



## A study on a combined process for the treatment of phenolic resin plant effluents

Shiva Agarwal, Ana E. Ferreira, M. Teresa A. Reis, M. Rosinda C. Ismael, Licínio M. Ferreira, Remígio M. Machado, Jorge M.R. Carvalho\*

Centre for Chemical Processes, Department of Chemical and Biological Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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### ABSTRACT

The removal of phenol and formaldehyde from phenolic resin plant effluents has been studied by using a combined process. In the first step, phenol was removed from effluent by solvent extraction. Special attention was paid to the effluent with a low content of phenol, which was treated by non-dispersive solvent extraction in hollow fibres. It was found that a single module of Liqui-Cel® 2.5 in. × 8 in. membrane contactor allowed processing ~24 L/h of effluent with 0.4–0.7 g/L phenol and attaining values as low as 0.5 mg/L in the raffinate. Formaldehyde, which was left in phenolic resin plant effluent after the removal of phenol, has been treated with hydrogen peroxide in alkaline medium and also in acidic medium (Fenton process). In alkaline medium, formaldehyde was oxidized with hydrogen peroxide to formate ion, which was recovered by solvent extraction. The oxidation of formaldehyde with Fenton process was also studied under several operating conditions. It was found that a large amount of hydrogen peroxide (i.e. mole ratio H<sub>2</sub>O<sub>2</sub>:HCHO > 6) was necessary to mineralize more than 90% HCHO in 1–2 h, at atmospheric pressure and 25 °C. The combination of pressure and high temperature strongly increased the kinetics of the process and allowed achieving a very high overall efficiency of the treatment under moderate H<sub>2</sub>O<sub>2</sub> dosage.

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### 1. Introduction

Phenol and formaldehyde are the main pollutants discharged by phenolic resin producing industries. As is well known, phenol produces many adverse effects on fish and aquatic ecosystem when chronically exposed even at a small concentration. For instance, phenol concentrations of over 2 mg/L are toxic to fish and concentrations in the range of 10–100 mg/L result in death of aquatic life within 96 h [1]. Also, formaldehyde has been found to critically damage DNA and cause mutations in mammalian cells and microorganisms [2]. Therefore, these toxic substances must be removed from effluents before releasing it in the environment. The usual treatments of phenolic effluents are biodegradation, thermal decomposition, extraction and adsorption [3–5]. Among them, biological treatment is limited to only less concentrated phenolic effluent, because microorganisms can not survive in higher concentration of such pollutants (i.e. up to 2.5 g/L phenol [3]). On the other hand, thermal decomposition and adsorption proved high energy consuming and costly methods [4,5]. More recently, Ferreira et al. [6] reported the application of the Membrane Aromatic Recovery System (MARS) for recovering phenol from resin production

condensates. The MARS unit was able to reduce the phenol concentrations to sufficiently low values (i.e. 0.1–0.3 wt.%) for further phenol detoxification by destructive processes. Other possibility that should be taken into account is the use of solvent extraction. In fact, solvent extraction method finds some advantages in treating phenolic wastewater, which is justified with the work published in literature [7,8]. Most recently, Juang et al. [9] reported the treatment of a phenolic wastewater by solvent extraction and membrane biodegradation in hollow fibres. Our research group also studied the removal and recovery of phenol and formaldehyde from a phenolic resin plant effluent by using solvent extraction [10,11]. The studies focused on the treatment of an aqueous phase containing 46 g/L phenol and 41 g/L formaldehyde and revealed that Cyanex 923 was found to be a more selective extractant for phenol than other tested extractants and also extraction of formaldehyde was almost nil. So the objective of the present work was to intensify the study on the removal of phenol with Cyanex 923 and to remove formaldehyde from the raffinate after the separation of phenol. It is worth emphasizing that there are two effluents commonly generated in phenolic resin plants: one presents a high concentration of phenol (typically 50 g/L) resulting from the condensates enriched with phenol and another one with a low concentration of phenol (<1 g/L) resulting mainly from rinse and refrigeration waters. Thus, the present study is mainly addressed to the removal of phenol from dilute streams and for that non-dispersive solvent extraction (NDSX) in hollow

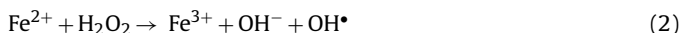
\* Corresponding author. Tel.: +351 218417311.  
E-mail address: [jcarv@ist.utl.pt](mailto:jcarv@ist.utl.pt) (J.M.R. Carvalho).

fibres was applied. Hollow fibres modules were chosen as contactors because these devices present the capability of treating a large amount of dilute solutions among several advantages [12]. On the other hand, NDSX also avoids many of the problems associated with conventional solvent extraction including solvent losses, emulsion formation, phase separation, and the shortcomings due to flooding and loading in traditional contactors [13].

