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Optimization study of the alkaline washing of mononitrobenzene

Thesis Project in the scientific area of Chemical Engineering, supervised by Professor Doctor Cristina Maria dos Santos Gaudêncio Baptista and Doctor Alejandro Ribeiro submitted to the Department of Chemical Engineering, Faculty of Science and Technology, University of Coimbra

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UNIVERSIDADE DE COIMBRA

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Supervisors:

Prof. Dr. Cristina Maria dos Santos Gaudêncio Baptista
Dr. Alejandro Ribeiro

Host institution:

CUF-Químicos Industriais.

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Note

Due to confidentiality reasons, main variables presented in this work were normalized.

Abstract

Mononitrobenzene (MNB) has an important role in the polyurethanes chain production, which is mainly used by the construction and automobile industry. MNB is produced by nitration of benzene and such process has side reactions that lead to the formation of dinitrobenzene (DNB), dinitrophenol (DNP) and trinitrophenol (TNP). These compounds are usually removed from the MNB by means of a reactive liquid extraction in alkaline medium.

At the nitration plant of CUF-QI, MNB's purification is carried out in two countercurrent washers (each one consists of a static mixer and a settler). Ammonia (NH_3) is used as alkaline agent since it promotes the extraction by reacting with the nitrophenols to form aqueous salts. In the plant, washing efficiencies for DNP and TNP are approximately of 0.57 and 0.43, respectively. This work was focused on the assessment of the operating conditions in the second alkaline washer of MNB at CUF-QI. The objectives were to study the influence upon the extraction of nitrophenols from the MNB of: the process temperature, the weight ratio R solvent /MNB and the composition of the solvent.

Experiments mainly consisted in carrying out the MNB's washing at laboratory scale. Experiments revealed that the extraction of nitrophenols's is promoted at lower temperatures, a decrease of 45% in temperature led to an increase in the washing efficiency of 0.13 and 0.05 for DNP and TNP, respectively (compared to plant conditions). It was demonstrated, at laboratory and industrial scale that, the solvent to MNB weight ratio could be reduced up to using only 20% of the current solvent flow rate, without any impact in both washers.

It was also confirmed that ammonium has different impacts on the extraction of nitrophenols, the rise in NH_4^+ concentration in the solvent promotes the DNP transfer while it decreases the TNP extraction. Moreover, it was demonstrated that ammonium carbonate acts as alkaline agent at very low concentrations of ammonium (around 0.03). When NH_4^+ concentration is in the plant range (around 0.4), ammonium carbonate decreases the washing efficiency due the common ion effect.

When washing without alkaline agent, near neutral conditions, TNP's washing efficiency was higher than DNP's. Carrying out the process using a stream from the process (MNB's tank water, $\text{pH} \approx 7$) and low solvent to MNB ratio (30 times lower than current plant's R) led to efficiencies of 0.68 and 0.79 for DNP and TNP, respectively. As an outcome of this study it is proposed to change the solvent composition in the plant: ammonia aqueous solution would only be added to the solvent in the first washer, and neutral conditions would be used in the second washer.

Resumo

O mononitrobenzeno (MNB) tem um papel importante na cadeia de produção dos poliuretanos, que por sua vez são usados principalmente como materiais na indústria da construção e de automóveis. O MNB é produzido por nitração do benzeno, ocorrendo reacções secundárias que levam à formação de subproductos, principalmente dinitrobenzeno (DNB), dinitrofenol (DNF) e trinitrofenol (TNF). Estes compostos são separados do MNB através de uma extracção líquida reactiva em meio alcalino.

Para a purificação do MNB na fábrica de nitração da CUF-QI são usados dois lavadores que operam em contracorrente (cada lavador é composto por um misturador e um decantador). Como agente alcalino é utilizada amónia que promove a extracção ao reagir com os nitrofenóis para formar sais solúveis em água. Normalmente na fábrica as eficiências de remoção do DNF e do TNF são 0.57 e 0.43, respectivamente. Neste trabalho avaliaram-se as condições operatórias do segundo lavador alcalino do MNB. Os objectivos foram avaliar o efeito de três condições operatórias na extracção dos nitrofenóis: temperatura do processo de lavagem, razão mássica solvente/MNB (R) e composição do solvente.

Os ensaios a diferentes temperaturas mostraram que a transferência dos nitrofenóis para a fase aquosa é favorecida com o abaixamento da temperatura: uma diminuição de 45% na temperatura face ao valor nominal de operação, traduziu-se num aumento da eficiência da lavagem de 0.13 e 0.05 para o DNF e o TNF, respectivamente (comparando com as condições da fábrica). Estudos de variação da razão mássica R (solvente/MNB) mostraram, à escala laboratorial e industrial, que a purificação do MNB pode ser efetuada só com o 20% do caudal de solvente usado actualmente na fábrica, sem causar impacto na eficiência dos lavadores.

Neste trabalho foi confirmado que o amónio tem diferentes efeitos sobre a extracção dos nitrofenóis: promove a transferência do DNF e diminui a extracção do TNF. Também foi demonstrado que o carbonato de amónio promove a extracção do DNF sempre que a concentração do amónio no solvente seja baixa

(aproximadamente 0.03). No entanto, se a concentração de NH_4^+ estiver na gama usada na fábrica (0.4), o carbonato de amónio diminui a eficiência de lavagem dos nitrofenóis devido ao efeito do ião comum.

Ao lavar o MNB sem agente alcalino, ou seja, aproximadamente em condições neutras, verificou-se que a eficiência da lavagem do TNF foi mais elevada que a do DNP, no entanto, em condições alcalinas a tendência é contrária. Ao lavar o MNB com uma corrente neutra do processo, água do tanque de MNB final, e com uma razão R baixa (30 vezes menor que a R da fábrica) obtiveram-se eficiências de 0.68 e 0.79 para o DNF e TNF. Na sequência deste trabalho sugere-se que na secção de lavagem de MNB da fábrica de nitração de CUF-QI o primeiro lavador funcione com o solvente actual, onde é adicionada a amónia, e o segundo lavador opere em condições neutras.

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List of symbols and abbreviations

$C_{j,in}$: Weight fraction of the compound j in organic phase of washer inlet stream (m/m)

$C_{j,out}$: Weight fraction of the compound j in organic phase of washer outlet stream (m/m)

DNP: 2,4-dinitrophenol

K_j : Partition coefficient of the compound j

MNB: Mononitrobenzene

MNB_A : MNB coming from the acidic wash

MNB_1 : MNB outlet of first washer, inlet to the second washer.

MNB_2 : MNB outlet of second washer

MNB_3 : stripped MNB; inlet to MNB tank

MNB_4 : Final MNB

NPs: Nitrophenols

pK_a : Acid dissociation constant, logarithm

R : Weight ratio between solvent and MNB in the washers

S_F : Fresh aqueous solvent with ammonium

S_1 : Solvent inlet to the first washer

S_2 : Solvent inlet to the second washer

S_3 : Water from the MNB tank

S_{purge} : Solvent purge for incineration.

TNP: Trinitrophenol.

$w_{s,ext}$: weight fraction of solute in the extract phase (m/m)

$w_{s,raf}$: weight fraction of solute in the raffinate phase (m/m)

η_j : Washing efficiency of the compound j .

CHAPTER 1

INTRODUCTION

The separation of components in a homogenous liquid mixture is a common problem in the chemical processing industry. Liquid-liquid extraction is a very important method since it allows the separation of compounds in such liquid mixtures (Laddha and Degalees, 1992). The basis of this process for separating components in solution is their distribution coefficients between two phases: gas-liquid or liquid-liquid. This study is focused on the extraction between two immiscible liquid phases and can also simply be referred to as liquid extraction or solvent extraction. This is a mass transfer process from one liquid phase into a second immiscible liquid phase (Perry, 1997).

Liquid-liquid extraction technique is used for separating and purifying organic compounds of commercial importance at large scale. According to Perry (1997) the first registered application of solvent extraction is probably that of Goering in 1883 for concentrating acetic acid from dilute solutions by extraction with a solvent such as ethyl acetate. However, a large scale application of this technique happened first in the petroleum industry with the separation of aromatic compounds from aliphatic compounds (Laddha and Degalees, 1992). Dow Chemical Company developed a process using a mixture of glycols and water as solvent, for achieving efficient separation of aromatic compounds from a mixture of other hydrocarbons (Fenske and Broughton, 1955).

Liquid extraction has also been used extensively in the coal tar industry, in the refining of vegetable oils, animal fats and purification of pharmaceutical and natural products (Alders, 1959). Solvent extraction is being used advantageously for the recovery of pollutant chemicals, such as phenols from effluent streams of petroleum cracking plants which are recovered using light catalytic oil (Marcé, 2000).

Mass transfer operations usually rely upon the uneven distribution of the substances to be separated between two immiscible phases. It involves an equilibrium spontaneously reached in a multiphase system; confining the

attention to one of the phases and considering that chemical potential of any substance is related to its concentration, equilibrium implies changes that lead to an uniform concentration of each component throughout the phase. This migration of substances, that leads to uniform composition, is the phenomenon of diffusion which is enormously accelerated by stirring, or otherwise mechanically agitating the liquid (Treybal, 1963).

According to Perry (1997), liquid extraction has demonstrated to be really useful in the following fields:

- Separation of close boiling point liquids;
- Separation of liquids of poor relative volatility;
- Substitute for high vacuum distillation of mixtures whose boiling points are very high;
- Substitute for expensive evaporation;
- Substitute for fractional crystallization;
- Separation of heat sensitive substances (particularly important in biochemical industry);
- Separation of mixtures that form azeotropes;

According to Laddha and Degalees (1992), the liquid-liquid extraction operation consists in the following steps:

1. Intimate contact of the solvent with the solution containing the component to be extracted, the solute, which will be transferred from the solution to the solvent.
2. Separation of the two immiscible phases.

In extraction operations, the solution from which the solute is to be removed is called the feed and the liquid used for extraction is the solvent. The solvent-rich product is called the extract, while the residual liquid from which most solute has been withdrawn is the raffinate (Sinha and Parameswar, 2012). The complete process may involve other separations such as distillation to recover the solvent from the extract and the raffinate phases.

Liquid extraction has an important application in the mononitrobenzene (MNB) production process. MNB is mostly used for producing aniline through its

hydrogenation. Aniline is an intermediate in methylenediphenyldiisocyanate (MDI) synthesis and the major demand drive for MDI is the polyurethane industry. The polyurethanes are used predominantly in foams for insulation (construction and automobile industry) and lately, especially in Asia, as synthetic leather and shoe soles (Lynch and Ryan, 2012). In Figure 1-1 molecular structure of MNB, aniline and MDI are represented.

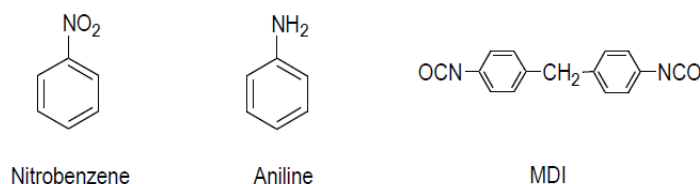


Figure 1-1.- Nitrobenzene, aniline and MDI molecules (Lynch and Ryan, 2012).

Side reactions during benzene nitration to produce MNB lead to dinitrophenol (DNP) and trinitrophenol (TNP) formation in concentrations that compromise MNB's specification. Dinitrobenzene (DNB) is formed as well during nitration, though its concentration is usually under 100 ppm in adiabatic technology (Lynch and Ryan, 2012). Reactors are operated with great excess of benzene, which consumes most of the nitric acid before significant amounts of DNB are formed. According to Quadros *et al.* (2004), the removal of byproducts from the MNB, mainly of nitrophenols (NPs), is demanded by the market. This study is focused on MNB purification by removal of nitrophenols. The crude MNB is purified in a two stages washing process: one acidic (for removing sulfuric and nitric acid) and the other one alkaline (for removing nitrophenols in a liquid-liquid extraction) (Boyd *et al.*, 2001). The alkaline washing is usually carried out countercurrently in a chain of washers. This work is focused on the alkaline washing process of MNB and aims at assessing the influence of operating conditions upon the efficiency of the extraction of NPs from the crude MNB. This work will mainly focus on the weight ratio between the solvent and MNB to be used in the washers, composition of the extraction solvent and the washing temperature.

The study was carried out at the nitration plant of the company "CUF-Químicos Industriais" (CUF-QI) located in Estarreja, Portugal. At CUF-QI,

MNB's purification is carried out by means of a reactive extraction in alkaline medium using a chain of two washers. This technique is routine in the industry, however, not thoroughly studied in MNB production process. Nitrophenols's presence in the hydrogenation of the MNB has negative impact in the aniline synthesis: it reduces the process yield, decreases selectivity and promotes the contamination of catalysts (Lynch and Ryan, 2012). Purification of the crude MNB is required, thus, the relevance of the washing process at industrial scale is clear and studying and optimizing of the process becomes pertinent.

Cardoso (2013) studied the solvent composition in the extraction process in the first washer at CUF-QI. It was demonstrated that the ammonia improves the washing efficiency of DNP while decreasing the TNP's one. This work continues the previous study, focusing now on the second washer and assessing the influence of other operating variables such as temperature and amount of solvent used upon the extraction efficiency.

CHAPTER 2

MNB PRODUCTION

2.1 History and market

Mononitrobenzene is produced by nitration of benzene using mixed acid, a solution of nitric acid and sulfuric acid. A key performance characteristic of mixed acid nitration process is the amount and type of nitro-hydroxy-aromatic byproducts formed. Nitration of benzene produces nitrophenols, nitration of toluene produces nitroresols and nitroxylenols are obtained during the nitration of xylene. Most nitrated aromatics are subsequently hydrogenated to their corresponding amine (in the case of CUF-QI, MNB is hydrogenated leading to aniline). It is common practice to remove nitro-hydroxy-aromatic byproducts from the nitroaromatic product, as these compounds have negative influence upon the hydrogenation catalyst performance (Boyd *et al.*, 2001).

