S 7.4 (supplementary information). The correlation coefficients, r_{jk}, are listed in Table S 7.5.

Table 7.5 - Criteria weight results using the CRITIC method.

Variable	Environmental				Technical				Economic		
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
σ_j	0.206	0.030	0.306	0.080	0.171	0.186	0.173	0.220	0.050	0.119	0.177
C_j	1.857	0.365	3.423	0.749	1.525	1.673	1.524	2.539	0.647	1.060	1.667
w_j	**0.109**	**0.021**	**0.201**	**0.044**	**0.090**	**0.098**	**0.089**	**0.149**	**0.038**	**0.062**	**0.098**
Importance	3	11	1	9	6	4	7	2	10	8	5
w_j sum	0.376				0.426				0.198		

Table 7.5 shows that the top three most important criteria are the microorganisms > ANC > GI, which are distributed between the environmental (C1 and C3) and technical (C8) categories. According to the CRITIC calculation methodology, the higher weight is obtained by the criterion with the higher standard deviation and lower correlation with other criteria (Aznar Bellver et al., 2011). The criteria with the lowest impact on the decision are biomass production (C2), drying energy cost (C9), and CO_2 emissions (C4). The values of these criteria (shown in Table 7.4) are very similar between the alternatives, and thus have a low influence on the decision. Globally, the local factors (C4, C9, C10 and C11) sum up a total weight of 0.248 out of 1, probably playing a minor role in the overall outcome.

7.3.3   Ranking the alternatives

The scores for selecting the adjuvant alternatives and drying temperatures using the MOORA and TOPSIS methods are listed in Table 7.6. For the MOORA method, the sum of the beneficial and non-beneficial criteria, and the final S_i score are shown. For the TOPSIS, the ideal distance D_i^+ using Eq. (7.11), the non-ideal distance D_i^- using Eq. (7.12), and the closeness coefficient CCi, using Eq. (13) are indicated. The weighted normalised decision-matrix calculated using Eq. (7.8) is listed in Table S 7.6 – supplementary information and the d_j^+ and d_j^- values are presented in Table S 7.7 – supplementary information. Figure 7.3 depict the final scores achieved with MOORA and TOPSIS methods, to highlight the worst (lowest scores) and the best (highest scores) ranked alternative.

Table 7.6 - Scores for the adjuvants' alternatives using the MOORA and TOPSIS methods.

Alternative	MOORA			TOPSIS		
	Beneficial Criteria	Non-beneficial Criteria	S_i	Ideal distance	Non-ideal distance	CC_i
CFA_70	0.145	0.070	0.075	0.175	0.063	0.264
CFA_130	0.267	0.066	0.202	0.162	0.100	0.382
GLD_70	0.289	0.047	0.242	0.094	0.157	0.626
GLD_130	0.381	0.041	0.340	0.073	0.167	0.695
ES_70	0.208	0.042	0.166	0.158	0.097	0.380
ES_130	0.303	0.037	0.266	0.145	0.112	0.436
RH_70	0.066	0.048	0.018	0.186	0.021	0.101
RH_130	0.184	0.042	0.142	0.171	0.068	0.285
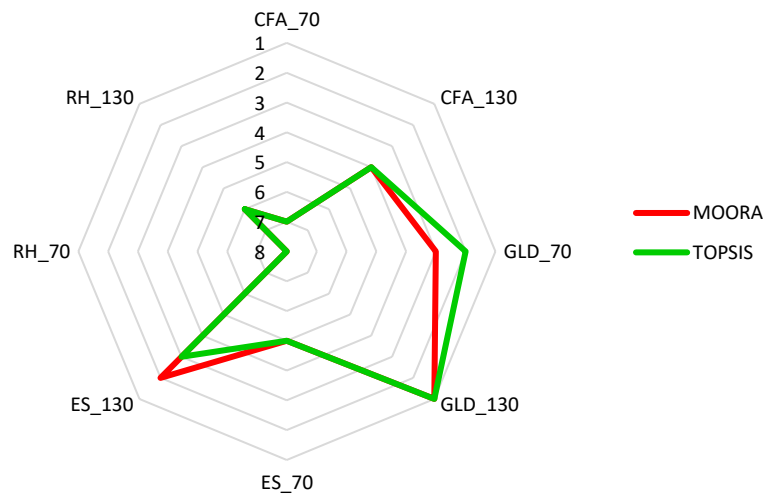
Figure 7.3 - Ranking for the selection of SS drying adjuvants (GLD, CFA, ES, and RH) at 70 and 130 °C.