Concerning the removal of formaldehyde from effluents, there are several methods cited in literature to obtain this purpose like solvent extraction, polymerization with urea, oxidation in alkaline medium, oxidation in acidic medium (Fenton process), photo-Fenton process, treatment with active charcoal and conversion to easily biodegradable formaldehyde disulfide. The extraction of formaldehyde with 1-decanol was already tested [11], but the stripping of the solvent was difficult and also the kinetics of the extraction was very slow. Equilibrium was reached in more than 6 h. Therefore, oxidation of formaldehyde in alkaline and acidic medium (Fenton process) was studied and the results are presented here. In presence of base, formaldehyde was oxidized with hydrogen peroxide to formate according to the following chemical equation [14]:



After oxidation, the resultant formate was acidified to formic acid. Further the recovery of formic acid was carried out by solvent extraction with Cyanex 923 and Alamine 336. In literature, some other works are also published related to formic acid extraction using phosphate containing extractants [15,16] and tertiary amines [17–19]. It is worth mentioning that formic acid is used in many industries such as textiles, natural rubber and leather processing. Also sodium formate is widely used in tanneries and its recovery is, therefore, of particular interest. Another study was the destruction of formaldehyde with Fenton process, as stated before. Oxidation with Fenton's reagent is based on ferrous ion and hydrogen peroxide, and exploits the very high reactivity of the hydroxyl radical generated in acidic medium by the catalytic decomposition of  $\text{H}_2\text{O}_2$  [20]:



A large number of hazardous and organic pollutants, including formaldehyde, can be oxidized and completely mineralized by using Fenton process [21]. However, Fenton oxidation is quite complex, the efficiency being affected by several parameters, like pH, concentrations of hydrogen peroxide and catalyst, temperature and pressure. Most studies on Fenton reaction published in literature have been carried out at mild conditions, i.e. normal temperature and atmospheric pressure. So, other goal of the present study was also to determine different experimental conditions leading to high mineralization degrees of formaldehyde with favourable kinetics.

## 2. Experimental

### 2.1. Solvent extraction

The organic phases were prepared by diluting the extractant in aliphatic diluents viz., ShellSol T and ShellSol D70 (Shell Chemical Ltd.). In the present study, Cyanex 923 was used as an extractant for phenol and formic acid (resulting from the oxidation of formaldehyde) as such as obtained from Cytec, Netherlands. Alamine 336 (Cognis, Ireland) was also tested as an extractant for formic acid but along with the modifier 1-decanol (Acros Organics, Belgium). Before use, Alamine 336 was washed with acidified water and then with water to remove impurities. A few tests were also carried out using the extractant Aliquat 336 (Cognis, Ireland) along with 1-decanol. 3 M NaOH (MERCK, p.a.) was used to strip loaded formic acid. Equilibrium studies were performed by agitation of the aqueous and

**Table 1**

Characteristics of the hollow fibre membrane module.

Type of module	G259 (contactor)
Module length	28 cm
Module diameter	7.7 cm
Case inner diameter	5.55 cm
Distribution tube diameter	2.22 cm
Number of fibres	~10,800
Fibre	X30–polypropylene
Effective fibre length	15.6 cm
Inner diameter of the fibres	240 $\mu\text{m}$
Outer diameter of the fibres	300 $\mu\text{m}$
Pore size	0.03 $\mu\text{m}$
Porosity	40%
Inner interfacial area	1.27 $\text{m}^2$
Outer interfacial area	1.58 $\text{m}^2$

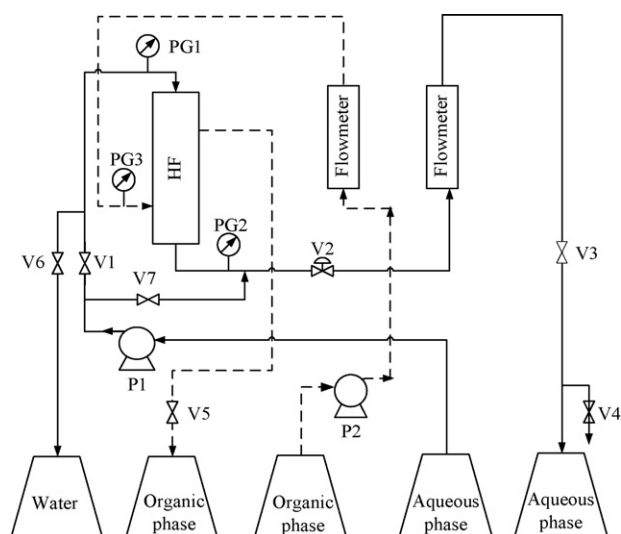
organic phases in an orbital agitator (Aralab Agitorb 160E) using several volume ratios, at 25 °C.

### 2.2. Formaldehyde oxidation

The experiments of chemical oxidation in alkaline medium were carried out at 22 °C in a 250 mL reactor with magnetic stirring using 130 Vol. hydrogen peroxide (José Manuel Gomes dos Santos LDA), sodium hydroxide (Panreac, p.a.) and potassium hydroxide (MERCK, p.a.). The concentration of the hydrogen peroxide solution was determined by titration with potassium permanganate in acidic medium [22]. The experiments of chemical oxidation of formaldehyde, using Fenton's reagent, at 25 °C, were carried out in a 2 L Pyrex glass insulated reactor with agitation. This reactor could withstand 0.6 bar external pressure. The experiments with high temperature and under pressure were conducted in a 1.5 L stainless steel 316 AISI insulated reactor with agitation. It is coated with Hypalon and a high temperature of 200 °C and 15 bar pressure can be maintained in this reactor. pH was adjusted by using dilute sulphuric acid. Heptahydrated ferrous sulphate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (MERCK, p.a.) was used as catalyst.