According to Guenkel (2013), the first adiabatic MNB plant began operating in 1979, in USA. Since then, MNB production increased from 1 million metric tons per year (MTPY) to 10 million MTPY in 2012. On the other hand, technology of mononitrobenzene's production evolved from isothermal to adiabatic, which is safer, more reliable and with higher yield.

Mononitrobenzene is a main reagent in the MDI-based polyurethanes production. MDI's world production was 0.4 million MTPY in 1988 and, according to Guenkel (2013), it was 6 million MTPY in 2013 and can be over 10 million MTPY by 2015 (MDI capacity estimates should be viewed only as "best guesses" since producers keep records confidential). Such growth of MDI production could only be achieved by the construction of new MNB plants. According to Lynch and Ryan (2012), much of the growth will take place in China. In 2010 the share of MNB production worldwide was about 25% for the USA, 30% for Europe, 25% for China and 20% for the rest of the world. China's share will probably exceed 50% in the next three years.

2.2 Benzene nitration process

Nitrobenzene production relies upon the reaction of benzene with the nitronium ion (NO_2^+). Benzene is mixed with a solution of nitric acid and sulfuric acid, such solution is usually referred as nitrating acid or mix acid. This liquid-liquid reaction is well known and the technology around MNB production is already mature according to Guenkel *et al.* (1994). The mechanism of nitration is represented in Equation 2-1 and Figure 2-1.

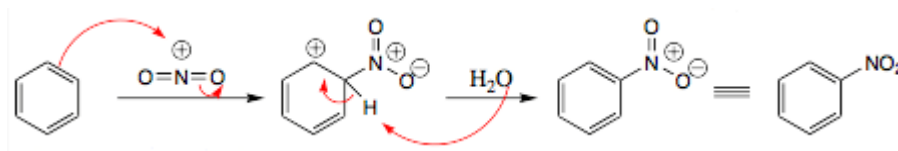
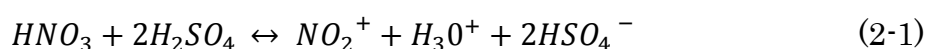
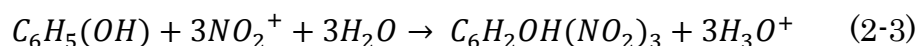
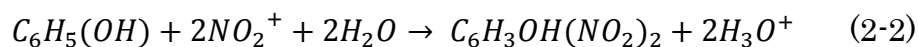


Figure 2-1.- Benzene nitration mechanism (Guenkel *et al.*, 1994).

Byproducts formed in nitrobenzene plants are mainly dinitrobenzene (DNB), dinitrophenol (DNP) and trinitrophenol (TNP). All of them with better affinity to the organic phase than to the acid phase. Quadros *et al.* (2004) refer that DNP and TNP reach mass percentages of 0.1% and 0.5% of the total MNB produced. In the reactors, diluted sulfuric acid is the main component of the aqueous phase. Lynch and Ryan (2012) state that nitrophenols can be formed when the nitronium ion becomes attached to the benzene ring through one of its oxygen atoms, instead of to its nitrogen atom, leading to phenol. The phenol then reacts with nitric acid to form nitrophenol, which can be further nitrated to dinitrophenol and trinitrophenol (picric acid). On the other hand, Burns and Ramshaw (1999) state that undissociated nitric acid that transfers to the organic phase might oxidize the benzene to form phenol. Phenol reactions, that lead to 2,4-dinitrophenol and trinitrophenol formation, are presented in Equation 2-2

and 2-3. Quadros *et al.* (2004) indicate that such reactions are instantaneous, once phenol is formed.



Benzene nitration reaction is exothermic, releasing about 113 kJ. mol⁻¹ (Lynch and Ryan, 2012). Sulfuric acid concentration in the mix acid is a key parameter in the benzene nitration. It promotes the formation of the nitronium ion and absorbs the water formed in the reaction. In other words, it is the catalyst of the reaction and does not enter in the stoichiometry. The mixed acid could have different compositions. Lynch and Ryan (2012) state that a sulfuric acid concentration of 65% in weight, 4% of nitric acid are desirable in the mixed acid.

Reaction is carried out in one or more continuous adiabatic reactors (nitration train) typically at temperatures between 80 to 150 °C with excess benzene to make sure the complete nitric acid conversion. The large volume of sulphuric acid helps to control the temperature in the nitrators by absorbing the heat of the reaction. The spent acid and benzene are fed at 50°C - 90°C (Guenkel, 2013).

The first processes developed used continuous stirred nitrators in series, while the second-generation technology, developed in 1988, uses plug flow nitrators. Most of the old isothermal plants have been shut down (Guenkel, 2013). Since the mixture is heterogeneous (organic and aqueous phases), a good dispersion is needed to guarantee high conversion of nitric acid and benzene (Santos, 2005).

After the reactors, the liquid-liquid mixture goes to a decanter where the two phases are separated. The organic phase goes to the purification stage, then, after being washed, the excess of benzene is stripped to produce the final MNB. Benzene is recycled back to the process. Figure 2-2 shows a simplified diagram of the benzene nitration process.

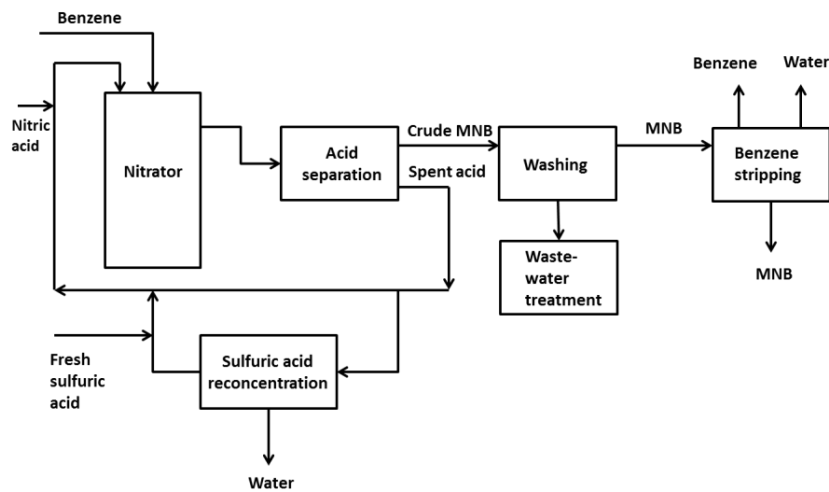


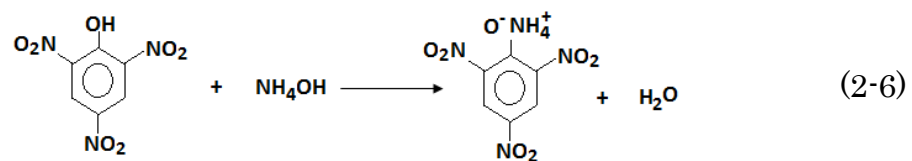
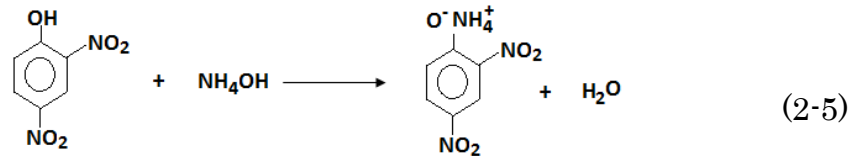
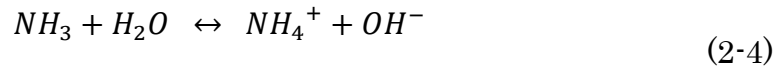
Figure 2-2.- Simplified industrial benzene nitration process (Ullmann, 2002).

2.3 Mononitrobenzene washing

After reaction, the spent acid and the crude nitrobenzene are usually separated using gravity settlers. This is done with high efficiency since MNB has poor solubility in water and in sulfuric acid. Centrifugal separation is also used in some plant designs. The spent acid is then reconcentrated and recycled (sulfuric acid reconcentration) (Lynch and Ryan, 2012). The organic phase follows to the washing process which includes two steps (Boyd *et al.*, 2001):

1. Acidic washing: The crude MNB from nitration is mixed with water to remove mineral acids, mainly sulfuric and nitric acids. Either fresh or process water can be used. The two phases are then allowed to separate.
2. Alkaline washing: Crude MNB from the acidic washing is sent to a multistage and countercurrent washing process. Under alkaline conditions, nitrophenols are extracted into the aqueous phase. The alkali source is commonly sodium hydroxide. When the effluent of the alkaline washing is incinerated, as in CUF-QI, ammonia solution is used instead of sodium hydroxide as no ash is produced from combustion. Extraction is possible since the nitro-hydroxy-aromatic salts formed have high solubility in water. The ammonia (NH_3) added is a base, receives a proton and forms

ammonium (NH_4^+), according to reaction in Equation 2-4. Then, NH_4^+ reacts with DNP and TNP to form salts (Equations 2-5 and 2-6).



Liquid-liquid extraction or washing, may be operated batchwise or continuously. The operation of mixing and separation of phases may be repeated if required (when several stages are needed, continuous flow becomes a better option). Representative types of equipment are mixer-settlers, centrifugal extractors and vertical towers of various kinds that operate by gravity flow or agitated tower extractors (McCabe, 1993).

The mixture of liquids leaving a mixer is a dispersion which must be settled, allowed to coalesce and separate into its liquid phases so they can be withdrawn separately from the stage. Unstable dispersions usually have drop diameters of about 1 mm or larger, and settle rapidly. Stable dispersions, or emulsions, are generally characterized by droplet diameters of about 1 μm or less (API, 1990). The unstable dispersions are preferred in liquid-liquid extraction operations and chemical-reaction systems involving two liquid phases that need to be separated (Perry, 1997).

At CUF-QI, MNB alkaline washing process is carried out in two alkaline washers with countercurrent flow. Each washer is considered as the combination of one static mixer and one decanter. In Figure 2-3 is illustrated a simplified diagram of the MNB purification process in the plant. The outlet stream of the

acidic washing (MNB_A) is mixed with the solvent stream S_1 , the phase separation occurs in the decanter 1 from where the organic phase (MNB_1) is directed to the second washer while the aqueous phase is recirculated to the first mixer. Same procedure is carried out in the second washer where a fresh stream of ammonia aqueous solution (S_F) is fed. A fraction of the second washer's solvent (S_2) goes to the first washer. A purge stream of solvent (S_{Purge}) is necessary to control the accumulation of the nitrophenols in the washing system.

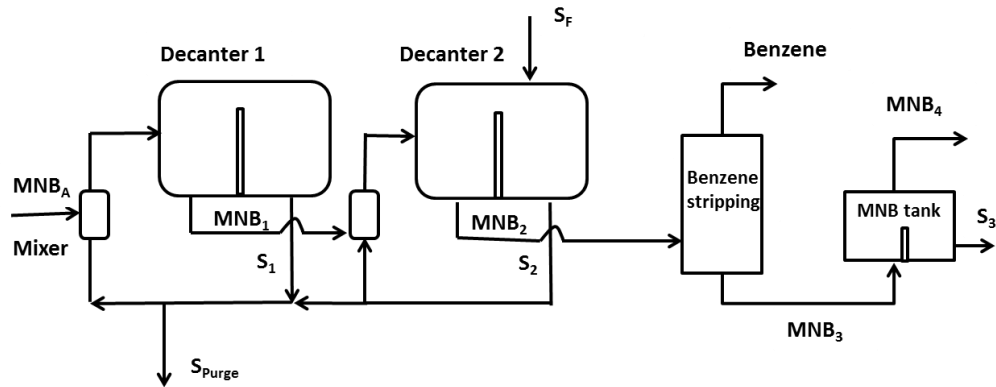


Figure 2-3.- Diagram of MNB's washing in the plant.

The stripped MNB (MNB_3) goes to a tank where the separation of the remaining water from the MNB takes place. Such water (S_3) has low concentrations of both nitrophenols and alkali agent.

CHAPTER 3

FUNDAMENTALS of LIQUID-LIQUID EXTRACTION

3.1 Ternary Equilibrium

The separation of components by liquid-liquid extraction depends primarily on the thermodynamic partition equilibrium of those components between the two liquid phases. Since two immiscible liquid phases are used, the thermodynamic equilibrium involves dealing with non-ideal solutions. In the simplest separation example, a feed F contains a solute that is to be transferred into an extraction solvent, S (Perry, 1997).

Systems containing four or more components, like the one in this study, become difficult to display in graphics (a common technique used to study phase equilibrium). Therefore in this chapter only three component liquid mixtures will be approached to serve as basic explanation of the phenomena under consideration. Data needed for the study are best represented by triangular diagrams, which are of two types: equilateral triangle and right-angled triangle, being the equilateral the most common (Laddha and Degalees, 1992). In an equilateral triangle, like the one shown in Figure 3-1, the perpendicular distances from any point within the triangle to the three sides represent the percentages or fractions of the three components (ternary systems). In Figure 3-1 the three apexes A , B and C represent 100% A , 100% B and 100% C respectively (McCabe, 1993).

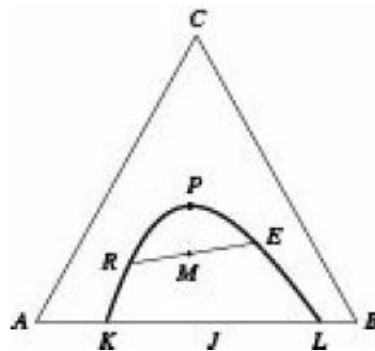


Figure 3-1.- System of 3 liquids, one pair partially miscible (McCabe, 1993).