According to the scores obtained from both MCDM methods, the alternative GDL_130 (drying of SS with GLD at 130 °C) is the best option, followed by ES_130 (MOORA method) and GLD_70

(TOPSIS method). Therefore, depending on the availability of each adjuvant, decision-makers can select among the highest scoring alternatives. Although CFA led to the highest DR value (C5) and kinetic constant, *k* (C7), and the least phytotoxicity (C1) comparing to the other materials studied, this adjuvant had no positive effect on ANC or microorganisms removal. Thus, CFA was not chosen as a principal option. Also, RH at 70 and 130 ºC are not advantageous alternatives. Indeed, Figure 7.3 shows that the worst alternatives are CFA_70 and RH_70 for both methods applied. In addition, the ranking obtained by the two MCDM methods is very similar, except for ES_130 and GLD_70, which exchange between the second and third positions.

7.3.4   Sensitivity analysis

Figure 7.4 shows the effect of changing the weights previously determined using the CRITIC method (w_j sum in Table 7.5) within the range of ±40%. Figure 7.4 (a) and (c) illustrates the variation of scores, and Figure 7.4 (b) and (d) the final ranking position using the MOORA and TOPSIS methods, respectively.

Figure 7.4 - Sensitivity analysis of the criteria weight. (a) and (c) Change of scores. (b) and (d) Final ranking using the MOORA and TOPSIS method, respectively.

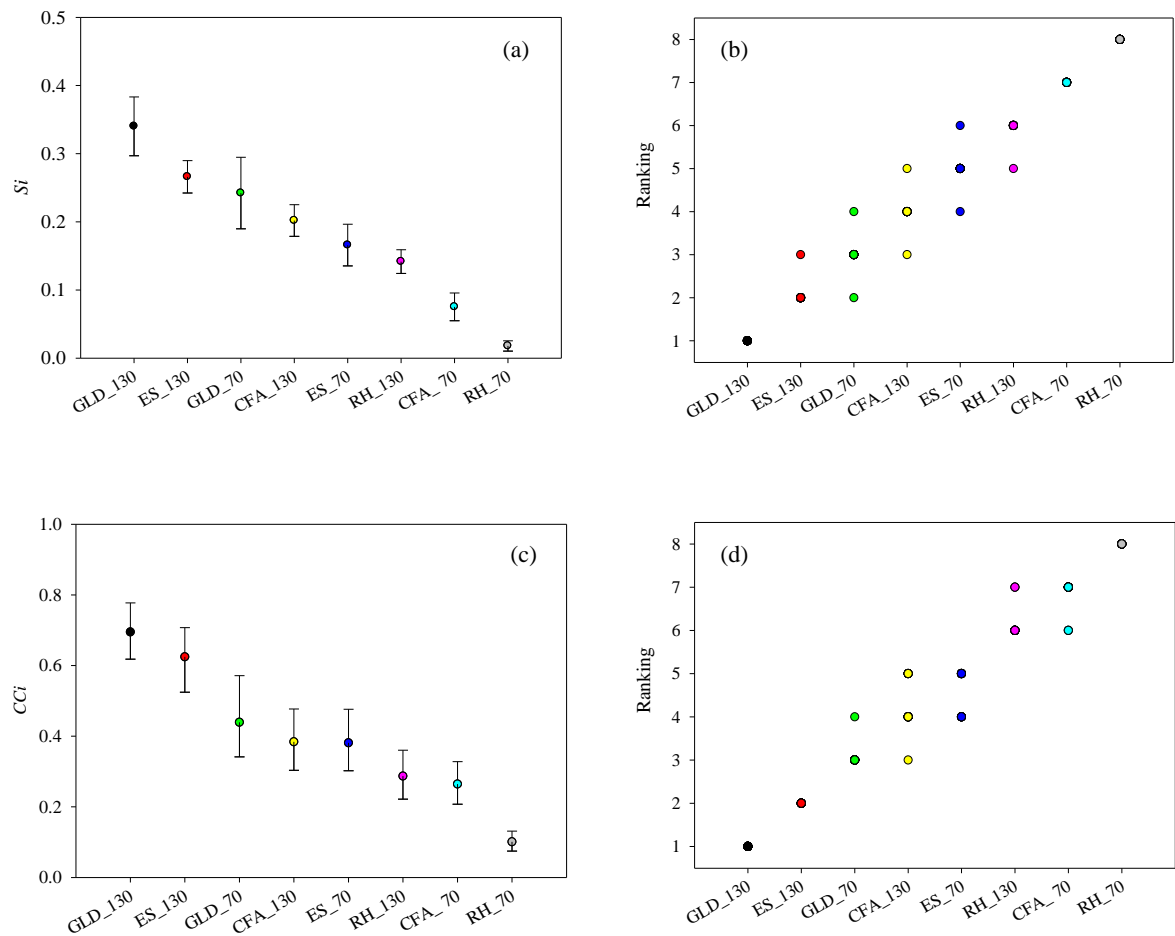The results indicate that the alternative GLD_130 is the preferred option by both MCDM methods, even after a change by 40% of the original criteria weights. According to the MOORA method, second place can be divided between ES_130 and GLD_70 depending on the weight attributed. For the TOPSIS method, ES_130 is always the second preferred option. RH_70 remains the last option for both methods.

