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Advanced oxidation processes for recalcitrant compounds removal comparison with biofiltration by *Corbicula fluminea*

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Abstract

Conventional treatments cannot remove the emerging contaminants due to their refractory character, therefore improved methodologies should be applied for obtaining their total removal. The need of development of suitable technologies to treat these recalcitrant compounds is related with the wastewater reclamation. Advanced oxidation technologies such as photocatalysis and ozonation appear as suitable solutions for recalcitrant compounds removal. Moreover, the biofiltration can be applied as a pest management approach integrated with wastewater treatment. Due to the invasive character of *Corbicula fluminea* their usage as biofilter hosts can work as a reduction of their impact over native species or industrial damage. These methodologies were used to promote the degradation of a mixture of SMX, CBZ and LRZ at initial concentration of 1 mg/L of each one. Single ozonation was capable to remove totally SMX and CBZ in 5 min. Whereas only 50% of LRZ were removed in 60 min. The weather can affect the sunlight radiation photon flux which will promote impact on the photocatalytic oxidation using 1 wt% of Ag and Pd-TiO2 as catalysts, for SMX, CBZ and LRZ abatement. *C. fluminea* was capable to remove about 30% of CBZ and LRZ in 24h.

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Keywords: Biofiltration; Corbicula fluminea; Photocatalytic oxidation; Ozonation; Sunlight radiation

1. Introduction

Modern society faces one of the major drawbacks of this century: water scarcity. Global warming and the exponential growth of population are considered as the main reasons for this problematic. Therefore, thinking on the minimization of impact of the scarcity of this resource, wastewater reclamation should be and option to be exploited [1]. However, the precautionary principle imposes that care must be taken in what regards the presence

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Nomenclature

AOPs	Advanced oxidation processes
CBZ	Carbamazepine
CEC	Contaminants of emerging concern
CPC	Compound parabolic collector
LRZ	Lorazepam
SMX	Sulfamethoxazole
TOD	Transferred ozone dose

of micropollutants in the recovered water so that its safety may be ensured. CEC appear on the water sources at different concentrations. In fact, CEC have been noted in the water courses such as rivers and with more frequency at wastewater treatment plants [2,3]. The appearance of higher number of antibiotic-resistance bacteria in the water courses promotes an increase of the consumption of antibiotics [4]. SMX is a typical antibiotic widely used. On the other hand, as consequence of work's and life stress due to the economic and industrial growth turns anxiety and depression common diseases due to the frustration of unreachable goals [5]. Therefore, CBZ and LRZ are typical used as antiepileptic/anticonvulsant and anxiolytic drugs, respectively. The conventional wastewater treatment cannot face these biorecalcitrant compounds; therefore, alternatives should be considered. The AOPs have been explored to improve conventional wastewater treatments. An approach often used as AOP technologies is ozonation, since ozone is a powerful oxidant that can promote the degradation of recalcitrant compounds such as emerging contaminants. The application of this technology for the abatement of emerging contaminants has been widely studied [6]. Molecular ozone can react with high electronic density compounds due to the electrophilic character [7]. Martini et al. [8] and Martins et al. [9] achieved complete SMX removal by single ozonation process, which reveals ozone reactivity with this molecule. Within these advanced oxidation processes can be considered a wide range of technologies. Another source that can be explored is photocatalysis using the sunlight as radiation source, allowing using suitable catalysts the degradation of CECs with low cost energy. However, for this it is necessary to use a material that can be active with this radiation. Typically, the most applied catalyst in photocatalysis is titanium dioxide due to its low cost and chemical stability. Nonetheless, TiO_2 band gap (3.2 eV) just can be broken with UVA radiation. Nevertheless, this energetic band gap can be reduced so that visible light application is possible with the incorporation of noble (Ag, Pd, Pt and Au) or non (N, B, S) metals [10,11]. In fact, the noble metals due to the surface plasmon resonance can absorb the visible light [12]. Another aspect important on the noble metals application is related with the load used onto the TiO_2 structure [13,14]. The high amount of noble metal can mean a high cost for the catalyst production and, if in excess, noble metal particles can trap the active sites of TiO_2, working as scavenger [14,15]. Another problem of sunlight radiation application is related with the variation of the photon flux available during the year. In fact, the photon flux can present really impact on the emerging contaminants degradation [16].

Corbicula fluminea is an invasive bivalve which can promote a serious economic and ecological impact [17]. The high capacity of dispersion and resistance to adverse conditions turns this species problematic. Thus, it needs suitable management strategies [18,19]. Typically, these bivalves are chemically controlled. However, their high biofiltration capacity makes them possibly suitable for emerging contaminants removal from water [20]. Ferreira et al. [21] using a winery wastewater proved that 100% of COD removal was possible to achieve in 3 days of contact with *C. fluminea* after application of Fenton's process as a pre-treatment. Moreover, the *C. fluminea* proved to be suitable for the biofiltration of bacteria *Escherichia coli*, virus and other metals providing from water [20,22].