Ternary liquid equilibrium systems may be of different types. In practice, the most frequent are systems with one pair of components partially miscible. In the equilibrium system shown in the triangular diagram in Figure 3-1 the two pairs of liquids B-C and C-A are completely miscible, while A and B are miscible only to a limited extent giving rise to two saturated solutions at K (A-rich) and L (B-rich). A binary mixture J, anywhere between K and L, will separate into two immiscible liquid phases of compositions K and L. Curve KRPEL is the bimodal solubility curve which shows the change in solubilities of A-rich and B-rich phases upon addition of C. Any mixture outside this curve is a single phase homogeneous liquid and hence unsuitable for extraction. Any mixture within this curve, such as M, will split into two saturated liquid phases R and E. The line RE is a tie line passing through M. There may be an infinite number of such tie lines (Sinha and Parameswar, 2012).

The tie lines are rarely parallel to an axis or between them, their slopes change slowly in one direction. Point P, where the A-rich and B-rich solubility curves converge, is known as the plait point (Perry, 1997). In Figure 3-1, the A-B mixture is meant to be separated using C as solvent to extract B; the tie line is tilted to the right (positive slope). This suggests that most of B could be extracted from A's phase using only a moderate amount of solvent C. If the tie lines were horizontal or tilted to the left, extraction would still be possible but more solvent would have to be used, since the final extract would not be as rich in B.

Triangular diagrams, as the in of Figure 3-1, are obtained for a given temperature, an operating parameter with a strong influence upon liquid-liquid equilibrium. In fact, there is a critical solution temperature above which A and B are completely miscible. Therefore, extraction must be carried out below such temperature (McCabe, 1993).

As mentioned before, study of equilibrium of systems with more than four components is complex and requires thorough laboratory experiments and modeling. In this study, the mixture contains mainly: water, benzene, MNB, DNP, TNP and ammonia. Liquid-liquid extraction in the MNB industry is possible due the formation of aqueous salts (nitrophenols-ammonium), leading to a reactive separation. According to Maurer (1996), data about the fundamental

relations governing phase equilibria in chemical reactive mixtures are scarce. Modeling of phase equilibria involves dealing with the effects of intermolecular forces upon macroscopic properties such as Gibbs energy, chemical potential, fugacity and activity. Detailed study of those properties is not in the frame of the present work.

3.2 Equilibrium partition ratios

Phase equilibrium is often characterized by partition coefficients, K , describing the distribution of solutes between the two immiscible phases (Wagner, 1999). The ratio of the weight fractions of solute in the extract phase ($w_{s,ext}$) and in the raffinate phase ($w_{s,raf}$) at equilibrium is also called the partition ratio K_s ; it is represented in Equation 3.1 where s stands for the solute to be extracted, in this case, DNP or TNP.

$$K_s = \frac{w_{s,ext}}{w_{s,raf}} \quad (3.1)$$

A partition ratio or coefficient is an empirical unit of measurement that attempts to account for various chemical and physical mechanisms that control the distribution of compounds between different phases (Wagner, 1999). In other words, it depends on the physical and chemical properties of the compounds to be transferred, properties of the liquid phases and temperature (Perry, 1997).

3.3 Solubility and acidity

Extraction of nitrophenols from the crude MNB is achievable since the solubility of the NP's salts in the aqueous and in the organic phases is different, being more soluble in the aqueous phase. Thus, it is important to take into account the factors that control the solubility of the compounds in this process.

Solubility may be defined as the maximum concentration of a substance that may be completely dissolved in a given solvent, at a given temperature and pressure; depending mainly on the polarity of the solute and on the solvent (Perry, 1997). DNP and TNP are partially polar molecules and when forming salts with an alkaline agent, their polarity increases, becoming more soluble in a polar solvent (as water for example). The relevance of understanding polarity is remarked by González and Requejo (2013), who suggest that solubility of benzene (an apolar molecule) increases in ionic liquids, when the polarity of the solvent decreases.

The solubility of any substance is a function of temperature (McCabe, 1993). The dissolution process is endothermic for most chemical compounds. For these substances, an increase in temperature leads to an increase in solubility. Liquids which form a homogenous system when mixed in any proportion are miscible (eg. water and ethanol). MNB and water are miscible to a certain extent; at a temperature lower than 60 °C, water solubility in MNB registers a strong decrease (CUF, 1998).

The dissociation constant (K_a) of a specific compound measures the separation of its molecule into two ions. It is often defined as the logarithm of the dissociation constant ($pK_a = -\log K_a$) (Guetta, 2006). Values of pK_a for DNP and TNP, the acids to be extracted from MNB, are 4.09 and 0.42 respectively (Marcé, 2000). It means that trinitrophenol will dissociate more easily, thus, in presence of an alkaline agent it will form a salt faster than dinitrophenol.

3.4 Common-ion effect

When a soluble salt, eg A^+C^- , is added to a solution of another salt (A^+B^-) containing a common ion (A^+), the dissociation of AB is inhibited. By the addition of the salt, AC , the concentration of A^+ increases (Guetta, 2006). Therefore, according to Le Chatelier's principle, the equilibrium will shift to the left in the Equation 3.2, thereby decreasing the concentration of A^+ ions in the

solution. So, the degree of dissolution of AB will be reduced and its precipitation will occur.



Common-ion effect could be described as the reduction in the solubility of a salt by the addition of a common-ion (Walter, 1981). Solubility of a salt changes, depending upon the presence or absence of a common-ion. The common-ion present in a solution decreases the solubility of a given compound, that will precipitate.

At CUF's nitration plant, ammonium carbonate ((NH₄)₂CO₃) has been detected in the washing section. This compound might be produced by reaction with carbon dioxide, a product of the oxidation of organic compounds during the nitration stage. Since in this plant an ammonia solution is used as the alkaline washing solvent for MNB, ammonium carbonate could have a negative impact on the extraction process. The ammonia (NH₃) added leads to ammonium (NH₄⁺), which reacts with the nitrophenols to form DNP and TNP aqueous salts enhancing their extraction from the MNB. As (NH₄)₂CO₃ is a salt, in an aqueous solution it dissociates adding NH₄⁺ and CO₃⁻² ions to the aqueous phase. According to the Le Chatelier's principle, excess of NH₄⁺ in the solution promotes its consumption, decreasing the dissociation of the nitrophenol salts (that will precipitate) and affecting their extraction in a negative way.

CHAPTER 4

MATERIALS AND METHODS

4.1 Streams characterization

Experiments in the laboratory were meant to simulate the washing process of the second washer in the MNB plant, thus, it was necessary to collect samples of the streams MNB_1 and S_2 (Figure 2-3). For a better understanding of the washing process and the variables that influence the nitrophenols extraction process, it is important to characterize other streams in the flow diagram in Figure 2-3. Samples of these streams were also collected and analyzed in the laboratory and their compositions are shown in Table A.1 in Appendix A. As referred in the introduction, this study is mainly focused on the optimization of the second washer (mixer and decanter 2) through assessment of its operating conditions.

The MNB_1 sample, in particular, required special attention since it has two phases: aqueous and organic and precipitation of solids had been previously observed in such mixture. In order to work with adequate and representative samples, before defining the experimental procedures it was necessary to study the best method to store and deal with MNB_1 samples.

4.1.1 Confirming nitrophenols concentration in a sample of MNB_1 over time

The influence of the time lag between collecting samples of MNB at outlet of the first washer and their analysis had not been assessed before. This is relevant for calculating the efficiency of the industrial washing process and to guarantee the use of representative samples in the laboratory experiments. A first experiment was carried out with the objective of evaluating the influence of time lag and temperature drop upon dinitrophenol and trinitrophenol concentration in the MNB_1 sample.

The sample of MNB₁ (approximately 1 liter) was collected on March 20th 2014 (10:30 am), and its normalized temperature was 0.85. A timer was set at sampling time. The vase (A) with MNB₁ was stored in the laboratory at room temperature. Samples of MNB₁ of approximately 2 grams were transferred to glass tubes (B) at different times, while registering the temperature. Pipettes were used for collecting and transferring the samples from A to B, while trying to always collect it at half of height of liquid in vessel A. Concentrations of DNP and TNP were measured by High Pressure Liquid Chromatography- HPLC (see section 4.6.1). The normalized concentrations of DNP and TNP concentrations in the MNB₁ are plot in Figure 4-1.

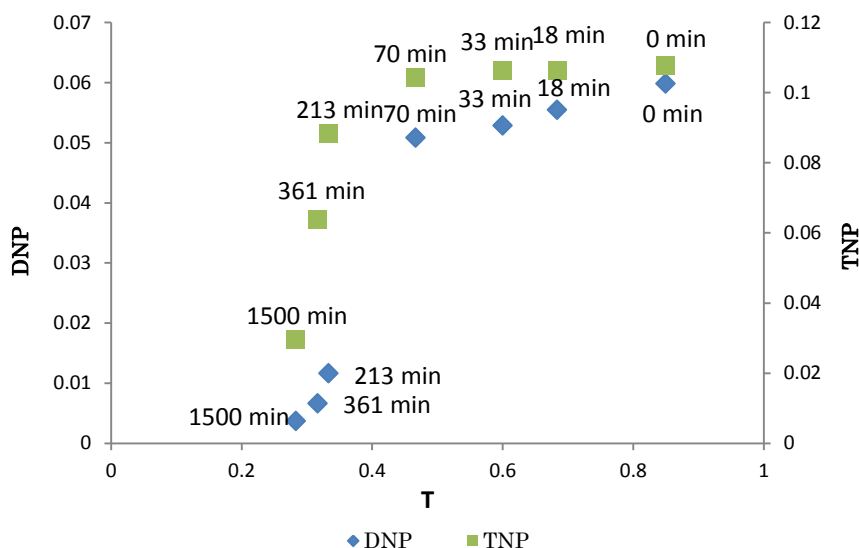


Figure 4-1.-Variation of nitrophenols concentration in MNB with time and normalized temperature.

Figure 4-1 shows that concentration of DNP and TNP decrease with time and as the samples cool down. During the first hour, decrease in NP's is smooth. After 70 minutes, it was registered precipitation and deposition of nitrophenols in the bottom of the vase A; the decrease in concentration of both NPs was sharp. This may be a consequence of nucleation phenomena happening and the rate of formation of crystals becoming higher. Figure B.1 in the Appendix B, show in

pictures the changes occurred to the sample due the time progress and thus, temperature decrease.

It is clear that DNP diminishes faster than TNP. This phenomenon may be caused by the differences in molecular structure between DNP and TNP, leading to an easier crystallization and precipitation of DNP. Moreover, when collected at the inlet of the second washer, the MNB₁ sample was a yellow liquid with emulsion's appearance. Two hours later there were two liquid phases: one clear, the other turbid, and solid crystals in the bottom of the vase.

For HPLC analysis just some millimeters of the sample are collected and regardless when the analysis is carried out, this sample should have the same composition as the one collected at washer inlet. Therefore, it is important to establish a standard procedure that ensures that all analysis are carried out at the same conditions and using a representative sample.

Although it was first planned to use the same MNB₁ sample for all experiments (a procedure aiming at reducing the variability of conditions) the results in Figure 4-1 confirm precipitation of NPs and change in composition with time and temperature. Therefore, for each experiment in this work different samples were collected in the plant, directly into glass tubes of 50 ml capacity previously weighted. The experiments were carried out from April to June 2014.

4.2 Reagents

In the experiments and analysis in the laboratory, besides the samples of streams MNB₁, MNB₂, S₂ and S₃ collected in the plant, the following chemical compounds and solutions were used:

- NH₃ aqueous solution (25% w/w). Sigma – Aldrich.
- (NH₄)₂CO₃ solid, Merck.
- NaOH (1 mol/L), Merck.
- HCl (1 mol/L and 0.05 mol/L), Merck.
- CaCl₂ aqueous solution (20 % w/w), Merck.

- Dihydrogen phosphate, Merck, >99.5%
- Demineralized water.

4.3 Mononitrobenzene washing at laboratory scale

Mononitrobenzene washing at laboratory scale was carried out in glass tubes, of 50 ml capacity. Samples of MNB were collected in the plant from washer's inlet streams (MNB_A and MNB₁) straight into the glass tubes. In each tube the MNB collected was mixed with a certain amount of solvent: washing water from the plant (S₂ in experiments 1 to 11), water from the MNB tank (S₃) or fresh water (experiments 12 to 14). Weight ratio R was defined as the relation between the mass of solvent and the mass of MNB to be washed (solvent/MNB).

For carrying out the process at the selected temperature (depending on experiment), tubes were immersed in a thermostated water bath (Model DC5, from Haake), until steady temperature was reached. Then, the tubes were agitated for one minute and submerged in the water bath at the same temperature for 5 minutes for settling

After the extraction, using a pipette, approximately 2 ml of the organic phase were transferred to another tube and mixed with NaOH, 1 M, to prepare the sample for High Pressure Liquid Chromatography analysis to measure the nitrophenols's concentrations (see section 4.6.1).

Washing efficiency, η_j , was the main parameter used for assessing the process performance at plant and laboratory. Equation 4.1 was used to calculate the extraction efficiency, where "c_j" is either DNP or TNP mass concentration in the MNB.

$$\eta_j = \frac{c_{j,in} - c_{j,out}}{c_{j,in}} \quad (4.1)$$

Since the washing at the laboratory was carried out batch wise (while washers in the plant are continuous), it was necessary to demonstrate that the method used reflects the industrial process. To achieve this, each experiment included a control tube: a sample of MNB₁ washed at same conditions as in the plant (same solvent composition, same R ratio and temperature). Analysis of the inlet and outlet samples of MNB allowed calculating the efficiency of washing in the plant. Washing efficiencies in the control tube and in the plant were in the same range for all experiments. This means that the washing method carried out at laboratory scale fits with the industrial process.

