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Selectivity control of benzene conversion to phenol using dissolved salts in a membrane contactor

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ABSTRACT

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Keywords: Liquid phase benzene oxidation to phenol Catalytic membrane contactor Selective oxidation Tar formation from benzene Salts and phenol extraction (from aqueous to organic) Effect of salts, pH, type of acids and anion sulphate in the synthesis and separation of phenol through the hydroxylation of benzene by using a Fenton reaction in a biphasic membrane contactor has been investigated. The results indicated that sodium sulphate (1 M) increased phenol extraction in the organic phase (76.3%) but also increased reaction kinetics promoting over-oxidation products and a black solid (tar) formation. The acids delayed and in some tests avoided the tar appearance as precipitate but also gave a reduction of phenol selectivity. The sulphate absence, obtained by using iron(0), did not avoid the precipitate formation but only caused its decrease favouring a significant increase of the ratio productivity/amount of black solid from 4.6 to 62.4.

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1. Introduction

Phenol is an important raw material for the synthesis of petrochemicals, agrochemicals, and plastics. The current worldwide capacity for phenol production is nearly 7 million metric tonnes per year [1]. Today, almost 95% of the worldwide phenol production is based on a three-step process with the so-called "cumene process". Despite its great success, the cumene process has some disadvantages: poor ecology, an explosive intermediate (cumene hydroperoxide) and a multistep character, making difficult to achieve high phenol yields with respect to benzene [2].

The search for new routes for phenol production based on the one-step direct benzene oxidation became more intensive in the last decade [3–10] but this reaction is a little selective because phenol is more reactive than benzene and over-oxygenated by-products occur.

To slow down consecutive catalytic reactions catalytic membrane reactors (CMRs) can be employed. These systems have attracted attention because of their advantages related to the synergy of the catalyst and membrane when implemented in the same device [11–13]. Within this family, the membrane contactors also permit to combine membrane separation and catalytic reaction in one unit operation. The separation of a product from the reaction mixture is one of the advantages in using a membrane in a reactor and permits to obtain improvements in terms of yield and selectivity in equilibrium-limited reactions and in consecutive catalytic reactions.

A membrane contactor is a device that achieves gas/liquid or liquid/liquid mass transfer without dispersion of a phase within another [14].

As common feature of these processes the separation performance is determined by the distribution coefficient of a component in two phases. The membrane, which can be defined as a permselective barrier between two homogenous phases, represents only an interface. It accomplishes a particular separation transporting a component more easily than another because of differences in physical and/or chemical properties between the membrane itself and the permeating components. Membrane contactors have a number of important advantages compared to conventional dispersed phase contactors. Some of them are: no flooding at high flow rates, no unloading at low flow rates, absence of emulsions, no density difference between fluids required. They reduce the volume of equipment and offer more interfacial area in non-dispersive contact across a membrane, leading to a decrease in the value of a height transfer unit (HTU). The membrane should be accurately chosen to enable as much as possible higher values of the mass transfer coefficient. Additional advantages of this technique are a high surface area per unit volume, when hollow fibre modules are used, and the possibility of changing the hydrodynamics of both phases independently. These contactors give any wanted shape of

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Fig. 1. Scheme of the reactor-membrane contactor.

fluid–fluid interface in contrast to conventional separation equipments where the shape of the fluid–fluid contact is an accident of nature. There are different membrane configurations like hollow fibre, flat sheet, rotating annular and spiral wound that have applications in wastewater treatment, VOC removal from waste gas, osmotic distillation, fermentation, pharmaceuticals, carbonation of beverages, protein extraction [14]. The most important drawback, however, is the slow mass transfer rate because of the additional mass transfer resistance offered by the pores of the membrane.

In our research group a flat-sheet membrane contactor was used for the one-step oxidation of benzene to phenol [15-18] reducing by-products formation employing a liquid-liquid membrane contactor. The membrane contactor system was formed by an aqueous phase, containing dissolved FeSO₄ as catalyst and hydrogen peroxide as oxidant, and by an organic phase containing benzene. The two phases were separated by a hydrophobic membrane. In this system the benzene permeates across the membrane from the organic phase to aqueous membrane interface where the interfacial oxidation reaction takes place. Then the formed phenol permeates back across the membrane to the organic phase where it takes shelter from over oxidation. The high value of phenol selectivity (98%) in the organic phase was obtained thanks to its extraction in the organic phase so avoiding further contact between phenol and the catalyst, which was soluble in the aqueous phase. The drawback of this system was the low rate of phenol extraction in the organic phase. Indeed, phenol that does not cross rapidly the membrane, reacts further to generate over-oxidation products such as 1-4 benzoquinone, biphenyl as trace and tars (black solid).