Furthermore, a set of scenarios listed in Table 7.3 were tested to evaluate the importance of the environmental, technical, and economic criteria weights. Figure 7.5 (a) and (b) illustrate the ranking results for the scenarios using the MOORA and TOPSIS methods, respectively.
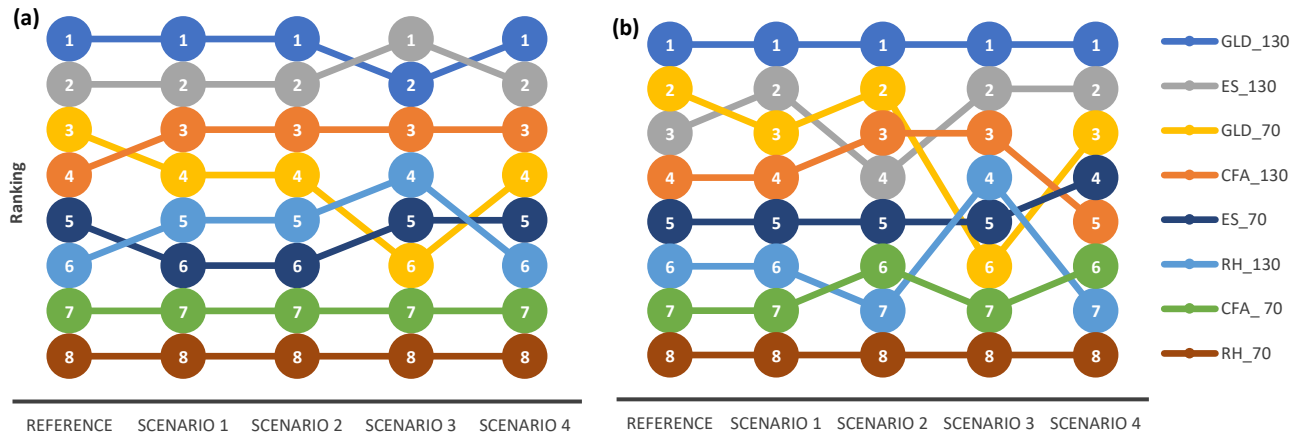

Figure 7.5 - Alternative ranking for the sensitivity analysis Scenarios 1 – 4 using the (a) MOORA and (b) TOPSIS methods.

The original weights calculated by the CRITIC method attributed 0.376, 0.426, and 0.198 to the environmental, technical, and economic criteria, respectively (Table 7.5). Thus, without the influence of the decision-maker, the economic criteria were considered the less important factors to the decision. However, the interested parties may want to attribute more importance to some specific criteria for the SS drying with adjuvants. Figure 7.5 (a) and (b) show the alternative ranking results for the weighting scenarios using the MOORA and TOPSIS methods, respectively. The Reference scenario corresponds to the ranking obtained with the original weights (Table 7.5). For both methods, GLD_130 and ES_130 alternatives are ranked in the highest positions, and RH_70 remains the least preferred alternative option. In general, scenario 3 causes more significant changes in the ranking of alternatives. In this scenario, the technical criteria account for 0.500 of the total weight, which means that criterion C5 – C8 weight 0.125 each. Therefore, the total weight of the environmental criteria is reduced to 0.250 (C1 – C4 accounting for 0.063 weight each), as well as the economic criteria (C9 – C11 account for 0.083 each). This change affects strongly the scores of GLD alternatives, which have the best performance in the microorganism removal (environmental criterion C3). Consequently, significant changes are observed for this adjuvant, more clearly when used at 70 ºC (GLD_70). Regarding the CFA alternatives, the longest collection distance (reflected on C4 and C10 criteria) has no significant influence on its ranking when compared to other criteria. Even when a higher weight is attributed to both criteria (C4 and C10), the ranking positions remain unchanged to these two alternatives.

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7.4 Conclusions

According to the scores obtained using two different multi-criteria decision methods, the alternative of drying SS using GLD at 130 ºC (GLD_130) is the best adjuvant and temperature option. However, ES_130 and GLD_70 also showed promising alternatives. On the other hand, the worst options were CFA_70 and RH_70 in both methods applied. The microorganisms > ANC > GI criteria were the most important, belonging to the environmental and technical criteria categories. Sensitivity analysis showed that despite changing the weight values by ±40%, GLD_130 and ES_130 alternatives are ranked in the highest positions. However, the GLD_70 ranking is highly affected when the importance of technical criteria is increased. In conclusion, the preferred adjuvant should be the one that assists the drying process and ensures soil pH buffering, while also considering the ability to inactivate pathogenic microorganisms. Nevertheless, the restrictions of regulations must be met in any case. In conclusion, this study demonstrated the usefulness of a strategy based on environmental, technical and economic criteria to select waste materials as drying adjuvants, in line with the circular economy.