In each experiment, a particular operating parameter was assessed, the others remaining constant. Five levels were tested in each experiment, 6 tubes were tied together (5 tubes for different washing conditions plus the control tube). With this procedure, in each experiment all tubes had the same conditions of agitation, temperature and settling. Figure 4-2 shows the model implemented.



Figure 4-2.- Arrangement for MNB washing in the laboratory.

4.4 Reducing the washing ratio between solvent and MNB in the plant

In the tests at the plant, samples of the inlet and outlet streams of the washer were collected before changing operating conditions, to analyze the composition of the organic and aqueous phases of these streams. Then, in order to change the

solvent/MNB weight ratio R , the flow rate of stream S_1 (experiment 8) or S_2 (experiments 5 and 6) was reduced according to the set point value for R . Approximately one hour elapsed before sampling, allowing steady state to be reached again in the plant.

4.5 Changing the concentration of ammonium and ammonium carbonate in the solvent

Assessing the influence of the ammonium and ammonium carbonate upon washing efficiency (section 5.3) required the change of their concentrations in the solvent used in the washing. In the laboratory, a sample of S_2 (approximately 600 ml) was heated in a heating plate (Thermolyne, Model Cicamarec 2), at a temperature of 1.33 promoting NH_3 and $(\text{NH}_4)_2\text{CO}_3$ evaporation until a concentration of 0.031 was reached for the ammonium. On the other hand, $(\text{NH}_4)_2\text{CO}_3$ in the solution dissociates in its ions which evaporate, thus, after the heating, $(\text{NH}_4)_2\text{CO}_3$ had a very low and residuals concentration.

Samples of MNB_1 were added to glass tubes and mixed with the pre-heated S_2 . For varying the concentration of ammonium or ammonium carbonate (depending of the parameter tested), a given volume of NH_3 solution, 25% or a specific mass of solid $(\text{NH}_4)_2\text{CO}_3$ were added to the tube which was shaken to homogenize.

4.6 Analytical methods

4.6.1 Measuring nitrophenols's concentration

High Pressure Liquid Chromatography (HPLC) was used for measuring DNP and TNP concentrations. A chromatograph "Hitachi Elite LaChrom" was used. Chromatography involves a sample being dissolved in a mobile phase (in this case, potassium dihydrogen phosphate). The mobile phase is then forced through an immobile, immiscible stationary phase placed in a column. In this case, the column from Tecknokroma (Mediterranean sea 18.5 μm , 25 x 0.4 cm – reference

TR-010038) was packed with C18 silica. A component of the mixture which is quite soluble in the stationary phase (TNP) will take longer to travel through the column than a component which is not so soluble in the stationary phase, as it is the case of DNP. As a result of these differences in mobility, sample components will become separated from each other as they travel through the stationary phase. The compounds are identified by means of an ultraviolet detector included in the HPLC equipment (Knauer, model K-2501). The results of each analysis are given in a plot (miliabsorbance as function of time) where the compounds detected appear as picks. The area of each pick corresponds to the concentration of a given compound; such area is calculated by a software in the equipment (DataApex). In Figure C.1 in the Appendix C it is shown an example of a chromatogram obtained in experiment E-12. Figures C.2 and C.3, also in Appendix C, show the calibration curves that allowed the calculation of nitrophenols's concentrations by the software.

As the sample to be analyzed must be soluble in the potassium dihydrogen phosphate (a polar compound) NPs in the MNB (which is an apolar organic molecule) must be transferred to an aqueous phase. This is done by mixing MNB with sodium hydroxide (NaOH), which promotes the extraction of NPs to the aqueous phase with a very high efficiency (Boyd *et al.*, 2001). For this reason, after each washing experiment, a sample of washed MNB was transferred from the tube to another flask, mixed with NaOH (1 M) in excess (5 times in weight), agitated and centrifuged. Two phases are obtained (an aqueous one, now rich in NPs, and an organic phase). The aqueous phase was then analyzed in the HPLC to determinate DNP and TNP concentration.

When determining NPs concentration in the washing water samples (S₁, S₂ and S₃) NaOH was not added since extraction of the nitrophenols was not necessary (NPs were already in an aqueous phase); adequate dilution was reached with demineralized water.

4.6.2 Measuring ammonium concentration in the solvent

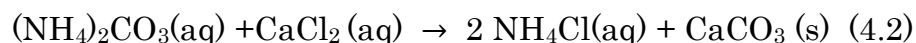
Information on NH_4^+ concentration in the washing solvent is of great importance since ammonium is the alkaline agent that promotes the nitrophenols's salts formation (Eq. 2.4 and 2.5) and its transfer to the aqueous phase. At CUF's plant, ammonium analysis follows a standard procedure: titration with hydrochloric acid using titration equipment from Metrohm, model 751 GPD, Titrino.

The equipment had already the titration curves programmed and was configured to titrate samples with high and low concentrations of NH_4^+ using HCl 0.05 and 1 mol/L, respectively. The results were obtained in weight percentage and the analysis took approximately 2 minutes for each sample.

4.6.3 Measuring ammonium carbonate concentration in the solvent

As referred in Chapter 3, it is known that the ammonium carbonate in the washing solvent influences the nitrophenols extraction. Thus, analysis of its concentration in the solvent must be performed.

Gravimetric analysis was carried out; for each test a sample of solvent was accurately weighted (approximately 20 grams) and mixed with calcium chloride in excess (CaCl_2 solution of 20 % w/w) showing a fast precipitation. The reaction is:



As observed in Equation 4.2, a double replacement reaction takes place.

The mixture was filtered under vacuum using a filter paper previously weighted. Then, the paper with the calcium carbonate was dried in a heating

plate until constant weight was reached. The paper with the dry solid was weighted again and the mass difference registered corresponds to the CaCO_3 precipitated. According to stoichiometry, the number of moles of CaCO_3 obtained is the same as the moles of $(\text{NH}_4)_2\text{CO}_3$ in the solution before reaction. Once the mass of ammonium carbonate was known it was possible to calculate the weight percentage of $(\text{NH}_4)_2\text{CO}_3$ in the solvent.

CHAPTER 5

RESULTS AND DISCUSSIONS

The results of the study on the influence of the different operating conditions upon the efficiency of the alkaline washing of nitrophenols in the crude mononitrobenzene will be presented in this chapter. The study was mainly focused on the performance of the second washer. The experiments were first carried out at bench scale. The promising results obtained allowed carrying out tests in the plant for validation during normal operation. The conditions tested in all the experiments are briefly described in Table 5-1.

Table 5-1.- Operating conditions in each experiment.

Experiment	Parameter tested	Scale
E-1	Temperature (R=1.32)	Laboratory
E-2	Temperature (R=0.26)	Laboratory
E-3	Weight ratio R (T=0.92)	Laboratory
E-4	Weight ratio R (T=0.5)	Laboratory
E-5 and E-6	Weight ratio R	Second washer- Plant
E-7	Weight ratio R for obtaining the minimum R (T=0.92)	Laboratory
E-8	Weight ratio R	First washer-Plant
E-9	Ammonium carbonate concentration in the solvent (solvent with $\text{NH}_3=0.03$)	Laboratory
E-10	Ammonium carbonate concentration in the solvent (solvent with $\text{NH}_3=0.5$)	Laboratory
E-11	Ammonium concentration in the solvent (solvent with $(\text{NH}_4)_2\text{CO}_3 \approx 0$).	Laboratory
E-12	Weight ratio R using demineralized water as solvent.	Laboratory
E-13 and E-14	Weight ratio R using water from the MNB's tank as solvent.	Laboratory

5.1 Temperature influence

In the first experiment (E-1) samples of MNB inlet stream in the second washer, MNB_1 , were washed with the solvent S_2 (Figure 2.3) using the same weight ratio between the solvent and MNB as in the plant ($R=1.32$). The extraction was carried out at different temperatures following the procedure described in section 4.3. Washing efficiencies, η (Eq. 4.1) and partition ratios, K (Eq. 3.1) obtained at different temperatures are shown in Figure 5-1a and 5-1b. In E-1, due to operational limitations, only 4 levels of temperature were tested (plus the control tube conditons).

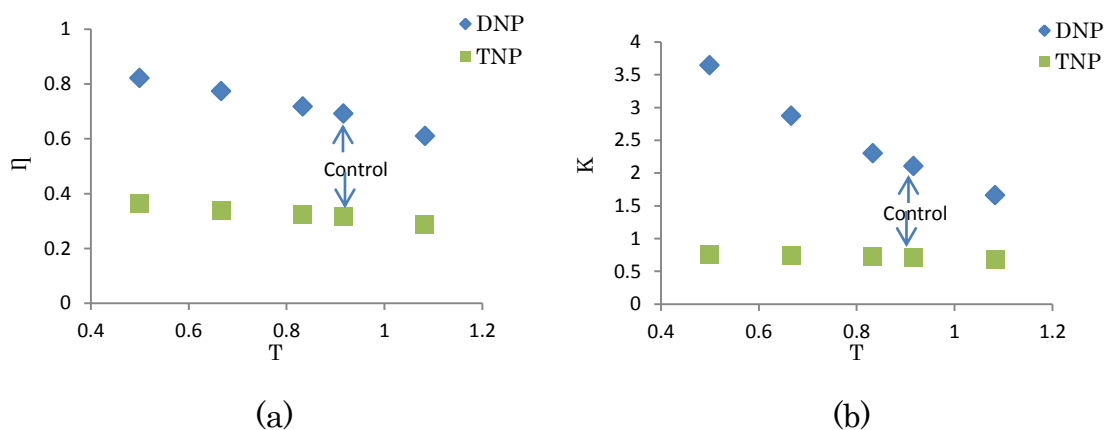


Figure 5-1. - Influence of temperature upon extraction of nitrophenols at $R=1.32$ (E-1): a) efficiency, b) partition ratio (S_2 composition: $NH_4^+=0.60$, $(NH_4)_2CO_3=0.45$, $DNP=1.69$, $TNP=3.36$).

Figure 5-1a shows a rise in the washing efficiency with the drop in temperature. Another important finding is that DNP extraction is more sensitive to temperature than TNP washing, confirming the results in Figure 4-1. Washing at lower temperature promoted the transfer of the byproducts to the aqueous phase which is an enhancement of the process when compared with the industrial operating conditions ($T=0.92$). For example, in Figure 5-1a, carrying out the washing at a temperature of 0.5, efficiencies of 0.82 and 0.36 were obtained for DNP and TNP, respectively, compared with the 0.69 and 0.31 at plant's temperature (control tube). In other words, extraction of DNP decreases

significantly as temperature rises. A possible explanation could be that solubility of the dinitrophenol in the organic phase improves with temperature (endothermic dissolution as referred by McCabe (1993)), due to this, transfer of DNP to the aqueous phase is diminished. This would increase the solubility difference of the byproducts in each phase, promoting better distribution coefficients for the DNP as is demonstrated in Figure 5-1b. A deeper study of nitrophenols's solubility in organic and aqueous media should be considered, to achieve a better understanding of the phenomena.

On the other hand, solubility of water in the MNB diminishes with decreasing temperature (CUF, 1998). Therefore, as temperature is lowered, the water in the organic phase transfers easily to the aqueous phase carrying the nitrophenols with it and improving the efficiency of the extraction. An important fact to take into account is that in the organic phase the water is dissolved and also dispersed (entrainment).

In a second experiment (E-2) NPs's extraction was tested varying temperature and setting ratio R at a lower value (0.26, which is 5 times less than plant's R). The day samples were collected, due to operation difficulties, it was not possible to collect an additional sample of MNB₁ to determine NPs concentration before extraction. Thus, washing efficiencies and partition ratios could not be calculated. For this reason in Figure 5-2 nitrophenols's concentration are shown instead of efficiencies, and the pattern allows discussing the results.

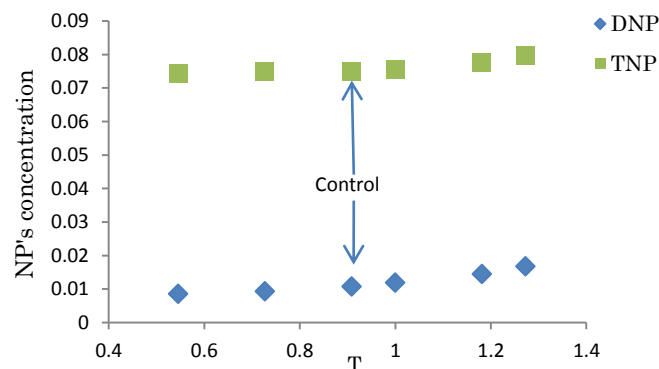


Figure 5-2. - Influence of temperature upon extraction of nitrophenols at R=0.26 (E-2) (S₂ composition: NH₄⁺=0.45, (NH₄)₂CO₃=0.40, DNP=1.59, TNP=3.37).

It is clear in Figure 5-2 that nitrophenols concentration in the organic phase increases with temperature rise; such results at low R, five times less than the R used at plant, match the ones of the first experiment. This suggests that the second washer could work with less solvent (S₂) and at a lower temperature, improving the efficiency of the process.

5.2 Influence of weight ratio R between solvent and MNB

The volume of solvent to be used is a key parameter of the washing process. Such solvent has NH₃ as alkaline agent. As can be seen in Figure 2-3, the water (S₁ and S₂) is recycled in the process, due to this it also contains (NH₄)₂CO₃, DNP and TNP. The objective of this third experiment (E-3) was to assess the influence of using lower volumes of water, or lower solvent/MNB weight ratios R, in the extraction. The final goal is to find out if the amount of aqueous solvent can be reduced without compromising the efficiency of the extraction.