### 2.3. NDSX experiments

Non-dispersive solvent extraction was carried out using a Liqui-Cel® Extra-Flow 2.5 in.  $\times$  8 in. membrane contactor (Celgard, USA). The aqueous phase flowed through the lumens (tube side) of the hollow fibres and the organic phase flowed through the shell side of the fibres. The overpressure on the tube side was about 100 kPa to stabilize the interface in the pores and to prevent any leakage of the membrane phase. The characteristics of the hollow fibre membrane module are presented in Table 1. The experimental setup for the extraction experiments is shown in Fig. 1. The equipment consists of a hollow fibre module (HF), two gear pumps (P1–P2) (DDS.38, Tuthill), two flow meters, three pressure gauges (PG1–PG3) and valves. To start the process, the organic phase was pumped through the hollow fibres to fill the shell side of the contactor. Next, the flow of the organic phase was stopped and deionized water was pumped through the fibres tubes upstream (valves V6 and V7 were opened) to remove the organic phase from the tube side. The valves V6 and V7 were then closed and the actual aqueous feed phase was introduced into the respective reservoir for replacing water. The valves V1 and V3 were opened allowing that the aqueous solution flowed through the lumen side. After ~0.5 L of the aqueous phase was expelled, the organic phase started flowing through the shell side and the extraction began. Both phases were pumped through the hollow fibre module in a once-through operation mode. Aqueous samples were taken for measuring the concentration of phenol till reaching a steady-state of the system. All the experiments were carried out at 25 °C.



**Fig. 1.** Experimental setup for the removal of phenol from effluent by NDSX using a hollow fibre module as contactor.

#### 2.4. Phenolic effluents and analyses

The effluents used in the present study were synthetic solutions and simulated phenolic resin plant effluents produced by a Portuguese company. Phenol was purchased from MERCK and was analytical grade (99.5% minimum purity). Formaldehyde was obtained from a formaline solution composed of 37% formaldehyde and 10% methanol (MERCK, p.a.).

The concentration of phenol in the aqueous phase was measured with a double beam ultra-violet/visible spectrophotometer (Hitachi U2000) at 270 nm under acidic medium. The concentration of phenol in the organic phase was obtained by mass balance.

Formaldehyde analysis was done by the Hantzsch reaction colorimetric method [23]. A double beam ultraviolet/visible spectrophotometer Hitachi U2000 was used for the analysis. Formate ion was analyzed by potentiometric titration with HCl solution (Titrisol, MERCK) in a Metrohm 682 Titroprocessor. Total organic carbon was determined by a Dohrmann Carbon analyzer. The measurement of pH was performed by a Metrohm 827 pH meter with a Metrohm combined electrode.

### 3. Results and discussion

#### 3.1. Removal of phenol from effluents

As stated before, phenolic resin plants produce different concentrated effluents. For instance, a Portuguese phenolic resin company discharges effluents namely 'High' and 'Low' containing 30–60 and 0.4–0.7 g/L of phenol, respectively. Concerning the concentration of formaldehyde in 'High' and 'Low' effluents, the values are 10–41 and 0.4–3 g/L, respectively. If the concentrated stream can not be reused directly in the process, it is possible to apply solvent extraction with Cyanex 923 for recovering phenol in a first step of treatment, as reported in a previous study [11]. The extraction of phenol with Cyanex 923 is particularly favourable in terms of equilibrium. Besides, the kinetics is very fast, which allows the use of columns as contactors in a continuous mode operation [10]. Fig. 2 shows the equilibrium isotherm for the extraction of phenol with 0.5 M Cyanex 923 in ShellSol D70 at 25 °C. As observed, a concentration of phenol higher than 200 g/L can be achieved in the organic phase, which is related to the ability of Cyanex 923 for forming solute-extractant complexes with several moles of phenol per mole of extractant [11].

Further, as shown in Fig. 2, the McCabe-Thiele graphical method revealed that three equilibrium stages were necessary to decrease the concentration of phenol of the effluent 'High' from 46 to less than 0.1 g/L with a partially phenol-loaded Cyanex 923 phase (i.e. with 5 g/L phenol) using a volume ratio aqueous:organic 3:1. Increasing the volume ratio to 5:1 (data not shown) increased the number of equilibrium stages to 5. So, the process of extraction ought to be easily feasible using a column in a continuous mode operation. It is worth mentioning that the concentration of phenol in the raffinate can be fixed, for instance, at 0.5 g/L, since this is a typical concentration of the effluent 'Low'. Therefore, the raffinate and effluent 'Low' can be mixed in order to be treated jointly. Concerning the loaded organic phase, which contains ~140 g/L phenol for the volume ratio aqueous:organic 3:1, this one can be easily stripped (i.e. with 5 M NaOH) in order to attain a desirable concentration of ~280 g/L phenol at stripping phase. This aqueous stream can be afterward recycled and used directly in the manufacture of phenolic resins.

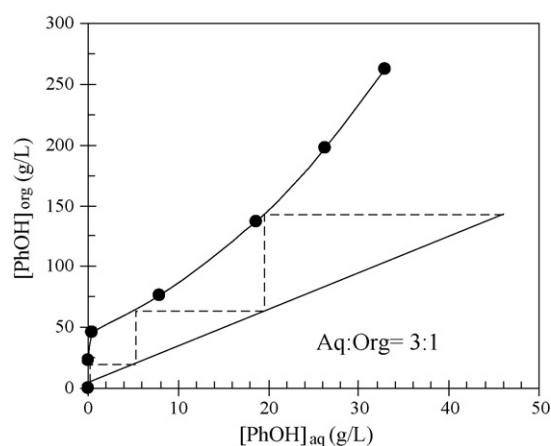
A few experiments of NDSX were then carried out using a hollow fibre module to check the feasibility of this technique for treating effluent 'Low'. For this, the effect of the concentration of Cyanex 923 in the range of 0.04–0.6 M on the extraction of phenol was tested. The hydrodynamics conditions were selected from a previous study [24]. The overall mass transfer coefficient based on the aqueous phase  $K_{aq}$  was obtained from the mass balance developed in the membrane module, which is valid in the once-through operation mode in conditions of minimal resistances in the membrane and solvent phases [25]:

$$K_{aq} = \frac{Q_{aq}}{A} \ln \frac{[\text{PhOH}]_{\text{initial}}}{[\text{PhOH}]_{\text{final}}} \quad (3)$$

where  $Q_{aq}$  is the aqueous flow rate and  $A$  is the membrane area at the interface (1.27 m<sup>2</sup>). The overall mass transfer coefficient was also evaluated by a conventional resistance in series model for making the comparison with the experimental values. When mass transfer is transport limited, the overall mass transfer coefficient of extraction, based on the aqueous phase in the tube side, is related to the individual mass transfer resistances as follows [26]:

$$\frac{1}{K_{aq}} = \frac{1}{k_t} + \frac{d_i}{m k_m d_{lm}} + \frac{d_i}{m k_s d_o} \quad (4)$$

where  $k_t$ ,  $k_m$  and  $k_s$  are the local mass transfer coefficients for the boundary layer in the tube side, diffusion through the pores and boundary layer in the shell side,  $m$  is the distribution ratio,  $d_i$  is the inner diameter of fibres,  $d_o$  is the outer diameter of fibres and  $d_{lm}$  is the logarithmic mean of fibre diameters. The first term on the



**Fig. 2.** Equilibrium isotherm for the extraction of phenol with 0.5 M Cyanex 923 in ShellSol D70 at 25 °C (effluent 'High' with 46 g/L phenol).

**Table 2**  
NDSX results: overall mass transfer coefficient of phenol extraction and relative resistances.

[PhOH] <sub>initial</sub> (mg/L)	[Cyanex 923] (M) (in ShellSol T)	[PhOH] <sub>final</sub> (mg/L)	Extraction (%)	Experimental $K_{aq}$ (m/s)	Local mass transfer coefficients			Contribution of individual resistance			Calculated $K_{aq}$ (m/s)
					$k_t$ (m/s)	$k_m$ (m/s)	$k_s$ (m/s)	Aqueous	Membrane	Organic	
400	0.04	1.9	99.5	$9.4 \times 10^{-6}$	$1.18 \times 10^{-5}$	$2.08 \times 10^{-6}$	$3.59 \times 10^{-6}$	84.5%	10.2%	5.3%	$1.0 \times 10^{-5}$
400	0.1	1.3	99.7	$1.0 \times 10^{-5}$	$1.18 \times 10^{-5}$	$1.94 \times 10^{-6}$	$3.32 \times 10^{-6}$	92.7%	4.8%	2.5%	$1.1 \times 10^{-5}$
400	0.5	0.2	99.9	$1.3 \times 10^{-5}$	$1.18 \times 10^{-5}$	$1.55 \times 10^{-6}$	$2.56 \times 10^{-6}$	97.9%	1.4%	0.7%	$1.2 \times 10^{-5}$
700	0.5	1.1	99.8	$1.1 \times 10^{-5}$	$1.18 \times 10^{-5}$	$1.55 \times 10^{-6}$	$2.56 \times 10^{-6}$	97.9%	1.4%	0.7%	$1.2 \times 10^{-5}$
400	0.6	0.5	99.9	$1.2 \times 10^{-5}$	$1.18 \times 10^{-5}$	$1.48 \times 10^{-6}$	$2.42 \times 10^{-6}$	98.3%	1.1%	0.6%	$1.2 \times 10^{-5}$
700	0.6	0.5	99.9	$1.3 \times 10^{-5}$	$1.18 \times 10^{-5}$	$1.48 \times 10^{-6}$	$2.42 \times 10^{-6}$	98.3%	1.1%	0.6%	$1.2 \times 10^{-5}$

[HCHO]<sub>effluent</sub> = 2 g/L; aqueous flow rate = organic flow rate = 24 L/h.

right side of Eq. (4) represents the resistance to mass transfer in the tube side, while the second and third terms denote, respectively, the resistance across the membrane and in the shell side. The local mass transfer coefficients  $k_t$ ,  $k_m$  and  $k_s$  were obtained from empirical correlations.

The mass transfer coefficient in the aqueous phase flowing inside the fibres was obtained from the Lévêque equation [26]. To calculate the mass transfer coefficient in the shell of cross flow module, as is the actual case, a correlation suggested by Schönner et al. [27] was applied. The mass transfer coefficient in the membrane  $k_m$  was also calculated from an equation published in the literature [26]. For these calculations, densities and viscosities of phases were measured and the diffusivities of solute were estimated from the Wilke-Chang equation [28]. The diffusivity of phenol in the aqueous phase was estimated to be  $1.03 \times 10^{-9}$  m<sup>2</sup>/s whereas the diffusivity of phenol-extractant complex in the organic phase was found to be within  $2.89$ – $4.05 \times 10^{-10}$  m<sup>2</sup>/s, under the range of concentrations tested. The molar volume of phenol at its normal boiling point was predicted by Schotte's contribution method [29], which gave a value of 102.0 cm<sup>3</sup>/mol. The molar volume of Cyanex 923 at its normal boiling point was determined to be 519.4 cm<sup>3</sup>/mol by the Le Bas method [30], which gave a value of 621.4 cm<sup>3</sup>/mol for the complex phenol-extractant. Other details related to the evaluation of individual mass transfer coefficients are published in a previous work [24]. The distribution ratio  $m$  was calculated for the initial conditions from the extraction constant  $K_{ex}$ , which was determined to be  $10^{3.02}$  M<sup>-1</sup> at 25 °C [24]:  $m = K_{ex} [\text{Cyanex 923}]_{\text{initial}}$ . For instance,  $m$  was 42 for 0.04 M extractant and was 524 for 0.5 M extractant. It is worth noting that the variation of the distribution ratio along extraction was not significant. Taking into account the equilibrium model published in a previous study [24] and the experimental results of extraction, the distribution ratio was found to decrease 10% for 0.04 M extractant but only decreased around 1% for 0.5 M extractant.