The aim of this work was to innovatively compare two different AOP's process (Ozonation and photocatalysis) and biofiltration with *C. fluminea* for the abatement of a mixture of SMX, CBZ and LRZ. In the photocatalysis experiments was also evaluated the effect of the presence of clouds and weather conditions on the photon flux, verifying its impact on the mixture degradation rate.

2. Materials and methods

2.1. Chemicals and catalysts

SMX, CBZ and LRZ were purchased at Sigma-Aldrich. The 1 wt% Ag and Pd doped TiO_2 catalysts were prepared by photodeposition method through UV–Vis light (1000 W Xe lamp) for 100 min, using $AgNO_3$ and $PdCl_2$ as respective precursors [14]. The main characterization is published elsewhere [14].

2.2. Experimental procedure: AOPs

The sunlight experiments were carried out in a 0.5 L cylindrical reactor with a CPC placed below, it covering all its surface. The load of photocatalyst placed in the reactor was 70 mg/L. This load was used based in previous works [23]. The reactor was covered with aluminum during 10 min before starting the experiment to avoid light penetration so that the adsorption of CECs on the photocatalysts could be attested. Samples were withdrawn at 0, 5, 10, 15, 30, 45 and 60 min. The solution recover in each time for analysis was filtrated by an acetate cellulose syringe filter with a pore size of 0.45 μm. The reaction homogeneity was guaranteed by the presence of axially placed porous stone which allows air bubbling. The photon flux and the spectrum of radiation was followed during the experiments through a radiometer (Oceans Optics USB 4000 fiber optic spectrometer). The sunlight experiments occurred at the roof of the Department of Chemical Engineering from the University of Coimbra (40.1865243º, −8.41797950º). These experiments were performed in two different seasons of the year, one in the middle of May and the other in the beginning of November of 2018.

The experiments with ozone occurred in a 2 L glass reactor. Ozone was obtained by a pure oxygen stream from an ozone generator (802N, BMT). The inlet and outlet ozone concentrations were measured by two gas ozone analyzers (BMT 963 vent and 964 vent, BMT). These analyses allow the calculation of the TOD needed to promote the drugs decontamination. In fact, with this powerful oxidant the limiting step it will be the ozone consumption which is very related with the time of reaction, as can be seen in Eq. (1).

$$\mathrm{TOD} = \int_0^t \frac{Q_{Gas}}{V_{Liquid}} \times \left([O_3]^{in} - [O_3]^{out}\right) \times dt \quad (1)$$

where Q_{Gas} represents the gas flowrate (0.2 L/min), V_{Liquid} is the volume of the effluent used in the reactor (2 L), $[O_3]^{in}$ and $[O_3]^{out}$ are the ozone concentrations incoming and leaving the reactor, respectively. TOD was expressed in mg O_3/L. The remaining ozone that leaves the reactor was destroyed by a solution of 2% (w/v) potassium iodide.

2.3. Experimental procedure: Biofiltration

Asian clams were collected from a well-established population at a canal in Mira, Portugal (N40°25'06.90"/W8° 44'13.18") [19]. The collection occurred at the beginning of 2019. The procedure for clam's acclimation and preparation for experiments can be seen [22]. The capacity to remove CECs from water was tested using glass biofilters of 0.5 L with 20 clams (clams dimension between 20–30 mm). The tests were performed in duplicate and the mixture without clams was also analyzed to attest if compounds self-decomposition occurred. The experiment was performed during 72 h and samples were taken at each 24 h.

2.4. Analytical procedure

The CECs used in the experiments were identified and quantified by high-performance liquid chromatography, equipped with a diode array detector (HPLC-DAD, UFLC, Shimadzu). The volume of injection of samples was 100 μL. The eluents at the ratio 60/40 monosodium phosphate in ultrapure water and acetonitrile were flowed throughout a Silia Chrom C-18 column with a flow rate of 1 mL/min under isocratic conditions. CECs quantification occurred at the wavelength of 255 nm.

3. Results and discussion

3.1. Photocatalysis: effect of season of the year

The use of sunlight as radiation source for photocatalysis has multiple advantages, such as the cost, the availability and the spectrum radiation which can present UVA and UVB radiation, that can promote the photolysis of a wide range of compounds. However, the weather can reduce the benefits of sunlight radiation due to the presence of clouds, smog and rain that can reduce photon flux. On this way, two situations were evaluated, one where sun was at its maximum of irradiation throughout all the reaction time and a second where the presence of clouds was noted at the middle of the reaction and which reduced the photon flux radiation.