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7.6 Supplementary information

- *Materials collection site and characterization*
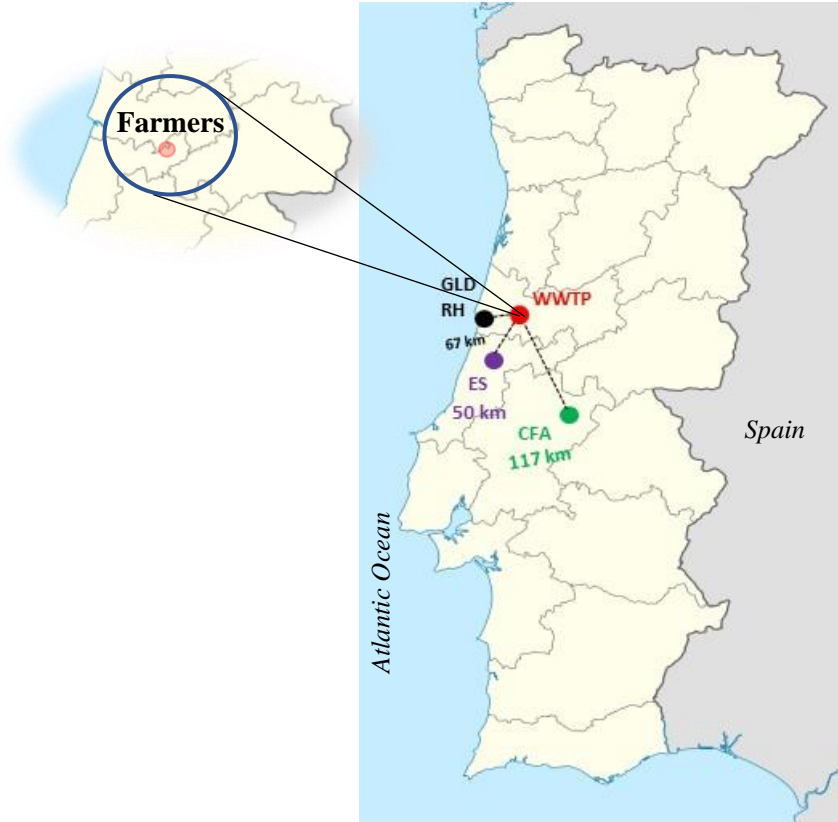
Figure S 7. 1 - Illustration of mainland Portugal showing the collection distances of the adjuvants and highlighting the sludge application area to the farmers (50 km).

Table S 7.1 summarizes the physical-chemical characterization of the materials used in this work.

Parameter [1]	Materials				
	SS	CFA	GLD	ES	RH
pH [2]	6.71	8.6	10.3	9.10	6.82
OM (%)	63.7	nd	nd	4.30	81.9
Moisture (%)	78.0	0.07	20.8	1.10	8.6
EC (mS cm^{-1}) [2]	1.70	0.49	16.6	0.21	0.88
Cl$^-$ (%)	0.13	0.02	0.63	0.02	0.19
$N_{Kjeldahl}$ (%)	3.90	nd	nd	nd	nd
P_2O_5 (%)	3.83	0.2	0.15	0.29	0.30
K_2O (%)	0.22	2.4	0.06	0.10	0.70
MgO (%)	0.38	1.5	16.8	0.72	0.30
CaO (%)	5.50	1.4	52.9 [3]	86.11 [3]	0.36 [3]
BaO (%)	0.02	0.11	0.04	nd	nd
TiO_2 (%)	0.15	1.1	0.02	nd	nd
SiO_2 (%)	4.05	50.8	2.91	nd	19.60
Al_2O_3 (%)	1.94	18.1	1.10	0.19	0.45

Table S 7.1 (cont.) - summarizes the physical-chemical characterization of the materials used in this work.