In this work, to avoid/reduce tar formation and enhance phenol recovery in the organic phase, different aspects have been studied: (i) use of dissolved salts in aqueous phase; (ii) pH and anion type of various acids; (iii) composition of aqueous phase before the black precipitate appearance; (iv) role of sulphate anion present in the reaction system by changing the FeSO₄ catalyst with Fe(0).

2. Experimental

2.1. Materials

Benzene (C_6H_6 , purity 99.8%) from Carlo Erba Reagenti was used both as substrate and as organic extracting phase. Phenol (C_6H_5OH , purity 99.99%), benzoquinone ($C_6H_4O_2$, purity 99.9%), biphenyl ($C_{12}H_{10}$, purity 99.99%), hydroquinone ($C_6H_6O_2$, purity 99%), resorcinol ($C_6H_6O_2$, purity 98%) and catechol ($C_6H_6O_2$, purity 99.5%) from Sigma–Aldrich were used for analytical calibrations. Acetic acid (CH_3COOH purity 99.9%), sulphuric acid (H_2SO_4 , purity 96%, $d = 1.84 \text{ g mL}^{-1}$), nitric acid (HNO₃, purity 63%, $d = 1.4 \text{ g mL}^{-1}$) from Carlo Erba Reagenti and hydrochloric acid (HCl, 37%, w/w solution in water) by Riedel-De Haën, were the acids tested to achieve acidic pH in the aqueous phase.

Sodium chloride and sulphate (NaCl purity 99.9%, Na₂SO₄ purity 99.0%,) from Sigma–Aldrich were used in the aqueous phase to modulate its ionic strength acting on phenol extraction.

Iron(II) sulphate (FeSO₄·7H₂O, purity = 99%) and iron(0) in powder form (Sigma–Aldrich) were employed as catalysts.

Hydrogen peroxide (H₂O₂, 30%, w/w solution in water) from Sigma–Aldrich was used as the oxidant.

Hydrophobic polypropylene flat sheet porous membrane (Accurel, manufactured by Membrana, thickness 142 μ m; pore size 0.2 μ m; porosity 70%) was used in the membrane contactor.

2.2. Methods and apparatus

Identification of the oxidation products was performed analysing the solutions by gas chromatography mass spectrometery (GC–MS QP2010S) from Shimadzu.

Concentrations of phenol and oxidation by-products in the aqueous and organic phases were measured by high performance liquid chromatography (HPLC, Agilent 1100 Series instrument) using a GEMINI C18 (250 mm × 4.60 mm) column by UV readings at 254 nm wavelength. The mobile phase consisted of an acetoni-trile/water/acetic acid solution 50/49/1 (v/v/v) fed at a flow-rate of 1.0 mL min^{-1} . The column pressure was 110 bar and the injection volume was 20 μ L.

Ultrapure water, used throughout the work, was obtained from Milli-Q equipment by Millipore. A pH meter (WTW Inolab Terminal Level 3), with a glass pH electrode SenTix 81 (WTW), was used for pH measurements.

Experimental tests were conducted in a lab-made membrane contactor built with a two compartment cell to separate the organic phase and the aqueous reacting phase (Fig. 1).

The two compartment cells (each one with a volume of 130 mL) were separated by a flat sheet polypropylene membrane with an exposed membrane surface area of 28.3 cm². In the compartment containing the aqueous phase the catalytic reaction takes place, while in the second one, containing only benzene in the double task of stripping solution and reagent, phenol is accumulated in the time. In particular, use of benzene, as both substrate and extractant, avoids use of other organic solvents with benefit in product recovery.

The phases were stirred by two motors and thermostated by a water bath at $35 \,^{\circ}$ C. This value was chosen on the basis of the results

obtained in our previous work [15]. Samples of organic phase were periodically withdrawn and analyzed. The aqueous phases were analyzed after quantitative extraction with diethyl ether at the end of the catalytic tests.