Table 2 lists the results obtained in NDSX experiments and presents the overall mass transfer coefficient data, experimental and predicted by the resistances in series model. Table 2 also displays the local mass transfer coefficients and the relative contribution of each resistance to mass transfer. For example, the fractional resistance in the aqueous phase (tube side) is given by  $(1/k_t)/(1/K_{aq})$  the overall mass transfer coefficient  $K_{aq}$  being calculated by Eq. (4). As Table 2 shows, there is a good agreement between the experimental data and the values predicted using the conventional resistance in series model. The transport in the aqueous stagnant layer was the main limiting step in the mass transfer, which confirms the results obtained in a previous study [24]. The contribution of the resistance due to the transport in the aqueous stagnant layer increased with the concentration of extractant and was found to be in the range of 85–98%.

Furthermore, the results show that the phenol content in the effluent after the single pass-through treatment in the hollow fibre module can be reduced to a value as low as 0.5 mg/L, which is acceptable in terms of environmental regulations. Since the level of phenol in the extract is low, the solvent may be reused in the treatment of effluent 'High' before stripping. A single module of Liqui-Cel® 2.5 in. × 8 in. membrane contactor thus allows treating ~24 L/h of effluent 'Low' using an adequate concentration of Cyanex 923. If the concentration 0.5 M is selected, more membrane contactors can be combined or a contactor with a larger membrane surface area can be applied for conducting the effluent treatment. For instance, the use of a module of Liqui-Cel® 4 in. × 13 in. membrane contactor (6.64 m<sup>2</sup> membrane area) will allow processing ~70 L/h of effluent 'Low' and attaining less than 0.1 mg/L phenol in the raffinate. It is noteworthy that this prediction was based on the overall mass transfer coefficient evaluated by the resistances in series model for this case.

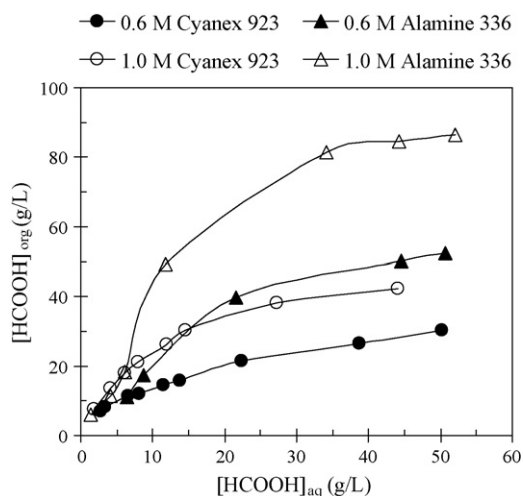


Fig. 3. Comparison of equilibrium isotherms for the extraction of 61 g/L formic acid solution with Cyanex 923 and Alamine 336 (0.6 and 1.0 M) in ShellSol T at 25 °C.

### 3.2. Removal of formaldehyde from effluents

#### 3.2.1. Oxidation of formaldehyde in alkaline medium and recovery of formate

The phenolic effluents, after the removal of phenol, contain formaldehyde which was treated with hydrogen peroxide in alkaline medium. The concentration of formaldehyde oxidized, by hydrogen peroxide in presence of either KOH or NaOH, was 41 g/L. The results showed that reaction is independent of the nature of the base as nearly 100% stoichiometric conversion of formaldehyde to formate was obtained in both cases. Further, kinetic study revealed that the reaction was over in less than 5 min.

The extraction of formate ion, obtained after oxidation, with tertiary amine and Cyanex 923 was tried but extraction was lower than 5%, since these reagents do not extract anionic species. Even though a quaternary ammonium salt (0.6 M Aliquat 336/20% 1-decanol) has been used, only 16% extraction was attained with a volume ratio aqueous:organic 1:1. So extraction of formate ion in the form of formic acid was tested. This is also supported by the work of Hu and Adeyiga [17] who used CO<sub>2</sub> to convert formate to formic acid before extraction with tertiary amines. Since the oxidation was performed in alkaline medium, the pH of the resultant solution was as high as 12. Therefore, the resultant formate solution was first acidified with concentrated sulphuric acid to decrease pH below pK<sub>a</sub> of formic acid (pK<sub>a</sub> = 3.56 [15]) and for that a reasonable amount of acid was used. To adjust the pH around 2.0 of the formate solution, 40 mL/L of concentrated sulphuric acid was required. This data shows that the removal of formaldehyde in the form of formic acid from waste water ought not to be very economical for industrial purpose. Nevertheless, bench scale studies were carried out to explore the potential of extraction and concentration. The extraction of formic acid was then tried with 0.6 and 1.0 M Cyanex 923 and the extraction capacity increases with the increase in concentration of extractant, as also obtained with Alamine 336. In case of extraction with Alamine 336, 10% 1-decanol was used as modifier. The equilibrium isotherms for the extraction of formic acid with Cyanex 923 were compared with those obtained with Alamine 336 and presented in Fig. 3.