Parameter [1]	Materials				
	SS	CFA	GLD	ES	RH
Fe_2O_3 (%)	nd	6.5	0.40	nd	0.10
Na_2O (%)	nd	1.3	8.01	nd	nd
LOI (%)[4]	nd	6.0	nd	nd	nd
PTM (mg kg^{-1}_{db}) [5]					
Cd	nd	nd	nd	nd	nd
Cr	161	162	42.3	nd	3.35
Cu	251	84.9	127	17.5	6.85
Ni	53.1	89.7	74.7	nd	nd
Pb	25.1	51.9	33.1	nd	2.25
Zn	628	189	161	10.1	28.0

[1] With the exception of moisture, the % was calculated in dry basis (TS); OM – organic matter; Electrical conductivity (EC); nd – not determined; [2] Measured at L/S = 10 L kg^{-1}; [3] these values are reported in $CaCO_3$; [4] LOI - Loss on ignition at 950 ºC; [5] Legal limit by *Decreto Lei Nº*. 276/2009 for soil application with $5.5 < pH \leq 7$: Cd = 20; Cr = 1000; Cu (1000); Ni = 300; Pb = (750), and Zn = (2500).

- *Drying kinetics*

Fick's second law was the model used to describe the constant rate period of the drying process (period I), Eq. (S 7.1). The Henderson & Pabis model, also known as the thin-layer model, described by Eq. (S 7.2), was used to model the second period of the drying kinetics (Figueiredo et al., 2015; Srikiatden and Roberts, 2007).

$$MR = \frac{M(t)-M_e}{M_0-M_e} = \sum_{n=1}^{\infty} \frac{4}{r^2 \alpha_n^2} \exp(-D_{eff}\, \alpha_n^2 t) \qquad (S\ 7.1)$$

$$MR = \frac{M(t)-M_e}{M_0-M_e} = ae^{-kt} \qquad (S\ 7.2)$$

where MR is the dimensionless moisture ratio (Danish et al., 2016); M_0 and $M(t)$ are the moisture content in the cylinder (gH$_2$O g^{-1} dry solid) at t_0 and t time, respectively; M_e is the moisture content in equilibrium (gH$_2$O g^{-1} dry solid); the roots of the Bessel function of zero order ($J_o(r\alpha_n) = 0$) allowed to determine α_n parameter; r is the radius of the cylinder (m); D_{eff} is the effective diffusion coefficient (m^2 min^{-1}) of water; *a* is a parameter of the thin-layer model; k is the kinetic constant (min^{-1}) and *t* is the time (min).

The modulus of drying rate, |DR|, expressed in gH$_2$O min^{-1} kg^{-1}SS$_{wb}$ was determined by Eq. (S 7.3),

$$|DR| = \frac{\partial M(r,t)}{\partial t} \approx \frac{\Delta M}{\Delta t} = \frac{M_i - M_{i-1}}{t_i - t_{i-1}} \qquad (S\ 7.3)$$

where M is the moisture in wet basis (gH$_2$O kg^{-1} SS$_{wb}$) and t is the time (min).

The energy (kJ kg^{-1} SS$_{wb}$) required for removing water to achieve MR = 0.30, expressed by E$_{0.30}$ was calculated for the Period I at 70 and 130 ºC, considering the drying rate at any time within this period, Eq. (S 7.4).

$$E_{0.30} = h \int_{t_0}^{t} |DR(t)| \, dt \tag{S 7.4}$$

where *h* is the latent heat of vaporization of water (kJ kg^{-1}), t_0 is the time at the beginning of Period I (min), *t* is the time to achieve MR = 0.30, and DR(t) is the drying rate at time t. The value of *h* was obtained considering the wet-bulb temperature during the Period I of the drying process (Cengel, 2003).

The drying kinetics of the different materials at 70 and 130 ºC can be observed in Figure S 7.2 (a) and (b), respectively.
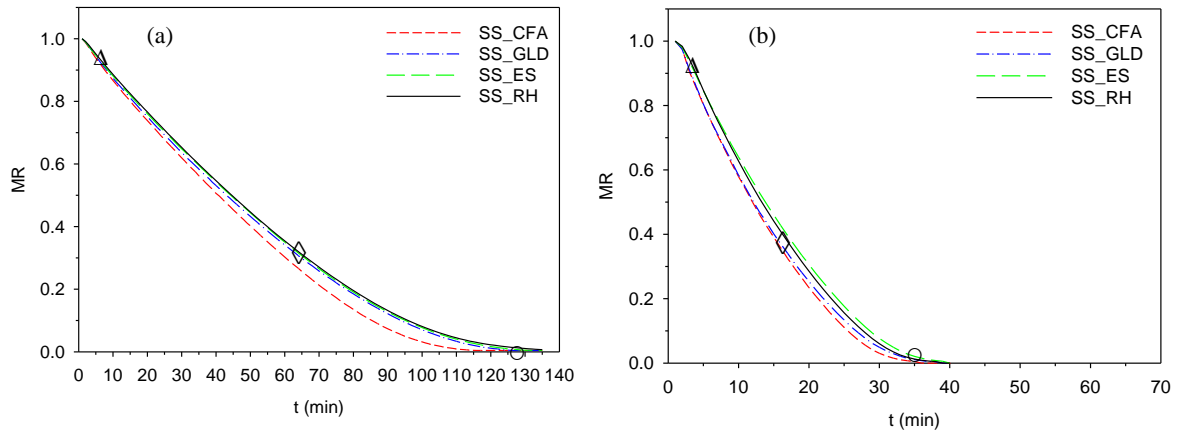
Figure S 7. 2 - MR evolution as a function of time for SS_CFA, SS_GLD, SS_ES, and SS_RH at (a) 70 ºC and (b) 130 ºC. The symbols Δ, ◊, and ○ refer to the end of the rising rate period, constant rate period (free water) and second drying period (bound water), respectively.