Samples of MNB₁ and water S₂ were collected on March 26th (11:15 am) from inlet streams of the second washer. Following experimental procedures described in section 4.3, the washing process of MNB₁ at laboratory scale was carried out at different R values using S₂ as solvent. The R ratio used in the plant is 1.32. The mixture was kept at temperature of 0.92 (conditions at plant's washer). The results are presented in Figure 5-3a and Figure 5-3b.

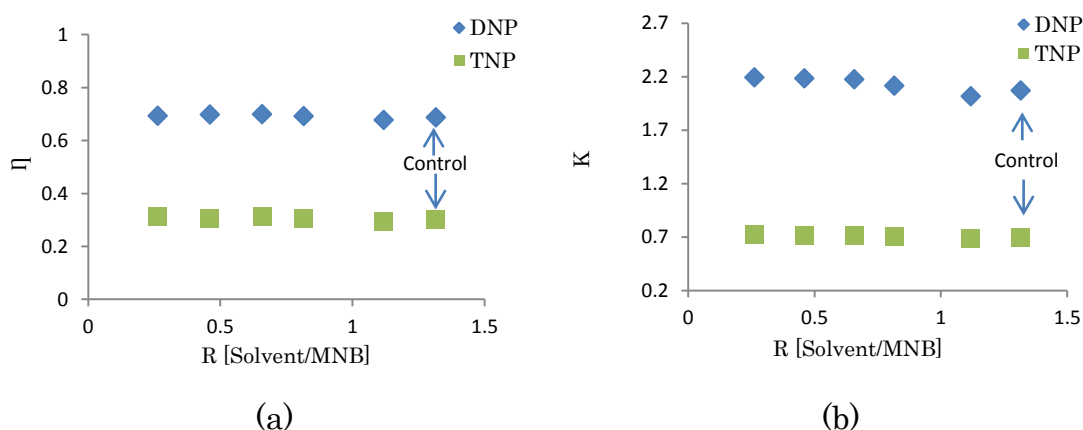


Figure 5-3. - Influence of washing ratio R upon extraction of nitrophenols at T=0.92 (E-3): a) efficiency, b) partition ratio (S₂ composition: NH₄⁺=0.6, (NH₄)₂CO₃=0.45, DNP=1.69, TNP=3.36).

As shown in Figure 5-3a, extraction efficiency does not change significantly with R. Even with a R of 0.26 it is possible to reach a separation very similar to the one obtained with the 1.32 ratio used in the plant. The volume of water to mix with the MNB guarantees the reaction of nitrophenols with NH_4^+ and the transfer of its salts to the aqueous phase. These results show that, at least at laboratory scale, it is possible to considerably reduce the mass of water used in the washing process.

Partition coefficients obtained are in the same range as the ones determined by Cardoso (2013) for the first washer. In Figure 5-3b it is clear that the partition coefficients are higher for DNP, which explains why its extraction has better efficiencies.

Washing ratio R did not influence the NPs mass transfer at $T=0.92$. Experiment E-4 was carried out to confirm this pattern at $T=0.5$, since experiments E-1 and E-2 demonstrated efficiencies improvement at lower temperatures. Experiments E-2 and E-4 were carried out the same day, and was not possible to collect a second sample of MNB_1 , washing efficiencies and partition ratios were not calculated. Though, the trend shown in Figure 5-4 allows analyzing the results. In E-4, the thermostated water bath was settled to $T=0.5$ and all tubes were immersed at the same time as detailed in section 4.3. Therefore, it was not possible to assess the control tube (that should be at plant's temperature, 0.92).

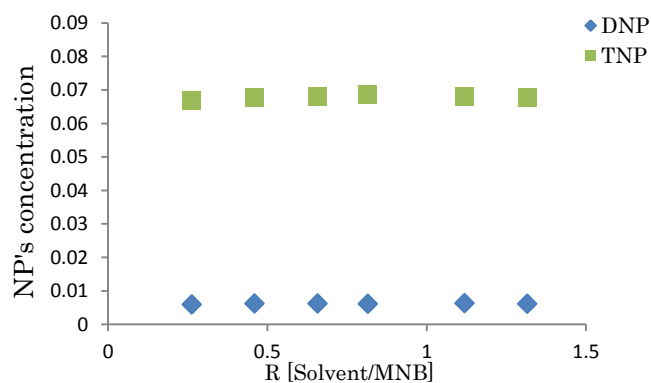


Figure 5-4. - Influence of washing ratio R upon extraction of nitrophenols at $T=0.5$ (E-4) (S_2 composition: $\text{NH}_4^+=0.45$, $(\text{NH}_4)_2\text{CO}_3=0.40$, DNP=1.59, TNP=3.37)

Washing with less solvent (lower R) did not influence the transfer of nitrophenols from the organic to the aqueous phase. Results of experiments E-1 to E-4 show that the washing process could be carried out at lower R without compromising the efficiency and even improving it, by operating at lower temperatures. Confirming these results at industrial scale would enable important improvements in the process. It is important to say that in experiment E-4, lower concentrations of NPs in the MNB were reached comparing to experiment E-3 where the washing was carried out at plant temperature, demonstrating again that the separation is enhanced at lower temperature.

In the plant, a change in temperature of the washing system is difficult to accomplish on account of energy integration between several units. On the other hand, a change in washing ratio R could be tested, and this was performed in experiment E-5.

During nitration plant operation, the inlet flow rate of water in the second washer, and therefore ratio R, were gradually reduced. Samples of outlet MNB stream, MNB₂, were collected and analyzed. The results of this experiment in the plant are plotted in Figure 5-5a and 5-5b.

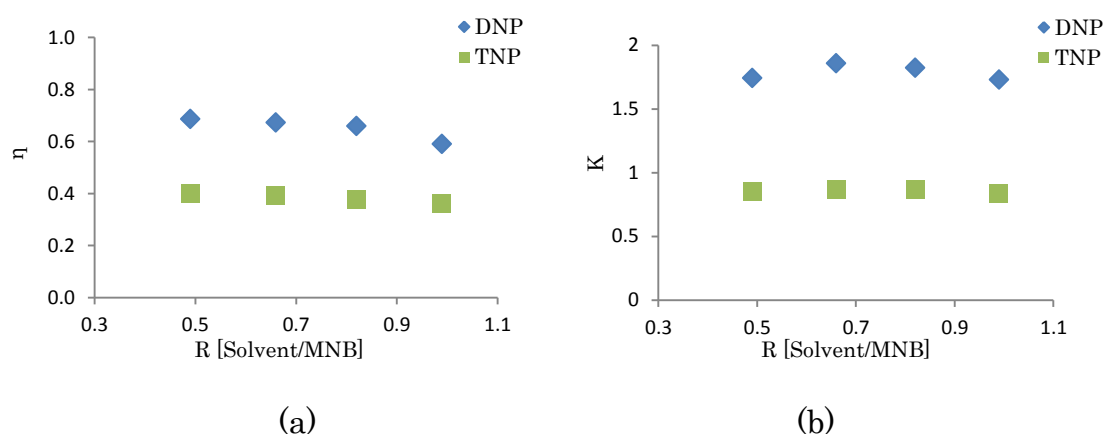


Figure 5-5. - Influence of reducing R ratio at plant's second washer (E-5) upon: a) efficiency, b) partition ratio (T=0.92; S₂ composition: NH₄⁺=0.43, (NH₄)₂CO₃=0.42, DNP=1.64, TNP=3.79).

Results of this experiment show that DNP and TNP washing efficiencies at plant are not influenced by the weight ratio R variation (in the range of R tested).

On average, the partition coefficients were 0.8 and 1.7 for DNP and TNP, respectively.

Performance of the washing system in the plant is not only influenced by temperature and the solvent/MNB ratio. The turbulence in the settling section is another parameter to take into account when discussing these results. A lower flow rate of the decanter inlet stream, due the S_2 diminution, is expected to lead to less turbulence in the vessel promoting a better separation of the phases. Another phenomenon to take into account is that mixing in the washing section is achieved in the static mixer before the decanter (Fig 2.3) and a decrease in flow rate could reduce as well the mixing efficiency. These factors, less turbulence in the decanter and less flow in the static mixer, seem to have no significant impact in the efficiency of the process for the range of R studied in experiment E-5.

To confirm the results, repetition of the experiment in the plant was carried out (E-6) on April 15th, following the procedures already described, and the results are presented in Figure 5-6a and Figure 5-6b.

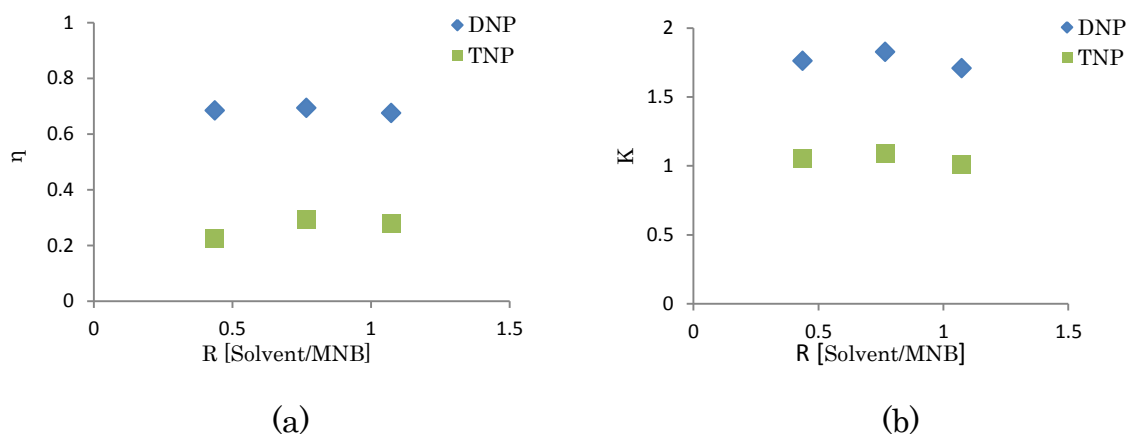


Figure 5-6. - Influence of decrease in ratio R at plant's second washer (E-6) upon: a) efficiency, b) partition ratio ($T=0.92$; S_2 composition: $NH_4^+=0.45$, $(NH_4)_2CO_3=0.36$, $DNP=1.85$, $TNP=3.26$).

Results confirm that washing efficiency in the second alkaline washer in the plant is not considerably affected by a reduction of the solvent/MNB ratio. Less water to be recirculated (S_2 decrease) means that a pump with less power could be used, saving energy and space if such a change was implemented in the plant.

Results of experiments E-3 to E-6 might be explained using theory of phase equilibrium. As referred in section 3.1, understanding of tie lines is of great importance for liquid extraction. With a solvent/MNB₁ ratio R of 1.07 or 0.44, the mixture seems to be located in the same tie line, which means that regardless of the variation in composition of the mixture, the same equilibrium will be reached and concentration of the different components will remain the same in the separated phases (till the mixture lies in another tie line). Additionally, results demonstrated that the washing is carried out with an excess of solvent.

Experiment E-7 was carried out to find out the minimum ratio R to be used in the extraction of nitrophenols in the second washer. Samples of MNB₁ were washed decreasing the amount of solvent S₂ used in each test (lower than 0.30). Results are shown in Figure 5-7a and Figure 5-7b.

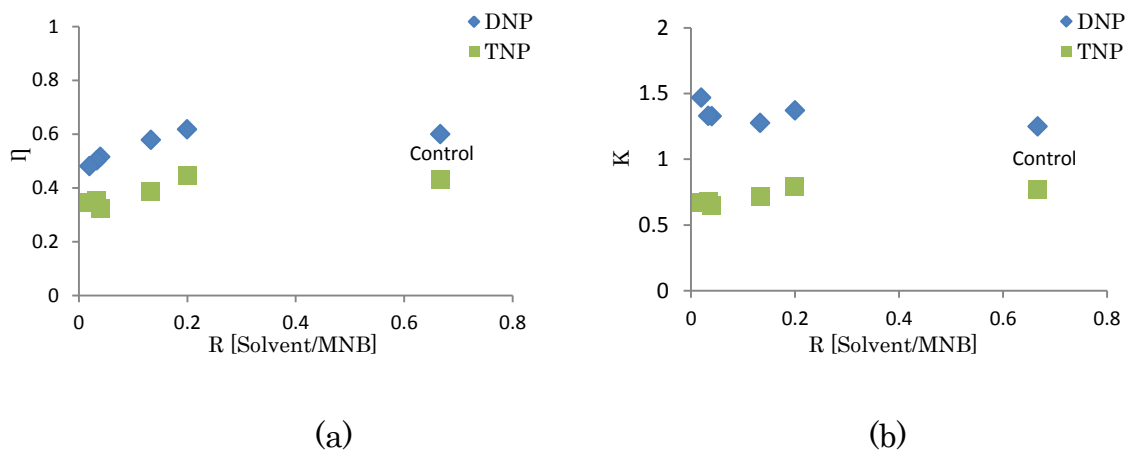


Figure 5-7- Minimum ratio R for MNB's washing (E-7): a) efficiency, b) partition ratio (T=0.92; S₂ composition: NH₄⁺=0.27, (NH₄)₂CO₃=0.29, DNP=2.22, TNP=2.85).

According to Figure 5-7a, it is possible to diminish the ratio R (even more than in E3 to E6) without compromising the washing efficiency. Nitrophenols's extraction began to decline when washing with an R below 0.20. In the plant, the R used is approximately 1.32, which means that as suspected, the process is carried out with a large excess of solvent (S₁ and S₂). It is possible to estimate that R=0.20 is the minimum R value to be used in the process. This result does not mean that the fresh solvent introduced (S_F) could be reduced since that would

lead to a rise of nitrophenols's concentration in S_1 and S_2 with a negative impact on the washing efficiency of the process.