From results, it is clear that the extraction with Cyanex 923 did not seem very promising when the extraction of a higher concentration of formic acid i.e. 61 g/L was performed. In fact, Alamine 336 provided much better extraction than Cyanex 923. Except few preliminary stripping studies with loaded Cyanex 923, the remaining stripping studies were carried out with 0.6 and 1.0 M loaded

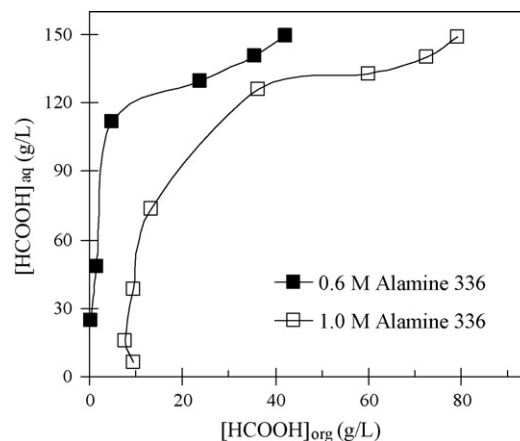


Fig. 4. Comparison of equilibrium isotherms for the stripping of formic acid from loaded Alamine 336 (0.6 M loading = 49.6 g/L, 1 M loading = 86.6 g/L) with 3 M NaOH at 25 °C.

Alamine 336 as shown in Fig. 4. As observed, a high concentration of solute (>100 g/L) could be attained in the aqueous phase using 3 M NaOH as stripping reagent. The stripping of the loaded 0.6 M Alamine 336 was found more favourable than the one with 1.0 M Alamine 336, which is in agreement with the effect of extractant on the equilibrium of extraction.

From the equilibrium data presented, it can be concluded that Alamine 336 allows concentration of formic acid in the form of formate by liquid–liquid extraction. However, the concentration ratio obtained from the waste solution with ~60 g/L of formate was just about 2 times. Moreover, as mentioned, a reasonable amount of sulphuric acid was required to adjust the pH before extraction. Therefore, some of these uneconomical aspects of the previous studies prompted us to try the removal of formaldehyde with Fenton process.

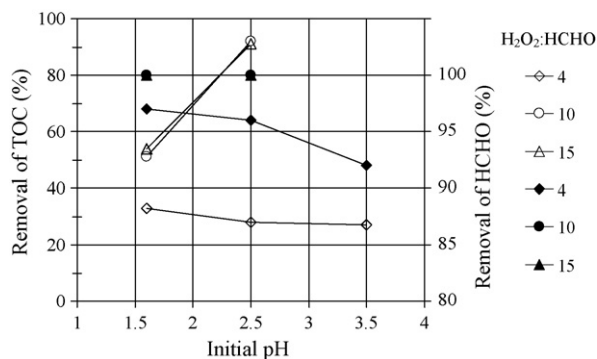
#### 3.2.2. Oxidation of formaldehyde using Fenton process

The oxidation of formaldehyde in acidic medium using Fenton's reagent was also carried out. Kajitvichyanukul et al. [2,31] also studied formaldehyde degradation using Fenton and photo-Fenton processes. They obtained almost complete removal of total organic carbon (TOC) content in 4 h [31]. The aim of the present study was to try other conditions to degrade formaldehyde in less time, which could be attractive for industrial purposes. Therefore, in all the experiments carried out, the reaction time was limited to 2 h only.

As mentioned before, a Portuguese phenolic resin company discharges effluents namely 'Low' and 'High' containing 0.4–3 g/L and 10–41 g/L formaldehyde respectively. So some preliminary experiments were carried out with varying initial concentration of formaldehyde in the range 2–40 g/L using the mole ratios of hydrogen peroxide to formaldehyde 2, 6 and 10. It was found that the initial concentration of formaldehyde had no significant effect on the % removal of TOC if all other conditions, namely mole ratio of hydrogen peroxide to formaldehyde, were kept the same. On the basis of these results, a low initial concentration of formaldehyde, i.e. 2 g/L was selected for all subsequent studies. In most experiments mole ratio of formaldehyde to ferrous ion was adjusted to 5 and this data was taken from literature [2].

The effect of pH on degradation of formaldehyde was studied at initial pH 1.6, 2.5 and 3.5 at different mole ratio of hydrogen peroxide to formaldehyde. The results are depicted in Fig. 5.

From Fig. 5, initial pH 2.5 allowed highest removal of TOC in case of ratio H<sub>2</sub>O<sub>2</sub>:HCHO 10 and 15. It is noteworthy that the removal of TOC strongly decreased at pH 1.6, except when the amount of H<sub>2</sub>O<sub>2</sub> was lower. So in all further experiments initial pH 2.5 was adjusted.