- *Phytotoxicity assays and growth tests*

The germination index (GI) was classified as non-phytotoxic if GI > 80%; mild phytotoxic 60% < GI < 80%; strong phytotoxic 40% < GI < 60%; and severe phytotoxic GI < 40% (Trautmann and Krasny, 1997).
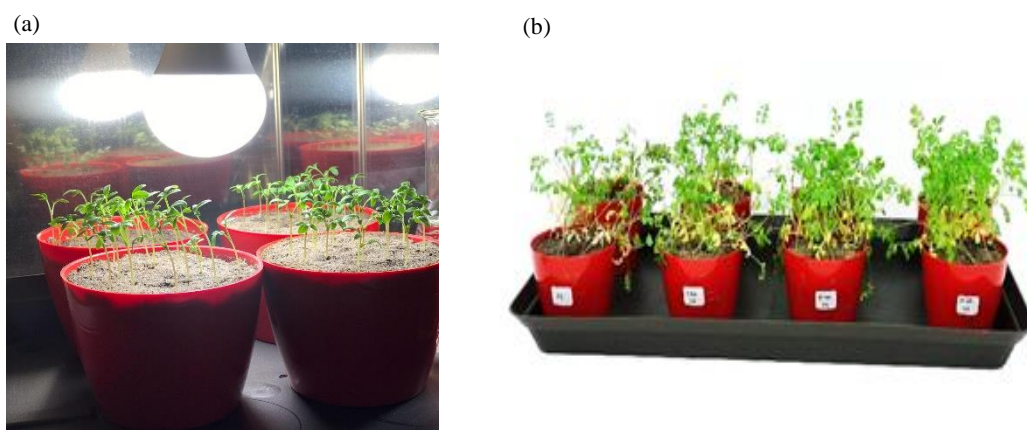
Figure S 7. 3 - Growth tests of *Lepidium sativum L.* with amendment soil (a) at incubator with light, temperature and relative moisture control (b) treatments after 4 weeks.

- *Intermediate calculations of selection criteria*

The CO_2 emissions during the transportation of adjuvants for the WWTP were calculated based on the steps present in Table S 7.2. The distances between the collection site and the WWTP are indicated in Figure S 7.1. About 1890 t year^{-1} of adjuvants will be necessary to mix with sewage sludge, which represents 105 loads per year in a truck with a capacity of 18 t. Table S 7.3 presents the intermediate calculations for the transport cost of the adjuvants.

Table S 7.2 - CO_2 emissions during transportation.

| Materials	Distance (km)	Annually loads	Distance of round trips (km year^{-1})	Adjuvants amounts (t year^{-1})	CO_2 factor (gCO_2 t^{-1} km^{-1})	CO_2 emissions (t CO_2 year^{-1})
CFA	117	105	24570	1890	50.6	2350
GLD	62	105	13020	1890	50.6	1245
ES	50	105	10500	1890	50.6	1004
RH	62	105	13020	1890	50.6	1245

Table S 7.3 - Adjuvants transport costs.

Materials	Distance (km)	Annually loads	Distance of round trips (km year^{-1})	Diesel average consumption (L km^{-1})	Diesel consumption (L year^{-1})	Diesel price (€ L^{-1})	Annually diesel price (€ year^{-1})
CFA	117	105	24570	0.35	8600	1.37	11781
GLD	62	105	13020	0.35	4557	1.37	6243
ES	50	105	10500	0.35	3675	1.37	5035
RH	62	105	13020	0.35	4557	1.37	6243

- *Multi-criteria decision making results*

The normalised decision-matrix calculated using Eq. (7.2) is reported in Table S 7.4.

Table S 7.4 - Normalised decision-matrix.