Experiment E-8 was carried out on May 06th looking forward to confirm if a decrease in the flow rate of recycled washing water in the first alkaline washer did not affect its efficiency (as was shown in the second washer in experiments E-5 and E-6). Two levels of R ratios were assessed. In this case, the MNB has higher concentrations of nitrophenols than in the second washer. Results are presented in Table 5-2.

Table 5-2. - Influence of decrease in ratio R upon washing efficiency in plant's first washer, $T=0.92$ (E-8) (S_1 composition: $NH_4^+=0.75$, $(NH_4)_2CO_3=0.71$, $DNP=5.23$, $TNP=3.89$).

R	DNPx10 ² TNP x10 ²		η		K	
			DNP	TNP	DNP	TNP
1.18	45.34	36.03	0.84	0.71	1.29	0.62
	7.06	10.51				
0.88	46.63	36.80	0.84	0.69	1.20	0.58
	7.60	11.29				

Results of experiment E-8 show that, within the range of R studied, the extraction of nitrophenols in the first washer is practically not affected by the decrease of $S_1/MNBA$ ratio. This is in agreement with the behavior registered in the second washer upon the decrease of R.

Results of experiments E-3 to E-8 allow suggesting an optimization by reducing the flow rate of water used. This means a pump of less power could be installed in both washers for solvent recirculation reducing energy consumption without compromising the efficiency.

5.3 Influence of solvent composition

5.3.1 Ammonium carbonate

As referred in section 3.4, ammonium carbonate, which is dissolved in the washing water in the plant, influences the extraction process. In experiments E-9 and E-10 the influence of ammonium carbonate in the solvent was assessed at two limiting concentrations of ammonium: solvent without ammonium (E-9) and solvent with ammonium's concentration registered in the plant, $\text{NH}_4^+=0.5$ (E-10). During the evaporation of ammonia from the solvent (see section 4.5), ammonium carbonate is released as well. In fact, ammonium carbonate is not present in the solvent after heating for 15 minutes (while usual ammonium carbonate concentration in S_2 is 0.36). Results of experiment E-9 are plotted in Figure 5-8a and Figure 5-8b.

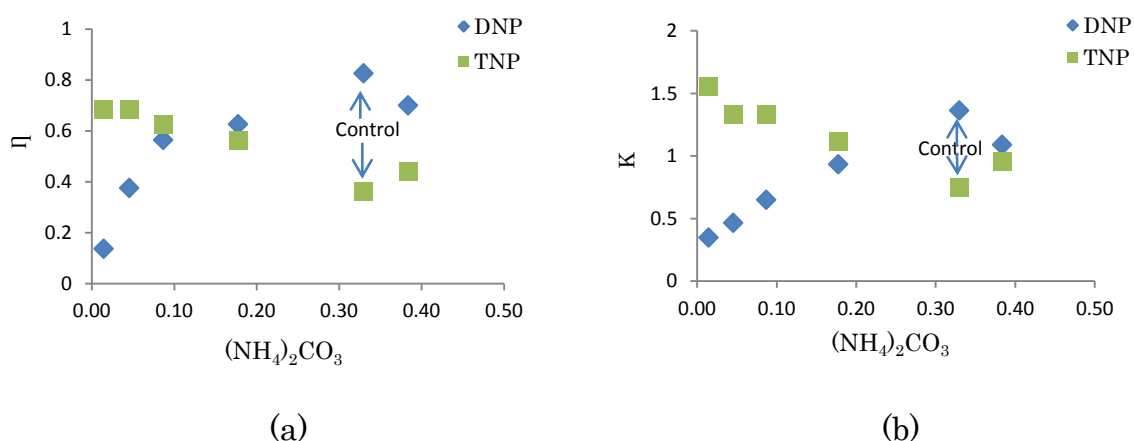


Figure 5-8. - Influence of ammonium carbonate concentration (E-9) upon: a) efficiency, b) partition ratio ($T=0.92$, $R=1$; S_2 composition: $\text{NH}_4^+=0.03$, $\text{DNP}=1.58$, $\text{TNP}=1.96$).

Figure 5-8a demonstrates that, in the absence of ammonia, ammonium carbonate acts as alkaline agent promoting nitrophenols's salts formation. At low concentrations of alkaline agent (ammonia), DNP extraction is poor, improving with ammonium carbonate addition. On the other hand, TNP extraction decreases as ammonium carbonate concentration rises. Again, as TNP salt is a bigger molecule, its transfer to the aqueous phase becomes more difficult. As referred in section 3.3, TNP has a lower pK_a than DNP (according to Marcé

(2000), values of pKa are 0.42 and 4.09 for DNP and TNP, respectively,) thus, trinitrophenol it is more acid, dissociates readily and forms the salt more easily than DNP. At low concentration of ammonium ion, most of it will react with the TNP. This would also explain the low efficiencies in DNP washing, that the data at low ammonium carbonate concentration in Figure 5-8a show. Results in Figure 5-8b demonstrate that the rise in ammonium carbonate concentration affects differently DNP and TNP partition coefficients; increases DNP distribution in the aqueous phase while it decreases the same parameter for TNP. Also, Figure 5-8b shows that for ammonium carbonate concentrations below 0.2, K_{TNP} presented higher values than K_{DNP} which is contrary to the results obtained in experiments E-1 to E-8. These findings match with the conclusions of Cardoso (2013). It is possible to suggest that TNP could be extracted at better rates operating without alkaline agent, in other words, near neutral conditions.

Same procedures of experiment E-9 were repeated but this time with the NH_3 concentration in the water S_2 as in the plant (approximately 0.5). Results are shown in Figure 5-9a and Figure 5-9ab.

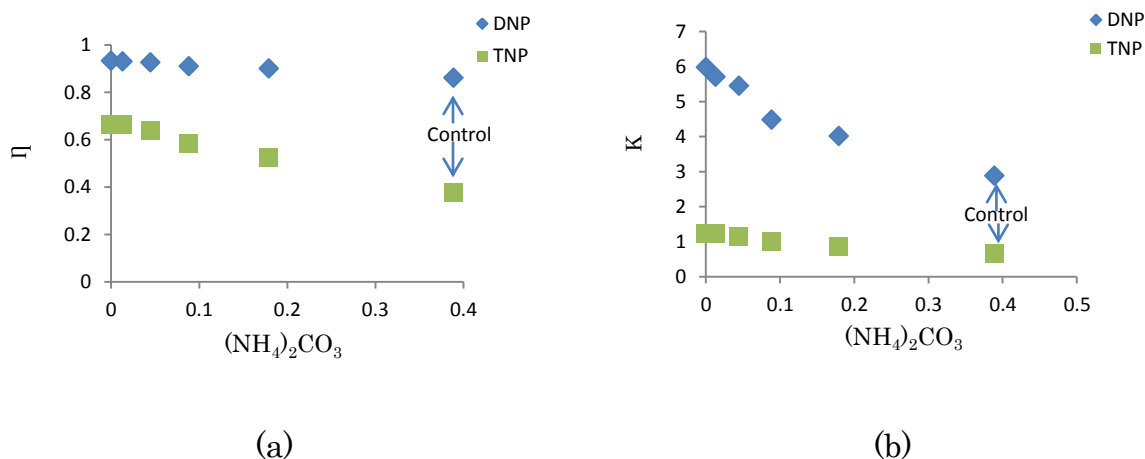


Figure 5-9. - Influence of ammonium carbonate concentration (E-10) upon: a) efficiency, b) partition ratio (T=0.92, R=1; S_2 composition: $NH_4^+=0.5$, DNP=1.58, TNP=1.96).

Figure 5-9a shows that, at an ammonium concentration of 0.5, the rise in ammonium carbonate concentration had a negative impact in the washing efficiency for both NPs, being less significant for the DNP. The solvent had already enough NH_4^+ for carrying out the extraction (as the first data show, $C_{(\text{NH}_4)_2\text{CO}_3} \approx 0$), thus, $(\text{NH}_4)_2\text{CO}_3$ addition leads to more NH_4^+ in the solvent and the common ion effect might occur as refers Walter (1981). As a consequence, NPs's salts would precipitate in the organic phase (decreasing the extraction efficiency).

Figure 5-9b shows a decrease in K partition coefficients values for both nitrophenols. Such behavior differs from results reported in Figure 5-8b (in E-9 ammonium's concentration was very low). This demonstrates the negative effect that ammonium carbonate has upon the extraction process; it decreases the solubility of the nitrophenols's in the aqueous phase.

On the other hand, when comparing results of experiments E-9 and E-10, efficiency and partition ratios of DNP were a lot higher in E-10 (high alkalinity medium) while, for TNP, both parameters did not change much between experiments.

5.3.2 Ammonium concentration

As referred in section 2.3, in this process the extraction of nitrophenols from MNB relies upon the reaction of nitrophenols with ammonium (Eq. 2.4 and 2.5), leading to the formation of salts, which are soluble in water. As ammonia has to be added to the process (leading to ammonium), it is important to assess the influence of ammonium concentration upon the extraction efficiency.

The influence of ammonium concentration in the washing water was tested in experiment E-11 following procedures detailed in section 4.5. Results are illustrated in Figure 5-10a and Figure 5-10b.

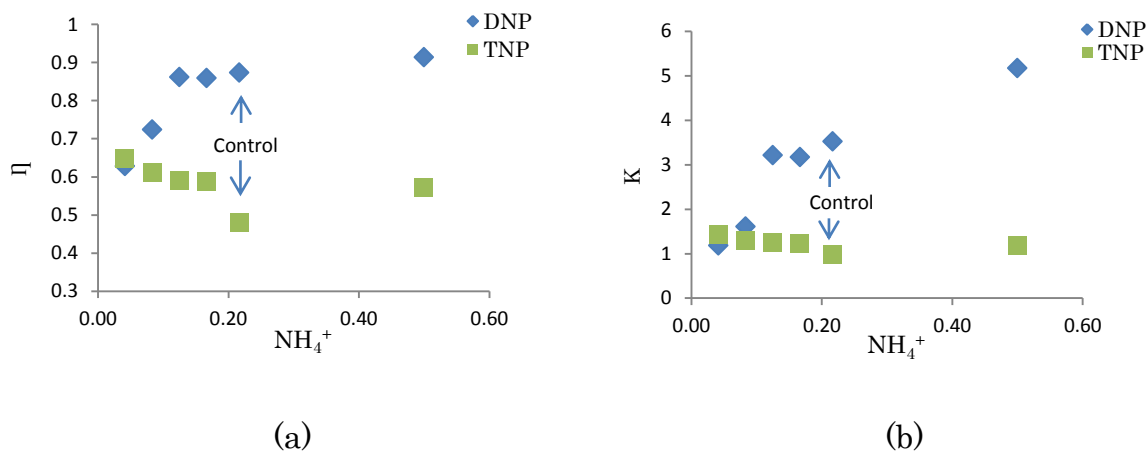


Figure 5-10. - Influence of ammonium concentration in the washing water (E-11) upon: a) efficiency, b) partition ratio ($T=0.92$, $R=1$; S_2 composition: $(\text{NH}_4)_2\text{CO}_3 \approx 0$, $\text{DNP}=1.99$, $\text{TNP}=3.02$).

Figure 5-10a shows that washing the sample of MNB_1 with higher concentrations of ammonium, in the absence of ammonium carbonate, improves DNP extraction. On the other hand, it has no significant influence upon TNP extraction as an increase of 0.45 in ammonium concentration only led to a decrease of 0.07 on TNP extraction efficiency. Analysis of Figure 5-10b reveals that partition coefficient of DNP is strongly affected by ammonium's concentration while values of K for TNP are less influenced. Nitrophenols's salts formed in the reaction with ammonium have different molecular structures, having the TNP a higher molar mass and being bigger than DNP's salt. This could explain why it is easier for the DNP to transfer to the aqueous phase. The TNP salt would require more residence time for transferring to the solvent phase.

Figure 5-8a to Figure 5-10a showed that ammonium has a negative effect upon TNP's extraction (which is the nitrophenol with higher concentration in MNB_1). Therefore, experiments E-12 and E-13 were carried out to test the washing process without ammonium and with very low concentrations of ammonium ($\text{pH} \approx 7$). Two conditions were tested: washing with demineralized water and with water coming from the MNB tank.

After being stripped (Fig. 2.3), the MNB is stored in a tank where water settling occurs. Such water ($\text{NH}_4^+=0.01$, $\text{DNP}=0.04$, $\text{TNP}=0.30$) was used for testing the washing process near to neutral conditions. The extraction process

was carried out at different ranges of ratio R for each solvent. Experiments E-12 and E-13 were carried out at the same time, three levels of mass ratio R were tested for each solvent (demineralized and tank water), to achieve this it was necessary to add a seventh tube to the experimental arrangement of tubes (Figure 4-2) which was used as the control tube. Results are compiled in Figure 5-11a and b and 5-12a and b.