In every test the aqueous phase contains 130 mL of ultrapure water, 4 mmol of catalyst and 4 mmol of acetic acid. The acetic acid was not used in the catalytic tests with different acids at constant pH. The oxidant (18 mmol total of a run) was added step by step (0.375 mmol every 5 min), last addition was done at 240 min and all run lasted 270 min.

Black solid samples were recovered at the end of the catalytic tests by filtration and weighed after being air dried. On the black solid some studies were carried out as elemental analysis and Fourier Transform Infrared Spectroscopy (FT-IR) analysis. Elemental analysis (C, H, N) was performed by the Microanalytical Service of the University of Calabria and FT-IR analysis by FT-IR spectrometer Spectrum One by Perkin Elmer.

Results of the experimental tests are reported using the following parameters:

- extraction quotient percentage $Q_E \approx (n_{org}/n_{tot}) \times 100$; where n_{org} is the mol number of phenol in the organic phase and n_{tot} is the sum of the mol number of phenol in the organic and aqueous phases;
- distribution ratio R_D = [Phenol]_{org}/[Phenol]_{aq}, which is the distribution of the compound between the two phases at the time *t*;
- phenol selectivity (%)=Ph/(Bq+Ph+Biph) × 100 where Ph, Bq and Biph are the mol numbers of phenol, benzoquinone and biphenyl, respectively, detected in the organic phase;
- phenol productivity $P = (g Ph_{org} + gPh_{aq})g_{cat}^{-1}h^{-1}$, which is the total mass (g) of phenol produced per unit mass of the catalyst per unit of time.
- Yield% = (Ph/18) × 100 where Ph is the mol numbers of phenol detected in the organic phase and 18 is the mol numbers of fed oxidant (limiting reagent).
- flux $(J_{\text{org Ph}})$ was calculated as variation of mmol of phenol in the organic phase per unit area of membrane and time (mmol m⁻² h⁻¹).

The separation performance of the membrane contactor was determined by the distribution coefficient and the flux.

2.3. Distribution coefficient

The distribution coefficient (K_D) of a component A between two phases is generally an index that characterizes the goodness of the separation. It is defined as the ratio of concentration of a component in the organic phase to its concentration in the aqueous phase of a two-phase organic/water system at equilibrium and at a specified temperature:

$$K_{\rm D} = \frac{[A]_{\rm org}}{[A]_{\rm aq}} \tag{1}$$

where $[A]_{org}$ is the concentration of the component A in the organic phase and $[A]_{aq}$ is the concentration of the same component in the aqueous phase at equilibrium.

The distribution coefficients of phenol between aqueous and benzene phases of different compositions were determined using different volume ratios of aqueous and organic phases (with a constant initial concentration of phenol in the aqueous phase) [19,20]. The phenol concentration in the organic phase was plotted as function of phenol concentration in the aqueous phase measured at equilibrium after each single extraction. The obtained equilibrium isotherm at 25 °C was a straight line passing from zero with

the slope corresponding to the distribution coefficient of phenol between the two phases.

Another important equilibrium parameter is the degree of extraction *E* defined as:

$$E\% = \frac{K_{\rm D}}{(K_{\rm D}+1)} \times 100$$
 (2)

when the values of organic and aqueous phases are equal.

It must be noted that the system studied in this work did not reach the equilibrium condition thus the parameters $Q_{E\%}$ and R_D previously defined have been used.

2.4. Flux

The transport of a component A through the membrane in a membrane contactor, from the feed phase to the permeate phase, occurs in three main steps: transport from the feed phase to the membrane interface, diffusion through the membrane and transfer from the other membrane interface to the permeate phase. Indeed, in the studied system the aqueous and organic phases are well stirred thus the liquid–liquid interfaces to both sides of the membrane and concentration polarization effects, due to accumulation of salt ions near the liquid–liquid interface, can be neglected.