Alternative	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
CFA_ 70	0.448	0.348	0.000	0.490	0.146	0.123	0.154	0.065	0.387	0.535	0.408
CFA_130	0.635	0.348	0.000	0.463	0.504	0.499	0.523	0.065	0.312	0.535	0.408
GLD_70	0.039	0.328	0.707	0.329	0.137	0.115	0.132	0.407	0.397	0.284	0.408
GLD_130	0.007	0.328	0.707	0.289	0.492	0.460	0.463	0.407	0.286	0.284	0.408
ES_70	0.378	0.331	0.000	0.295	0.134	0.114	0.132	0.571	0.400	0.229	0.408
ES_130	0.409	0.331	0.000	0.260	0.448	0.459	0.463	0.571	0.306	0.229	0.408
RH_70	0.116	0.403	0.000	0.334	0.137	0.114	0.127	0.065	0.411	0.284	0.000
RH_130	0.265	0.403	0.000	0.294	0.475	0.524	0.472	0.065	0.300	0.284	0.000

The correlation coefficient r_{jk}, determined using Eq. (7.4), or applying the function CORREL (Matrix1; Matrix2) on Excel is shown in Table S 7.5.

Table S 7.5 - Correlation coefficients between evaluation criteria.

Criteria	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
C1	1	-0.071	-0.739	0.548	0.211	0.232	0.282	-0.201	-0.138	0.593	0.271
C2	-0.071	1	-0.471	0.024	0.003	0.067	-0.003	-0.731	0.068	0.009	-0.966
C3	-0.739	-0.4713	1	-0.254	0.019	-0.042	-0.035	0.341	-0.093	-0.239	0.333
C4	0.548	0.0245	-0.254	1	-0.163	-0.185	-0.123	-0.655	0.216	0.974	0.219
C5	0.211	0.0028	0.019	-0.163	1	0.993	0.997	-0.050	-0.982	0.061	0.009
C6	0.232	0.0675	-0.042	-0.185	0.993	1	0.993	-0.073	-0.975	0.037	-0.056
C7	0.282	-0.0031	-0.035	-0.123	0.997	0.993	1	-0.061	-0.973	0.100	0.029
C8	-0.201	-0.7307	0.341	-0.655	-0.050	-0.073	-0.061	1	-0.028	-0.664	0.557
C9	-0.138	0.0679	-0.093	0.216	-0.982	-0.975	-0.973	-0.028	1	-0.011	-0.063
C10	0.593	0.0093	-0.239	0.974	0.061	0.037	0.100	-0.664	-0.011	1	0.239
C11	0.271	-0.9659	0.333	0.219	0.009	-0.056	0.029	0.557	-0.063	0.239	1

The normalized weighted decision matrix calculated using Eq. (7.8) is shown on Table S 7.6.

Table S 7.6 - Normalized weighted decision-matrix.

Alternative	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
	Max	Max	Max	Min	Max	Max	Max	Max	Min	Min	Max
CFA_70	0.049	0.007	0.000	0.022	0.013	0.012	0.014	0.010	0.015	0.033	0.040
CFA_130	0.069	0.007	0.000	0.020	0.045	0.049	0.047	0.010	0.012	0.033	0.040
GLD_70	0.004	0.007	0.142	0.014	0.012	0.011	0.012	0.061	0.015	0.018	0.040
GLD_130	0.001	0.007	0.142	0.013	0.044	0.045	0.041	0.061	0.011	0.018	0.040
ES_70	0.041	0.007	0.000	0.013	0.012	0.011	0.012	0.085	0.015	0.014	0.040
ES_130	0.045	0.007	0.000	0.011	0.040	0.045	0.041	0.085	0.012	0.014	0.040
RH_70	0.013	0.009	0.000	0.015	0.012	0.011	0.011	0.010	0.016	0.018	0.000
RH_130	0.029	0.009	0.000	0.013	0.043	0.051	0.042	0.010	0.011	0.018	0.000

The d_j^+ and d_j^- values that correspond to the ideal (best) and non-ideal (worst) values of the normalized decision-matrix depending on the objective to maximize and minimize a criterion, are presented in Table S 7.7.

Table S 7.7 - d_j^+ and d_j^- values.

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
	Max	**Max**	**Max**	**Min**	**Max**	**Max**	**Max**	**Max**	**Min**	**Min**	**Max**
d_j^+	0.069	0.009	0.142	0.011	0.045	0.051	0.047	0.085	0.011	0.014	0.040
d_j^-	0.001	0.007	0.000	0.022	0.012	0.011	0.011	0.010	0.016	0.033	0.000

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8.   CONCLUSIONS AND FORTHCOMING WORK

This work aimed to study the drying process of sewage sludge (SS) at different temperatures (70, 85, 100, 110, and 130 ℃) and with the addition (0.15 g adjuvant g^{-1} SS_{wb}) of different residues (weathered coal fly - CFA, green liquor dregs - GLD, eggshell - ES, and rice husk - RH), to obtain a product for agronomic applications. Based on the experimental results and the modelling studies, the following conclusions can be outlined:

- The limits imposed for potentially toxic metals (PTM) in SS in the Portuguese legislation were not surpassed for any PTM studied. Furthermore, the low PTM concentration in adjuvants does not compromise the possibility of its application in the soil;

- Since the soil in Portugal is predominantly acidic (pH < 5.5) and contains low organic carbon, the utilization of SS in the soil seems a viable possibility;

- The ranking of detrimental metals in germination index (GI) with *Lepidium sativum L.* seeds in root elongation was $Cd > Cu > Cr(VI) > C(III) \sim Zn \sim Ni > Pb$;

- The ecological risk showed that the geoaccumulation index of Cd, Cu, and Zn corresponded to "moderate to high pollution level". However, the pollution index and potential ecological risk index revealed that no contamination is expected if the sludge is applied to the soil;

- SS contained interesting quantities of nutrients (3.9% of $N_{Kjeldahl}$ and 3.8 % of P_2O_5), and a low concentration of K, while CFA contains 2.4% of K_2O. Therefore, SS combined with CFA may improve the agronomic quality of the final product;

- The utilization of CFA as an adjuvant (0.15 g CFA g^{-1} of SS_{wb}) had a positive impact on the drying process of SS for all the temperatures tested (70, 85, 100, 115, and 130 ℃). However, the isothermal drying at 130 ℃ was the best alternative (effective diffusion coefficient of 1.27×10^{-7} m^2 min^{-1}; drying rate equal to 31.61 gH_2O kg^{-1} SS_{wb} min^{-1}; energy consumption 864 kJ kg^{-1} SS_{wb});

- The positive effect of the use of adjuvants on the diffusion coefficient (D_{eff}) at 100 ℃ in Period I, compared to the control sample, was 1.11, 16, and 19%, for CFA, ES, and RH, respectively. However, GLD decreased D_{eff} by about 7%. The properties of GLD such as a high water absorption capacity, large surface area, small particle size, and low hydraulic conductivity probably hindered the drying process;

- GLD contains about 70% by weight of $CaCO_3$, and thus revealed good buffering capacity. However, it may increase the ionic strength in the soil (15.6 mS cm^{-1} measured in an L/S 10);

- GLD decreased the pathogenic microorganisms (86%) contamination;

- This study showed that in all the experiments, the mathematical models based on Fick's second law (Period I) and thin-layer model (Period II) described adequately the kinetics of drying and allowed the determination of the most relevant process parameters;

- The GI with *Lepidium sativum L.* with CFA extracts was always superior to 70%, which indicates that the inhibition of seed germination and growth is mild. CFA mixed with SS reduced the phytotoxic effect and enhance EC_{50} (66%);

- The GI measured in extracts with ES is higher than 60%, which indicates that the phytotoxicity is low;

- Pot experiments demonstrated that CFA boost the growth of plants (e.g., shoot length), and increases the soil pH from 6 to 7; while GLD, ES, and RH did not demonstrate a significative effect on plants;

- ES revealed a high acid neutralization capacity (19.7 meq g^{-1});

- The screening of four adjuvants showed that GLD and ES are the best adjuvants, considering technical, economic and environmental criteria;

- The choice of the ideal temperature for the drying process depends on the adjuvant and its ability to produce a final material that does not represent a risk to the environment and public health;

- The results of this work allowed to establish a new route for the management of specific residues as SS drying adjuvants, to produce material for soil applications, and contribute to the circular economy.

8.1 Forthcoming work

This study constitutes a first insight into the feasibility of a drying process of SS with different adjuvants to obtain a product for agronomic applications. The studies conducted on the thesis still require further analysis to complete specific issues. The following topics are proposed as future studies:

- The drying process must be evaluated for different solid shape with different percentages of adjuvants (w/w), to investigate the effect on the different falling rate periods;

- Study the effect of the adjuvants on the shrinkage during the drying process;

- Deepen the knowledge on the effect of adjuvants on sludge sanitation with and without drying;

- Study the effect of OM biodegradability on soil and PTM mobility in the soil and in plants;

- Perform respirometry studies (soil, SS, SS with adjuvants, and adjuvants) to determine the stability of the materials;

- Remove ammoniacal nitrogen content in the SS to reduce the phytotoxic effect on crops;

- Investigate through ecotoxicological approaches (e.g., cytotoxic, genotoxic, and mutagenic tests) other effects of the sludge in the soil, to contribute to the decision-making on the SS management;

- Test the produced material at full-scale in different types of soils and crops to assess the agronomic effect on physicochemical properties (e.g., water holding capacity, cation exchange capacity, aeration, drainage, porosity, soil erosion) and on microbiological aspects.