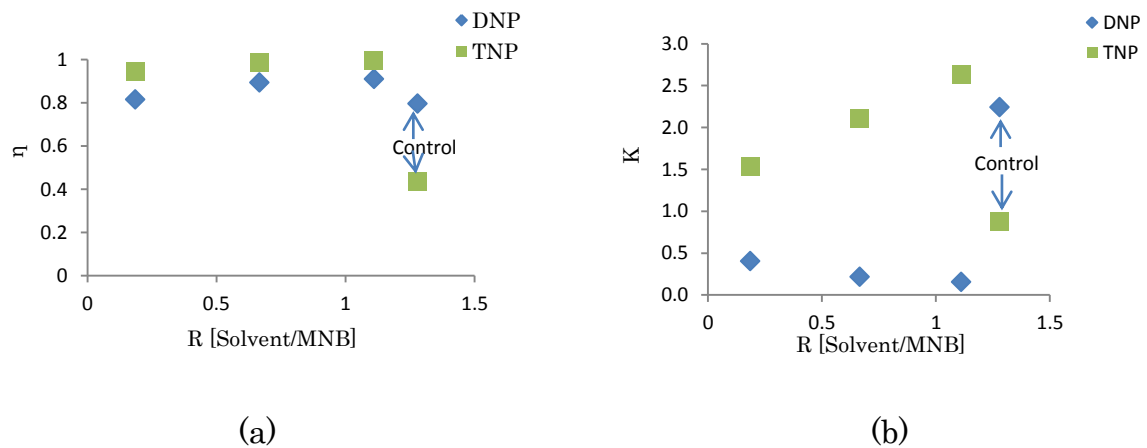


Figure 5-11. - Washing with demineralized water (E-12) - influence of solvent/MNB₁ ratio, R upon: a) efficiency, b) partition ratio (T=0.92; solvent composition: (NH₄)₂CO₃=0, NH₄⁺=0, DNP=0, TNP=0).

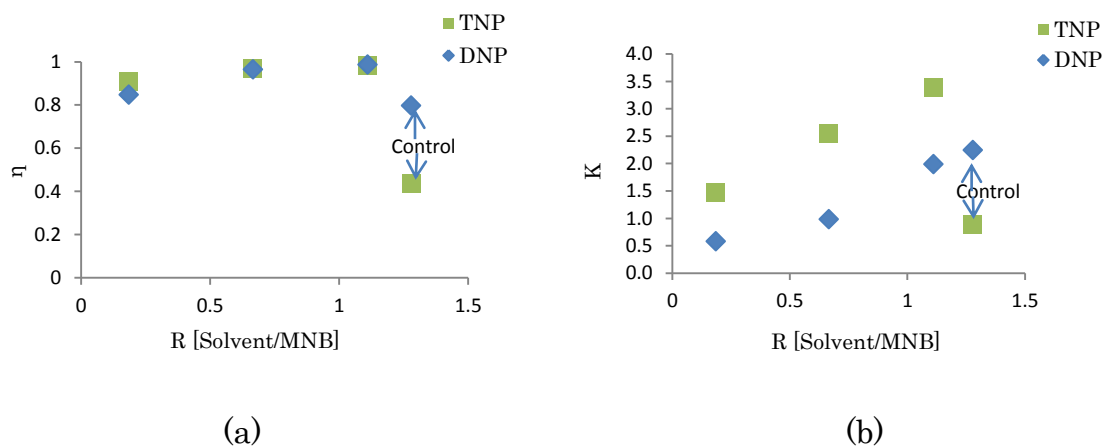


Figure 5-12. - Washing with water from the MNB tank (E-13) - influence of solvent/MNB₁ ratio, R upon: a) efficiency, b) partition ratio (T=0.92; solvent composition: (NH₄)₂CO₃=0, NH₄⁺=0.01, DNP=0.04, TNP=0.30).

Results of these experiments reveal a great positive impact of neutral conditions upon the efficiency of the second MNB's washer (comparing with plant conditions). Efficiencies obtained in the control tube were 0.79 and 0.44 for DNP and TNP, respectively ($R=1.32$) while in the laboratory, under neutral conditions and $R= 1.11$, this efficiency increased to 0.91 and 0.99 (using demineralized water) and 0.98 and 0.99 (using water from the MNB tank).

Comparing results of experiments E-12 and E-13, DNP's extraction was better when using tank water (due the presence of NH_4^+). On the other hand, TNP's extraction with demineralized water showed slightly higher efficiency than with tank water.

Tank water has low concentrations in ammonium (0.014 compared with 0.50 in the plant washing water) and demineralized water is NH_4^+ free. Due to this, it would be expected that DNP's washing efficiency was better at plant conditions. Nevertheless, as seen in Figure 5-11a and 5-12a, better extraction of dinitrophenol was reached using tank water and demineralized water. This is due to the low concentration on NPs in these waters (absence of NPs in demineralized water and 0.33 in tank water, while the average concentration of NPs in S_2 is 4.85). This means that in experiments E-12 and E-13 the gradient of NPs concentration between phases was bigger than in plant operating conditions, which also explains the high efficiencies reached.

High efficiencies obtained in E-12 and E-13, indicate that carrying out the process with a liquid with lower concentration of nitrophenols increases the extraction efficiencies. In the plant, the solvent recirculates in the washers, thus, there is accumulation of nitrophenols in S_1 and S_2 . Such accumulation is controlled with a purge stream (S_{purge}) and with addition of fresh solvent with ammonia (S_F). Washing with a "cleaner solvent" would mean an increase in the consumption of water, moreover, the solvent that leaves the washers is incinerated in a process that demands natural gas. Feeding more water seems unfeasible at industrial scale due to environmental and economic reasons.

Experiment E-14 was carried out for testing the extraction of nitrophenols at a lower range of solvent/MNB₁ ratio, R (0.02-0.11) being these conditions feasible application at plant scale. As indicated above, feeding fresh water at industrial

scale represents additional costs, this is why in this experiment only water from the MNB tank was tested. Results are presented in Figure 5-13a and Figure 5-13b.

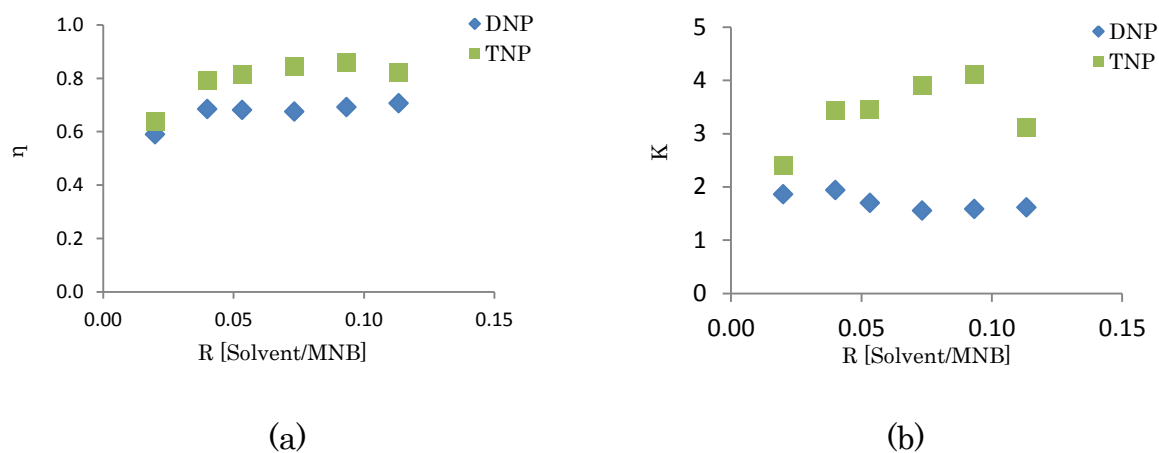


Figure 5-13. - Influence of extraction with water from the MNB tank (E-14): a) efficiency, b) partition ratio (T=0.92; solvent composition: $\text{NH}_4^+=0.01$, DNP=0.04, TNP=0.30).

Results of E-14 demonstrate that washing with very low amounts of tank's water allows a better extraction than washing with a higher R with the solvent S_2 used in the plant (efficiencies obtained in the control tube were 0.65 and 0.42 for DNP and TNP respectively while K values were 1.2 and 0.8). This can be explained having in mind that the tank's water has low ammonium content and low nitrophenols's concentration, promoting the TNP extraction (which is the compound with the higher concentration in MNB_1). An optimization of the washing process would be operating the second washer at neutral conditions. With this procedure, in the first washer most of the DNP would be extracted while in the second one TNP extraction would take place.

In Figure 5-13b it is clear that, under this washing conditions, partition coefficients are higher for TNP. In fact, higher partition coefficients for TNP were only registered for low alkaline agent concentration in the solvent.

The results obtained in this study are summarized in the Table 5-3, where it is shown the influence of the increase of each parameter upon the washing efficiency of both nitrophenols.

Table 5-3.- Influence of the increase in operating parameters upon the washing efficiency.

Parameter	η	
	DNP	TNP
Temperature	Decreases	Slight decrease
Weight ratio R (between 0.2 – 1.32)	No influence	No influence
(NH ₄) ₂ CO ₃ (NH ₄ ⁺ free)	Improves	Decreases
(NH ₄) ₂ CO ₃ with NH ₃ concentration at plant's range.	Decreases	Decreases
NH ₄ ⁺ ((NH ₄) ₂ CO ₃ free)	Improves	Decreases

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

Mononitrobenzene is a precursor of MDI that in the last decades experienced a rapid and steady growth in production, due this, it is important to optimize its production processes. This work was focused on the optimization of the purification process of MNB, a reactive liquid-liquid extraction in alkaline media. Several operating conditions were assessed: temperature, solvent's composition and weight ratio R between solvent and MNB.

It was demonstrated that extraction of nitrophenols is enhanced at lower temperature. This is due to decrease of water solubility in the MNB when temperature diminishes, which promotes the separation of the organic and aqueous phases. It is also explained by the increase of the solubility of nitrophenols in the MNB with temperature.

A decrease in the second washer's temperature by 45%, compared to the current temperature, would lead to an efficiency improvement of 0.13 and 0.05 for DNP and TNP extraction, respectively. However, due to current energy integration between several operations of the MNB purification process at CUF-QI nitration plant, a change in temperature would imply a redesign of the whole purification section. For new plant design or future revamping at CUF, washer's performance at a lower temperature than the current one must be considered, since the process efficiency might be improved.

Decrease in the amount of ammonia's aqueous solution used as solvent in the extraction had not affect upon the transfer of byproducts from the MNB to the aqueous phase. In other words, it was demonstrated that decreasing the R weight fraction between solvent and MNB at laboratory and industrial scale (in both washers) has not a negative impact in the washing efficiency at the range of R studied (a decrease up to 80% of the R currently in use was tested). Solvent is clearly in excess. In practice, it is possible to operate the washers with lower flow

rates of S_1 and S_2 streams, thus, installing pumps of less power is feasible, meaning less energy consumption.

Ammonium promotes the nitrophenols transfer from the MNB phase to the aqueous one (due the formation of nitro-hydroxy-aromatic salts). It was revealed that extraction of 2,4-dinitrophenol is greatly influenced by changes in ammonium concentration. A decrease of 82% in NH_4^+ concentration in the solvent (regarding to current plant's condition) led to a decrease of 0.23 in the washing efficiency of DNP. On the other hand, efficiency of TNP extraction had a light improvement (0.06). An opposite effect of the ammonium upon the extraction of nitrophenols was registered: improves DNP extraction while it decreases TNP's one.

Trinitrophenol is the byproduct with the higher concentration in the second washer, since NH_3 diminishes the extraction of TNP, washing without ammonium in the solvent was tested by using demineralized water and process water from the MNB tank which has very low concentration of NH_3 (S_3). Washing efficiencies obtained were above 0.90 for both nitrophenols, since the solvent used is NPs free and this promotes their transfer to the aqueous phase. Even at very low R ratios, the extraction was very effective (0.68 and 0.79 for DNP and TNP with an R of 0.04). Typical extraction efficiencies at the second washer in the plant are 0.57 and 0.43 for DNP and TNP respectively with an R of 1.32.

Ammonium carbonate is present in the washers as byproduct of the nitration stage and its influence upon the nitrophenols extraction was assessed. In the absence of ammonium, $(NH_4)_2CO_3$ acts as alkaline agent promoting the extraction of DNP and slightly decreasing TNP's extraction. Washing MNB with solvent (containing NH_4^+ at plant's concentration) and adding $(NH_4)_2CO_3$ led to a slight decrease in the extraction of both NPs due the common ion effect. This demonstrates the negative effect that high ammonium carbonate concentration has in the process.

Mononitrobenzene samples from the inlet stream to the second washer (MNB_1) are very sensitive to time and temperature change; at room temperature nitrophenols's precipitation and phases separation occurred 70 minutes after sampling. Then, analyses in the laboratory for determining washing efficiency in

the plant are notoriously affected. It is recommended to adopt a standard procedure at CUF-QI specifying that MNB₁ samples analysis must be carried out one hour after being collected, maximum.

The results achieved in this study allow suggesting a modification of the solvent feeding system. The first washer could be fed with the usual concentration of ammonium (extracting mostly DNP), while the second could operate at neutral conditions, using water from the MNB tank, for example, extracting most of the remaining TNP.

Several optimization suggestions are put forward: decreasing washing temperature for an improved efficiency; a reduction in flow rate of solvent (washers could be operated with only 20% of the current S₂ stream) which would allow installing pumps with less energy consumption. Moreover, operate the second washer under neutral conditions, without alkaline agent, by using the water stream coming from the MNB tank.

The present study accomplished its objectives since it was possible to reach new knowledge about the washing process in the plant and allowed new perspectives for future redesign of the mononitrobenzene purification process.

6.2 Future work

Looking forward to achieve a better understanding of the liquid-liquid extraction, a study of nitrophenols solubility in aqueous and organic phase is recommended.

It would be of interest to carry out an economic and technical study on the viability of the improvements proposed in this work. Mainly, it is important to assess energy integration of the MNB purification section aiming at decreasing the washing temperature. Redesign of the solvent feeding to the washers would also require a deeper study in the plant.