The flux (J_A) of component A, expressed in terms of overall mass transfer resistance coefficient $(k_{ov,A})$, is as follows:

$$J_{\rm A} = k_{\rm ov,A} \,\Delta c_{\rm A} \tag{3}$$

with

$$\frac{1}{k_{\rm ov,A}} = \frac{1}{k_{\rm A}({\rm feed})} + \frac{1}{k_{\rm A}({\rm membrane})} + \frac{1}{k_{\rm A}({\rm permeate})} \tag{4}$$

If the mass transfer resistance in the membrane phase is dominant then Eq. (3) reduces to

$$J_{\rm A} = \frac{dC}{dt} = \frac{D_{\rm A}K_{\rm A}}{l}\,\Delta c_{\rm A} \tag{5}$$

where Δc_A is the bulk concentration difference between feed and permeate phases, *l* is the membrane thickness, D_A is the diffusion coefficient of A in the membrane pores and K_A is the distribution coefficient of component A between the feed phase and the solution into the pores of the membrane phase. In most applications of liquid/liquid extraction the lowest membrane mass transfer resistance is obtained if the pores are filled with a fluid in which the solute is highly soluble. This suggests the use of a hydrophilic or hydrophobic membrane for a low or high K_A solute, respectively. That is, a low K_A solute is more soluble in a polar solvent than in a non-polar one, and the polar solvent will wet the pores of a hydrophilic membrane, the situation is analogous for high K_A solute and a hydrophobic membrane [14].

3. Results and discussion

3.1. Distribution coefficient and extraction percentage

The effects of addition of salts in the aqueous phase on the distribution coefficient of phenol between water and benzene have been observed as comparison with the system performance without salt (water-benzene system only).

The benzene–water distribution coefficient (K_D) of phenol and its extraction percentage (E%) were determined at 25 °C using the method described above and the results are reported in Table 1. It can be observed that K_D increases significantly when Na₂SO₄ is added; in particular, the addition of 2 M Na₂SO₄ or 3 M NaCl allows an increase of the distribution coefficient more than 3 times compared with no salt addition (from 2.1 to 7.2).

The observed increase can be explained by a salt solvation phenomena. Indeed, the studied salts can be considered as strong

Table 1

Distribution coefficient and extraction percentage at 25 °C of phenol in the system water:benzene without and with salts in the aqueous phase.

	E (%)	K _D
No salt	68.0	2.1
Na ₂ SO ₄ 1 M	79.7	3.9
Na ₂ SO ₄ 1.5 M	83.4	5.0
Na ₂ SO ₄ 2 M	87.8	7.2
NaCl 1 M	77.4	3.4
NaCl 1.5 M	79.7	3.9
NaCl 2 M	83.4	5.0
NaCl 3 M	87.8	7.2
NaCl 4 M	88.0	7.3

electrolytes completely dissociable permitting the formation of more or less solvated ions. This solvation leads to a decrease in the amount of water available for solvation of phenol which acquires more affinity for organic phase thus decreasing its concentration in the aqueous phase [21,22].

The obtained data indicate that using salts dissolved in the aqueous phase it is possible to transport phenol in the organic phase at higher flux (according to Eq. (5)) thus avoiding its subsequent oxidation.

3.2. Catalytic tests using dissolved salts in the aqueous phase

The catalytic tests, performed in the membrane contactor using sodium sulphate (at concentrations of 1, 1.5 and 2 M) and sodium chloride 4 M, were monitored for 240 min. The results (Table 2) were compared using the parameter Q%, R_D , selectivity%, phenol productivity, yield%, phenol flux and amount of black solid.

From Table 2 it is seen that using a greater amount of Na₂SO₄, dissolved in the aqueous phase, a greater amount of phenol is recovered in the organic phase (Q% = 83.7%), according to the previous results of liquid–liquid extraction. Despite this advantage the other effects of salt addition on the catalytic reaction were negative concerning selectivity, productivity, yield% and flux. Indeed the phenol productivity decreased from 0.64 to 0.30 g_{ph} g_{cat}⁻¹ h⁻¹ using sodium sulphate from 1 M to 2 M, respectively. This behaviour could be explained by the work of Le Troung et al. [23] where the authors studied the effects of sulphate ion on the oxidation rate of ferrous ion by H₂O₂ showing that in presence of sulphate the oxidation rate of Fe(II) was faster and also depended on the sulphate concentration Furthermore, the sulphate ion may have an effect on the efficiency of Fe(II)/H₂O₂ and Fe(III)/H₂O₂ systems owing to sulphate complexes formation with Fe(II) and Fe(III) [24].

This means that reduction of phenol productivity was probably caused by an increase of phenol degradation to other by-products. As a result, also tar formation increased by increasing the sodium sulphate concentration while phenol concentration, yield% and selectivity decreased.