The most difficult compound to degrade was CBZ (Fig. 1b) and it can be related with the tricyclic structure difficult to break through hydroxyl radicals. SMX (Fig. 1a) was easily removed for all the conditions tested.

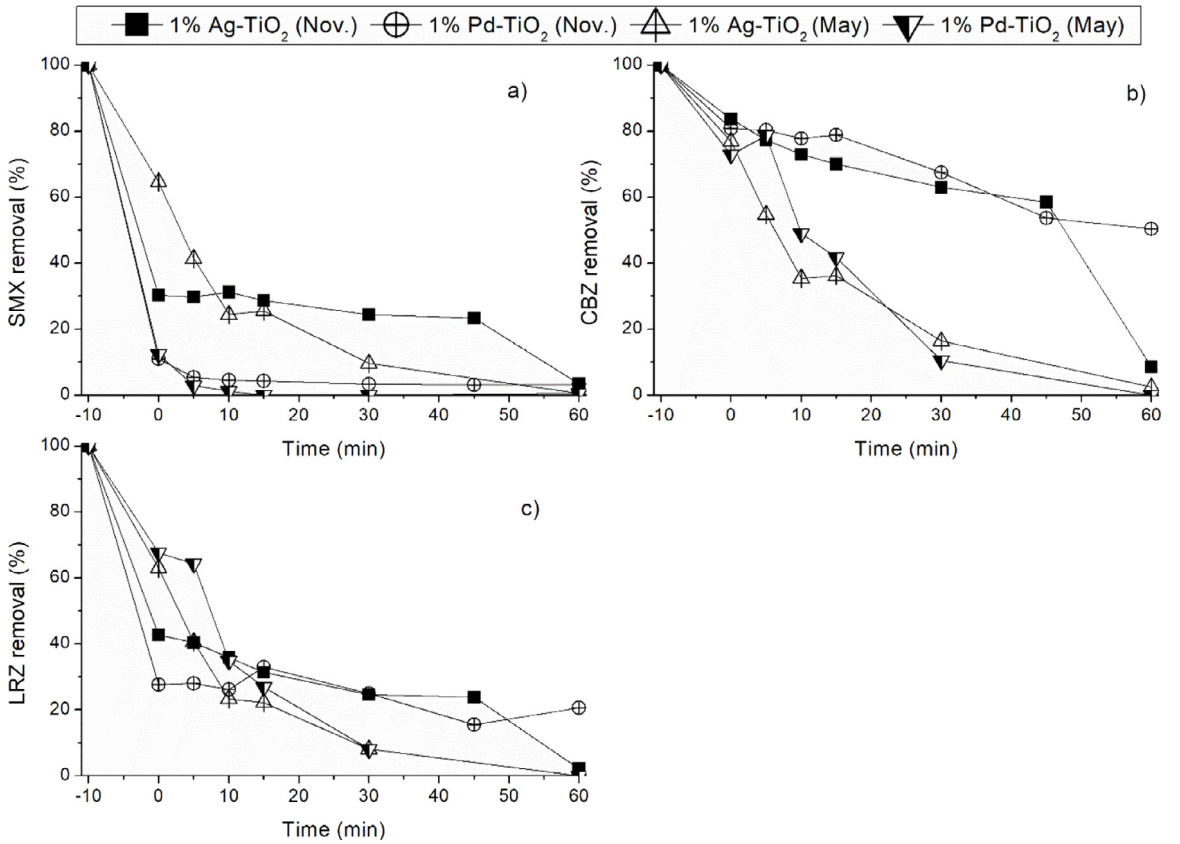

Fig. 1. Season of the year impact on photocatalytic oxidation for sunlight using Ag and Pd-TiO_2on degradation of (a) SMX, (b) CBZ, (c) LRZ.

Until the 15 min of reaction for Pd-TiO_2 experiments in November, the photon flux radiation was almost 440 ± 10 W/m^2 similar with the obtained for the same catalyst in May during complete reaction time 430 ± 20 W/m^2. The main difference is related with the contribution of UVA and UVB spectrum since the intensity was smaller for these two in November. But looking to Fig. 1 the results indicate that until this time the degradation obtained for both conditions was similar. However, after that, due the appearance of clouds the photon flux reduced to 130 ± 40 W/m^2. This reduction promotes the lower degradation of CECs after this period. The same occurs with Ag-TiO_2 until 45 min, but at the last point the photon flux increases again to the maximum of radiation and the degradation achieved was almost complete for all the CECs tested.

3.2. Ozonation and biofiltration

The photocatalytic oxidation proves that this process can be efficient for the degradation of CECs. However, the weather can affect its performance. Therefore, alternatively ozone will be evaluated in this section for CECs degradation.