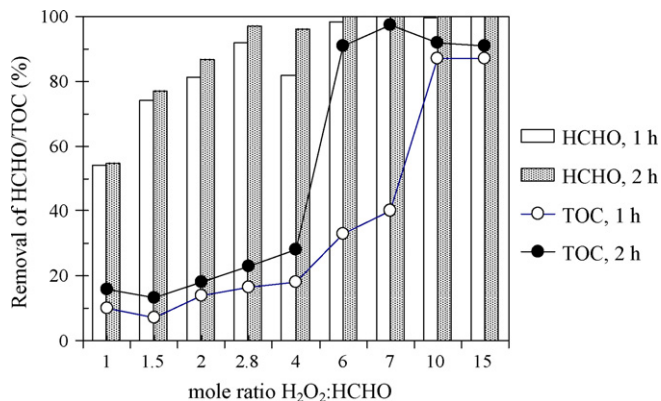


**Fig. 5.** Effect of initial pH on degradation of HCHO with Fenton process for mole ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  4, 10 and 15; time = 2 h,  $[\text{HCHO}] = 2 \text{ g/L}$  (0.067 M),  $[\text{Fe}^{2+}] = 0.013 \text{ M}$ ,  $T = 25^\circ\text{C}$  (open symbols: TOC removal, solid symbols: HCHO removal).

It is interesting to note here that pH 3.5 decreased to 2.5 after 2 h, whereas pH 2.5 decreased less than 0.1. Usually, the Fenton process has the highest efficiency when the pH is around 3 [32]. Bautista et al. [33] reported the application of Fenton process for treating cosmetic wastewaters and obtained the highest removal of TOC at pH 2.5–3. These authors observed a significant decrease in the efficiency of the process at lower and higher pH values. Also, Rivas et al. [34] found the optimum pH in the range of 2.5–3 in their study on the treatment of olive oil mill wastewater by Fenton's reagent. At low pH, the reaction between  $\text{OH}^\bullet$  and  $\text{H}^+$  becomes important and  $\text{H}_2\text{O}_2$  is stabilized as  $\text{H}_3\text{O}_2^+$  [33], which are deleterious for the oxidation process. On the other hand, when the concentration of  $\text{H}^+$  is too high, the regeneration of ferrous ion will slow down as well as the production of  $\text{OH}^\bullet$  [32]. Also the precipitation of ferric ion as  $\text{Fe}(\text{OH})_3$ , which is promoted by higher pH, is disadvantageous for the process. The formation of  $\text{Fe}(\text{OH})_3$  inhibits the regeneration of ferrous ion and enhances the decomposition of  $\text{H}_2\text{O}_2$  thus decreasing the production of  $\text{OH}^\bullet$  [35].

Kajitvichyanukul et al. [2] also examined the effect of initial pH on the removal of formaldehyde using a photo-Fenton process. They noticed that the initial pH in the range investigated, pH 2.6–4, had no obvious influence on the decomposition of formaldehyde. However, the oxidation rate of formaldehyde was found to increase as the pH value decreased and the highest removal was achieved at pH 2.6 [2]. Concerning the removal of formaldehyde in the present study, almost 90–100% was achieved in most cases. On the other hand, the removal of TOC was considerably lower, unless a large dosage of  $\text{H}_2\text{O}_2$  was employed. Therefore, intermediates might be formed during the course of oxidation, which can be more resistant to degradation than the parent compound. For instance, the decrease in the pH occurred during the oxidation process may be due to the formation of carboxylic acids (i.e. formic acid). Moreover, the presence of methanol in the solution of formaldehyde also inhibits the complete mineralization. A few determinations of methanol by gas chromatography in the residual solution confirmed that the removal of methanol was always lower than the removal of formaldehyde. These results are consistent with that observed by Kajitvichyanukul et al. [2,31].

Further, the influence of the amount of hydrogen peroxide on mineralization of formaldehyde was also studied and the results of % of TOC removal in variation with mole ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  after 1 and 2 h are shown in Fig. 6. As observed, the removal of formaldehyde exceeded 85% after 2 h with ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  2 but the removal of TOC was as low as 18% under the same condition. The increase in the  $\text{H}_2\text{O}_2$  dose above ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  4 strongly increased the removal of TOC. With ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  6, around 91% of TOC removal was achieved after 2 h, whereas 33% TOC was removed after 1 h. The mineralization was almost complete with

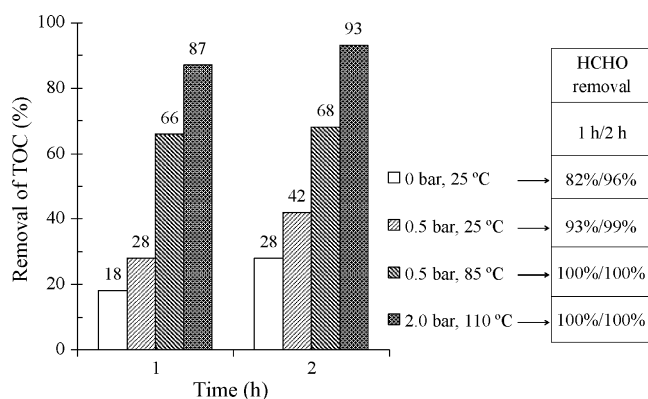


**Fig. 6.** Effect of amount of  $\text{H}_2\text{O}_2$  on degradation of HCHO with Fenton process;  $[\text{HCHO}] = 2 \text{ g/L}$  (0.067 M),  $[\text{Fe}^{2+}] = 0.013 \text{ M}$ ,  $T = 25^\circ\text{C}$ , initial pH 2.5.

ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  7 after 2 h and further augment in the amount of  $\text{H}_2\text{O}_2$  decreased the oxidation yield of the process. As pointed out in the literature [2,33], the higher the concentration of  $\text{H}_2\text{O}_2$  the faster it is decomposed thus increasing the reaction rate. However, the reaction rate can be inhibited when  $\text{H}_2\text{O}_2$  is in a large excess because of the occurrence of auto-scavenging reactions, i.e., the reaction of  $\text{H}_2\text{O}_2$  with  $\text{OH}^\bullet$ , or the combination of two radicals  $\text{OH}^\bullet$  [2]. It is worth emphasizing that the  $\text{Fe}^{2+}$  dose was kept constant and the efficiency of the process also depends on the ratio  $\text{Fe}^{2+}:\text{H}_2\text{O}_2$ . In fact, the increase in the concentration of ferrous ion was tested in a few experiments and the mineralization rate also increased. For instance, the removal of TOC after 1 h with ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  7 increased from 40 to 60% when the  $\text{Fe}^{2+}$  concentration increased from 0.013 to 0.023 M. Nevertheless, the results obtained showed that a high amount of  $\text{H}_2\text{O}_2$  (i.e. ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  10) was necessary to mineralize around 90% HCHO only in 1 h.

Some experiments were then carried out under pressure and a higher temperature to try to avoid the use of such a large excess of hydrogen peroxide. As known, when the temperature of the reaction medium is increased, oxidation proceeds at a faster rate but above 40–50 °C the decomposition of  $\text{H}_2\text{O}_2$  into oxygen and water is accelerated. Guedes et al. [36] studied the oxidation of cork cooking wastewater with Fenton's reagent and reported that a progressive increase in the temperature above 30 °C led to a decline in the overall efficiency. Bautista et al. [33] also checked the effect of temperature on TOC removal from a cosmetic wastewater and concluded that a combination of high temperature and high  $\text{Fe}^{2+}$  dose becomes detrimental for the efficiency of the Fenton process. So, the use of high temperature for increasing the mineralization rate will require the use of pressure to minimize the decomposition of  $\text{H}_2\text{O}_2$  towards  $\text{O}_2$ . Martínez and López [37] pointed out that carrying out Fenton process up to 3 atm allows rising temperature above 100 °C without risk in decomposition of hydrogen peroxide. Therefore, the use of pressure and the increase in temperature have been tried to improve the kinetics of Fenton process under moderate  $\text{H}_2\text{O}_2$  dosage. The results obtained are presented in Fig. 7. It is evident that under relative pressure of 0.5 bar, % TOC removal was higher than that obtained under atmospheric pressure, which indicates that pressure can be an important parameter in Fenton process. Besides, under pressure, the increase in the temperature was allowed without significant problems in decomposition of hydrogen peroxide.

As shown in Fig. 7, the combination of high temperature and pressure strongly enhanced the kinetics of the process. The removal of TOC increased to 66% (relative pressure 0.5 bar and  $T = 85^\circ\text{C}$ ) and 87% (relative pressure 2.0 bar and  $T = 110^\circ\text{C}$ ) after 1 h. Since the results are very promising, the influence of these parameters should be explored and optimized, the study being addressed towards the treatment of real effluent. Therefore, future work will be focused



**Fig. 7.** Effect of pressure and temperature on degradation of HCHO with Fenton process;  $[\text{HCHO}] = 2 \text{ g/L}$  (0.067 M),  $[\text{Fe}^{2+}] = 0.013 \text{ M}$ , mole ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  4, initial pH 2.5.

on the establishment of optimal operating conditions for degrading formaldehyde from effluent using Fenton's reagent. Finally, the formation of iron sludge after neutralization must be considered in terms of waste disposal issues. The residual iron content in the effluent after treatment as well as other parameters, whose limits are imposed by environmental legislation, must be taken into account.

#### 4. Conclusions

Phenolic resin plant effluents can be treated by using a combined process. In the first step, phenol can be removed from effluents and recovered by solvent extraction with Cyanex 923. Non-dispersive solvent extraction in hollow fibres showed to be very promising in treating effluents with a low content of phenol. A single module of Liqui-Cel® 2.5 in.  $\times$  8 in. membrane contactor allowed treating  $\sim 24 \text{ L/h}$  of effluent with 0.4–0.7 g/L phenol. In the second step of treatment, chemical oxidation with hydrogen peroxide in alkaline medium and Fenton process were used to prevent stream pollution from formaldehyde. The oxidation of formaldehyde with hydrogen peroxide in alkaline medium allowed stoichiometric conversion of formaldehyde into formate ion, which could be recovered by solvent extraction. Cyanex 923 and Alamine 336 were used as extractants and with the latter better results were achieved. It is possible to concentrate about 120 g/L of formate using 3 M NaOH as stripping phase. In continuation of oxidation of formaldehyde, Fenton process was also investigated by varying some parameters at atmospheric pressure and 25 °C like pH and amount of hydrogen peroxide. The removal of formaldehyde was very high in most cases. It was found that ratio  $\text{H}_2\text{O}_2:\text{HCHO}$  7 provided 97% removal of TOC after 2 h and larger amounts of  $\text{H}_2\text{O}_2$  were necessary to mineralize around 90% HCHO in 1 h, at atmospheric pressure and 25 °C. The combination of pressure and high temperature strongly increased the kinetics of the process and allowed achieving a very high overall efficiency of the treatment under moderate  $\text{H}_2\text{O}_2$  dosage. Further studies are necessary to optimize the treatment process of real effluents.

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