In the catalytic test with NaCl 4 M a further reduction of selectivity, productivity and flux was observed. The chloride ion also increased the oxidation rate of Fe(II) [23] but, in the present study, biphenyl was not produced and an almost equal amount of phenol (selectivity = 53%) and benzoquinone, was obtained. The high value



Fig. 2. Concentrations of detected products at the end of a run in aqueous and organic phases using H_2SO_4 . (Operative condition: T=35 °C; H_2O_2 = 18 mmol; catalyst = 0.4 mmol FeSO₄; pH = 2.8; run time = 270 min).

of Q% (95.5%) reported in Table 2 when using NaCl is misleading: it was caused by a disappearance of phenol in the aqueous phase to form benzoquinone and not by an increase of extraction in the organic phase.

3.3. Catalytic tests at different pHs and different acids

Some catalytic tests at different pHs were carried out by using sulphuric acid to change the pH of the aqueous phase from the value of 2.8, obtained with 4 mmol of acetic acid alone, to 1.5, 1.1 and 0.8, respectively. The acetic acid has been used in many works which study the benzene oxidation to phenol as it is considered a co-catalyst in the Fenton reaction [5,9]. Indeed, also in our previous work [15] the high phenol production (1560 mg) was obtained when acetic acid was used at pH 2.8. This co-catalyst did not avoid tar formation thus, in the present work, a study on the combined effect of the co-catalyst and an inorganic acid at different pHs has been performed.

Other oxidation tests were carried out to investigate the influence of anion type of the acid (HCl, HNO_3 and H_2SO_4) on tar formation.

From Fig. 2 it can be observed that too acidic condition (pH=0.8) slow down the reaction kinetics reducing both phenol and by-

Table 2

	Results of	catalytic	tests with	salts at	different	concentrations
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Salts	Q(%)	R _D	Selectivity (%)	Productivity $(g_{ph} g_{cat}^{-1} h^{-1})$	Yield%	Flux (mmol $h^{-1} m^{-2}$)	Amount of black solid (g)
Na ₂ SO ₄ 1 M	76.3	3.2	91	0.64	13.2	188.5	0.27
Na ₂ SO ₄ 1.5 M	76.3	3.2	90	0.40	8.1	116.2	0.47
Na ₂ SO ₄ 2 M	83.7	5.1	88	0.30	6.8	97.3	0.70
NaCl 4 M	95.5	-	56	0.07	1.8	25.8	0.17

Operative condition: T = 35 °C; H₂O₂ = 18 mmol; catalyst = 0.4 mmol FeSO₄; pH = 2.8 with 4 mmol of acetic acid; run time = 270 min.

344 **Table 3**

Results of catalytic tests at different pHs.

рН	Q(%)	Selectivity (%)	Productivity $(g_{ph} g_{cat}^{-1} h^{-1})$	Yield%	Flux (mmol $h^{-1} m^{-2}$)	Amount of black solid (g)
0.8	82.3	89	0.21	4.8	68.6	0.094
1.1	55.6	88	0.38	5.8	82.3	0.154
1.5	46.4	95	0.91	11.4	162.9	0.197
2.8	-	98	3.59	38.5	594.5	0.150

Operative condition: T = 35 °C; H₂O₂ = 18 mmol; catalyst = 0.4 mmol FeSO₄; acid = 4 mmol acetic acid and H₂SO₄ 1 M to reach the reported pH; run time = 270 min.

Table 4

Results of catalytic tests using different inorganic acids.

Type of acid	Q (%)	Selectivity (%)	$\begin{array}{l} Productivity \\ (g_{ph} g_{cat}^{-1} h^{-1}) \end{array}$	Yield%	Flux (mmol $h^{-1} m^{-2}$)	Amount of black solid (g)
HCl	71.5	71	0.15	2.9	41.6	0.195
HNO ₃	75.1	80	0.05	1.1	15.0	0.234
H_2SO_4	79.4	75	0.08	1.7	23.9	0.598

Operative condition: T = 35 °C; $H_2O_2 = 18$ mmol; catalyst = 0.4 mmol FeSO₄; pH = 2.8 adding 1 M acid solution; run time = 270 min.



Fig. 3. Detected products and selectivity% in the organic phase versus the time in the catalytic tests using nitric acid. (Operative condition: T=35 °C; $H_2O_2=18$ mmol; catalyst=0.4 mmol FeSO₄; pH=2.8; run time=270 min).

Table 5

Results of catalytic tests stopped when a cloudy solution appeared.