During this work and the one developed by Cardoso (2013), significant data of the washing process of MNB at the plant of CUF-QI were obtained, mainly

efficiencies and partition coefficients at different operating conditions. It would be of great interest developing a mathematical model for the nitrophenols's extraction from the organic to the aqueous phase. In the literature consulted is not possible to find this information. A suitable mathematical model of the process would greatly contribute to the optimization of the alkaline washing of mononitrobenzene.

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Appendix

A – Streams characterization

Table A.1 Plant's streams characterization and equipment efficiency.

Stream	Experiment	Day/Time	DNP $\times 10^2$	TNP $\times 10^2$	%NH ₃	%(NH ₄) ₂ CO ₃	η	
							DNP	TNP
MNB ₁	E-1 + E-3	26-03-14/ 11:15	4.4	12	0.60	0.45	0.61	0.31
MNB ₂			1.7	8				
S ₂			169.2	337				
MNB ₂	E-2 + E-4	31-03-14/ 14:45	1.1	3	0.45	0.40	0.62	0.49
S ₂			159	338				
MNB ₁	E-5	04-04-14/ 10:29	3.7	9.7	0.43	0.42	0.57	0.23
MNB ₂			1.6	7.5				
S ₂			163.7	379.2				
MNB ₁	E-6	15-04-14/ 10:45	5.6	7.5	0.45	0.36	0.67	0.28
MNB ₂			1.8	5.4				
S ₂			185.2	326.1				
MNB ₁	E-7	09-06-14/ 10:35	7.6	10.8	0.27	0.29	0.58	0.42
MNB ₂			3.4	6.1				
S ₁			222.2	284.8				
MNB _A	E-8	06-05-14/ 10:30	45.3	36.0	0.75	0.71	0.84	0.71
MNB ₁			7.1	10.5				
S ₁			523.1	389.3				
MNB ₁	E-11	15-05-14/ 10:00	7.6	9.9	0.22	0.02	0.54	0.42
MNB ₂			3.5	5.8				
S ₂			198.9	302				
MNB ₁	E-9	21-05-14/ 11:30	6.6	7.8	0.12	0.04	0.57	0.60
MNB ₂			2.8	3.1				
S ₂			157.5	195.6				
MNB ₁	E-12 to E-14	11-05-14/ 15:00	5.8	9.2	0.38	0.34	0.62	0.34
MNB ₂			1.3	4.7				
S ₂			159	284.6				
MNB ₃			8.1	11.3				
MNB ₄			0.7	0.8				
S ₃	51	70	0.05	0.03				
MNB ₁	E-10	14-05-14/ 10:30	7.8	6.5	0.20	0.36	0.57	0.43
MNB ₂			3.4	6.0				
S ₂			187.8	299.7				

B – Phases separation in a sample of monitrobenzene from the inlet stream to the second washer.

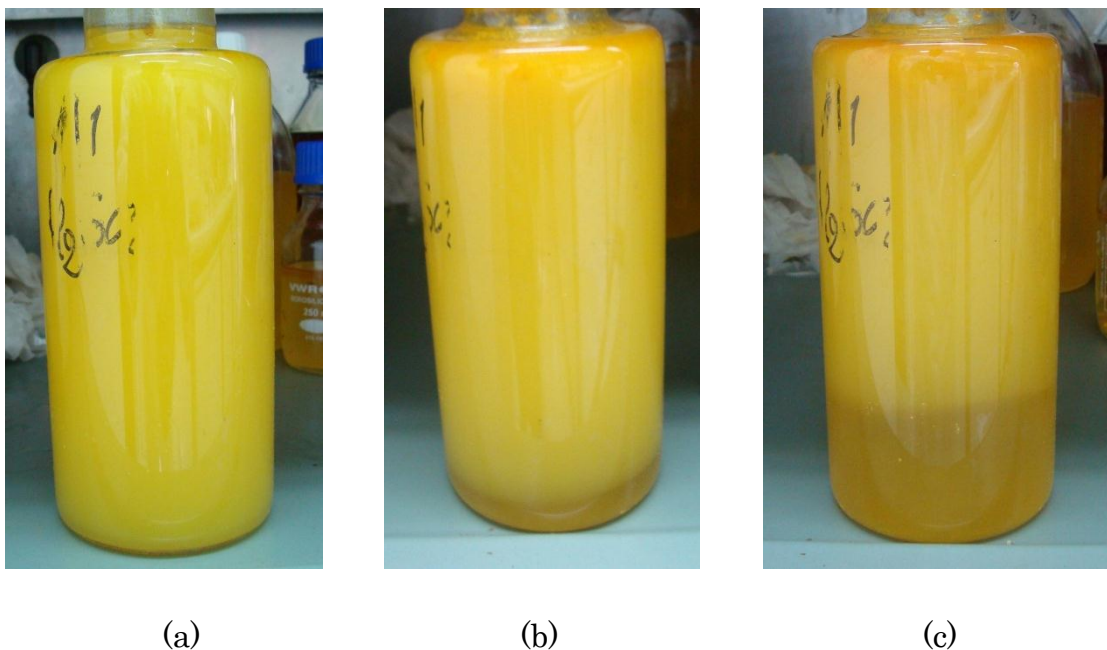


Figure B.1 Changes in a MNB sample from inlet stream to the second washer. Time and temperature after collecting: a) 5 minutes and 0.81; b) 55 minutes and 0.54 b) 360 minutes and 0.32.

C – HPLC results.

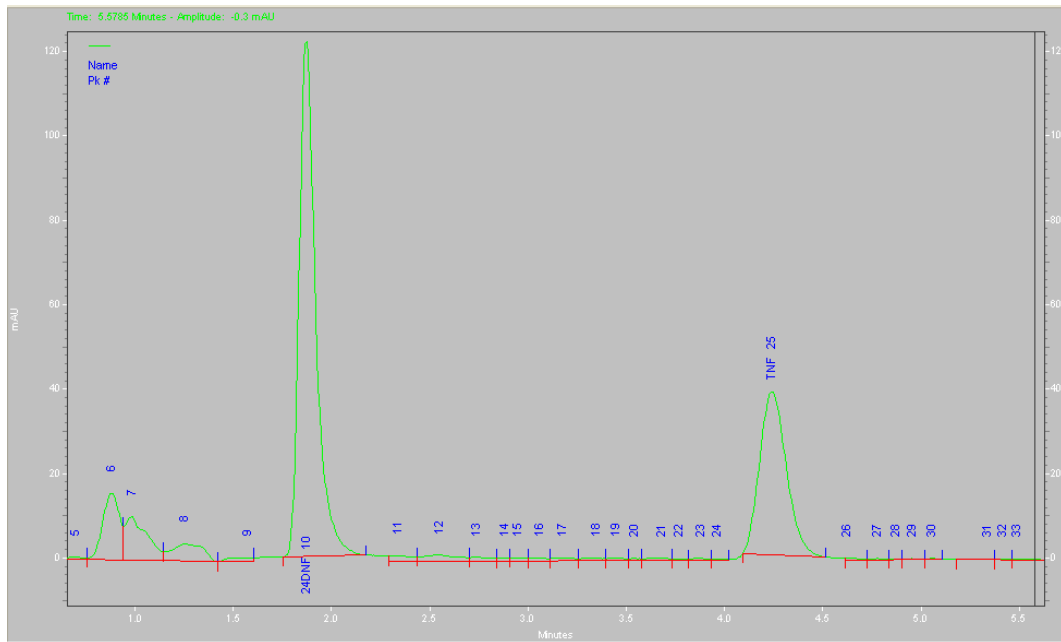


Figure C.1.- HPLC chromatogram with different compounds in MNB

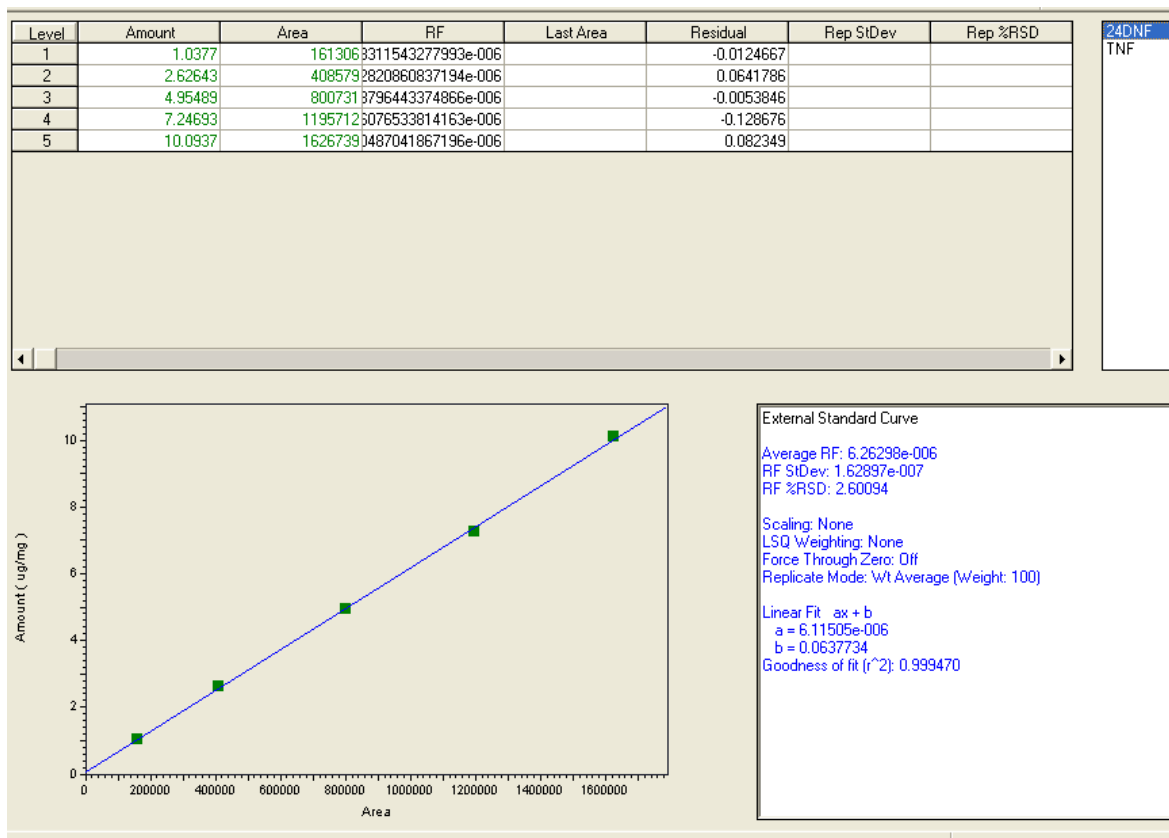


Figure C-2.- Calibration settings of the DataApex software for determining dinitrophenol concentrations.

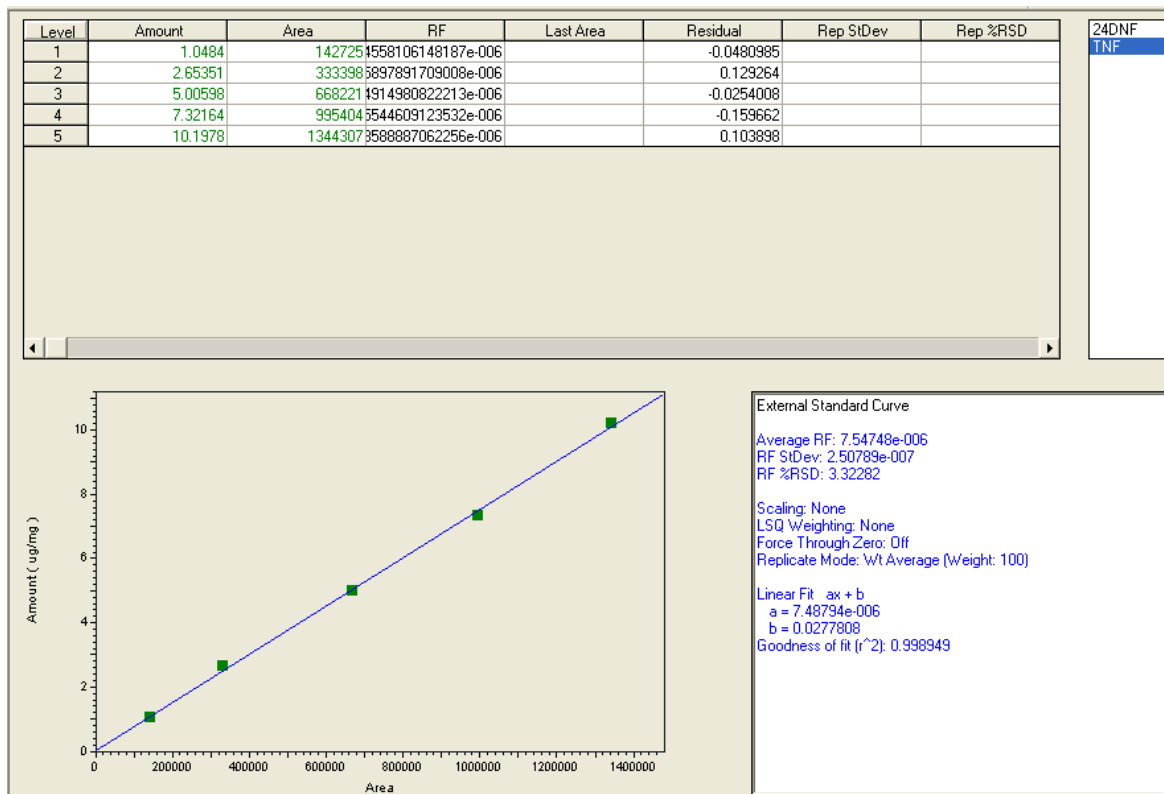


Figure C-3.- Calibration settings of the DataApex software for determining trinitrophenol concentrations.