Ozone proven to be a good oxidant for the CECs considered degradation in this experiment (Fig. 2a). SMX and CBZ were quickly degraded. In just 5 min of reaction it was possible to remove all initial concentration (this time corresponds to a 2.4 mg/L of TOD). However, only 50% of LRZ was removed after 60 min. This lower efficiency can be related with the low electrophilicity of the LRZ molecule. Cl is an electron withdrawing group in the benzenic ring which may reduce the molecule reactivity with molecular ozone.

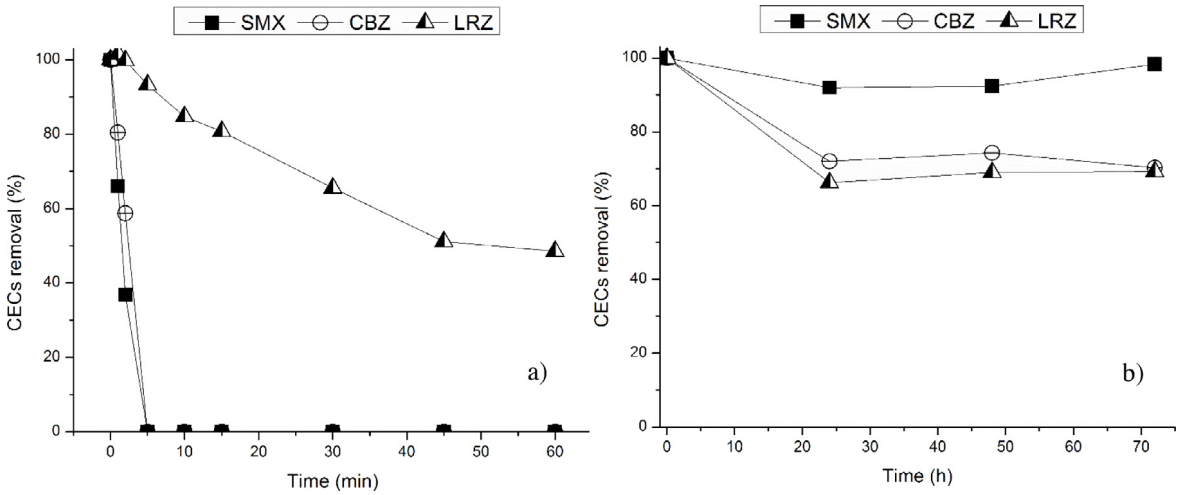

Fig. 2. CECs degradation by (a) single ozonation and (b) biofiltration by *C. fluminea*.

The Asian clams biofiltration process was tested as an alternative to AOPs. In fact, their resistance to adverse conditions and biofiltration capacity can be positive for CECs removal. On the other hand, the ecological and industrial impact of this invasive species turns their application for CECs removal as an environmental approach that can works as a pest management strategy [20]. The CECs removal was evaluated during 72 h of contact with 20 bivalves in 0.5 L of synthetic effluent. The concentration of CECs in the blank solution where the solution was only aerated did not suffer any abatement during this test period. The Asian clams can remove about 30% of CBZ and LRZ in 24 h (Fig. 2b). Until the 72 h, the pollutants concentration did not suffer further significant changes (Fig. 2b). This absence of alterations during this period can be related with the clam's saturation. Possibly with more clams it would be possible to achieve higher removals. Clams was not capable to remove SMX. Therefore, it seems that clams present a selective behavior regarding CECs removal. The mechanism of removal should be explored to verify if clams just work as adsorbent or can bioprocess these contaminants. After 144 h of contact, CECs concentration in water was again analyzed and no variation was verified (data not shown). Thus, even if probably saturated, the clams did not release the retained compounds.

4. Conclusions

The water courses have been constantly contaminated with contaminants of emerging concern, CEC, from pharmaceutical products usage. In fact, the increase on the consumption of such compounds promote the pollution of water courses. Therefore, in this work were studied different approaches to promote the abatement of a mixture of three CECs. The ozonation proven to be a strong oxidant for SMX and CBZ. Otherwise, LRZ present more resistance possible due to the low electrophilicity which promote the reduction on the activity. Moreover, the photocatalysis shows that the weather conditions can promote significant impact in terms of degradation efficiency. The presence of clouds was analyzed and besides the photon flux reduction also degradation of CECs was affected.

This is an important condition since the perfect sunlight radiation was not available all the year. Therefore, during the reactor project it must be needed in account this reduction on the efficiency. Alternatively, to AOPs methodologies was tested biofiltration through the *C. fluminea.* The clams in 24 h was able to remove about 30% of LRZ and CBZ. Moreover, during the 144 h the concentration of the both contaminants remains constant which reveals that the clams biofilter and does not release in the water.

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