Catalytic medium	Q(%)	Selectivity (%)	$Productivity(g_{ph}{g_{cat}}^{-1}h^{-1})$	Yield%	Flux (mmol $h^{-1} m^{-2}$)	Stopped time (min
FeSO ₄ 4 mmol + Na ₂ SO ₄ 2 M	59.9	66	0.88	1.8	25.4	30
FeSO ₄ 4 mmol	44.1	95	1.98	8.8	126.2	80
FeSO ₄ 1 mmol	75.6	96	1.90	10.7	152.6	240

pH = 2.8 using 4 mmol acetic acid.

products concentration as well as black solid amount (Table 3). At higher pH (1.1 and 1.5) process performance improves compared to pH 0.8, but the amount of black solid increases giving values higher than that obtained at pH 2.8 with acetic acid alone. Thus this last acid gives best results on reduced tar formation and improves selectivity, productivity, yield and flowrate compared to the inorganic acid.

In Table 4 the influence of the anion type of the mineral acid on tar formation, operating at pH 2.8, is reported. It should be noted that acetic acid was not added and that effect of the inorganic anions is a general decrease of the selectivity promoting over oxidation products (tar formation) compared to the presence of acetic acid alone (see Table 3). The sulphate anion gave the worst performance promoting the formation of black solid (0.598 g) at the expense of phenol productivity (0.08 $g_{ph} g_{cat}^{-1} h^{-1}$) and selectivity (75%).

The hydrochloric acid in the acidic aqueous phase generates chloride that leads to the formation of the FeCl⁺ complex and various chlorinated inorganic radicals. Among these ones, the dichloride radical anion Cl₂•⁻, which is predominant in the presence of millimolar concentrations of chloride, is a strong electron acceptor [23]. Thus a greater loss of selectivity and phenol productivity is observed although tar formation did not increase.

Similar behaviour was obtained when nitric acid was used. The concentration trend of phenol (Fig. 3) showed a very slow initial increase and then reached a plateau. This behaviour can be caused by the nitrate anion which is a good electron acceptor and compete with the catalyst regeneration as can be seen by the higher standard



Fig. 4. Detected products in the aqueous phase (a) and in the organic phase (b) in the stopped catalytic tests using different concentrations of catalyst and presence of sodium sulphate. Numbers on the bars indicate concentrations of products in mg/L. (Operative condition: $T = 35 \degree C$; $H_2O_2 = 18$ mmol; catalyst = 0.4 mmol FeSO₄; pH = 2.8 using 4 mmol of acetic acid).



Fig. 5. Concentration of phenol, benzoquinone and biphenyl and phenol selectivity in the time in the catalytic tests using suspended powder iron(0) at pH 2.8. (Operative condition: *T* = 35 °C; H₂O₂ = 18 mmol; catalyst = 0.4 mmol Fe(0); pH = 2.8 with 4 mmol of acetic acid; run time = 270 min).

Table 6

Results of catalytic tests using suspended powder of Iron(0).

Catalyst	Q(%)	Selectivity (%)	Productivity $(g_{ph} g_{cat}^{-1} h^{-1})$	Yield%	Flux (mmol $h^{-1} m^{-2}$)	Amount of black solid (g)
Iron(0)	66.1	94.3	8.11	12.7	181.0	0.13

Operative condition: T = 35 °C; H₂O₂ = 18 mmol; catalyst = 0.4 mmol Fe(0); pH = 2.8 using 4 mmol acetic acid; run time = 270 min.



Fig. 6. Further oxidation reactions of phenol.

(Elaborated from Bremner, 2006 [26]).

potential of nitrate:

 ${\rm Fe}^{3+} + {\rm e}^- \rightarrow ~{\rm Fe}^{2+}~~(E^\circ~=~0.77\,{\rm V})$

 $2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$ ($E^\circ = 1.25V$)

 $Cl_2^{\bullet^-} + e^- \rightarrow 2Cl^- \quad (E^\circ = 2.09 V)$

Also the dichloride radical anion $Cl_2^{\bullet-}$, with an high standard potential, can compete with the catalyst regeneration. Probably it reacts also with organic substances in the solution [23] and then



Fig. 7. FT-IR analysis in ATR (Attenuated Total Reflectance) of black solid.

the catalyst deactivation was not evidenced as in the case of nitric acid. Taking into account the above considerations the combined effect of nitrate-acetic acid and chloride-acetic acid was not tested experimentally.

3.4. Catalytic tests stopped before tar appearance

Some oxidation tests were carried out to stop the reaction just before the black precipitate appearance in order to analyze the composition of the aqueous phase when it started to become turbid. The results (Table 5) evidenced that precipitate formation was not caused by saturation of an oxidation product (in Fig. 4 no particular increase of benzoquinone and biphenyl is observed) and that black solid appears at very different reaction times depending on the composition of the catalytic medium. Indeed, in the tests carried out using 4 mmol FeSO₄ and 2 M Na₂SO₄ the time of black appearance was 30 min while using 4 mmol FeSO₄ and 1 mmol FeSO₄, without the salt, the appearance time was 80 and 240 min, respectively. Thus, a higher initial amount of sulphate anion in the aqueous phase causes solution clouding in lower time confirming that this anion is involved in the black solid formation.

3.5. Catalytic tests using iron(0)

The last aspect studied in this work was the use of suspended powder Fe(0) as catalyst to investigate the difference of the catalytic performance compared to the sulphate anion present in the reaction system when FeSO₄ was used. The classical Fenton oxidation process utilizes the reaction of iron(II) with hydrogen peroxide to generate hydroxyl radicals, which then give chemical oxidation or degrade organic pollutants. Recently, an advanced Fenton process (AFP) has been described, which uses metal iron surfaces in acidic conditions in conjunction with hydrogen peroxide to generate hydroxyl radicals [25,26]. The corrosion of the metal iron generates in situ ferrous iron giving rise to a potent Fenton-type reaction. Particular advantages of this process are the cost-savings owing to the use of metal iron rather than iron salts.

The results of the tests carried out using Fe(0) as catalyst in terms of products detected in the organic phase are reported in Fig. 5. The increasing phenol concentration in the time and an almost constant and very low concentration of benzoquinone and biphenyl can be observed.

In Table 6 the results indicate enhanced values of phenol productivity $(8.11 g_{ph} g_{cat}^{-1} h^{-1})$ and flux $(181.05 \text{ mmol } h^{-1} \text{ m}^{-2})$ maintaining a good selectivity (94.3%) and a fairly good phenol recovery in the organic phase (66.1%).

Despite the improved results, the sulphate absence did not avoid completely the black solid formation, but only gave its decrease. It must be noted that the ratio productivity/amount of black solid changes significantly: it is 62.4 using Fe(0) as catalyst compared to a value of 4.6 using iron sulphate (at pH 1.5 in Table 3).

Thus the black solid amount increased with the sulphate presence as it is confirmed by the work of Bremner et al. [26] who indicates that one of the compounds present in the black solid is a complex of iron (Fig. 6) which contains $C_6H_6O_4$, H_2O and sometime also sulphate.

FT-IR analyses, reported in Fig. 7, confirm the presence of $C_6H_6O_4$ in the mixture of the black solid. Indeed, infrared spectroscopy with a wide band between 2500 and 3300 cm⁻¹ indicates the presence of OH groups such as the OH stretching at 3373 cm⁻¹

generated by the presence of intermolecular hydrogen bonds and the C=C bonding, which is indicative of the presence of aromatic ring, generated by the signal at around 690 cm^{-1} . Other functional groups are present as the group C=O which absorbs at 1770 cm^{-1} .

The elemental analysis of tar on an instrument that was able to analyze only C, N and H gave: C = 63.92% and H = 3.36%. The difference could be mainly attributed to oxygen. These values are only indicative because the tar is a complex mixture of various compounds [26] and an "*ad hoc*" study should be carried out to find the exact composition.

4. Conclusions

The effects of salts, pH, type of acids and anion sulphate in the synthesis of phenol through the hydroxylation of benzene using a membrane contactor and a catalytic Fenton system have been investigated. The best results were obtained using powder of iron(0) as catalyst. Indeed a phenol concentration of 1650 mg/L in the organic phase and of 845 mg/L in the aqueous phase was obtained recovering 66.3% of phenol with a selectivity of 94.3% and a transmembrane flux of 181.05 mmol h^{-1} m⁻².

The sulphate absence, obtained by using iron(0), did not avoid tar formation but it was the only cause of its decrease giving a significant increase of the ratio productivity/amount of black solid (from 4.6 to 62.4).

Further studies will be devoted to test other catalysts that will avoid or reduce tar compounds and enhance phenol formation and recovery using also different membrane configurations.

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