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Direct benzene conversion to phenol in a hybrid photocatalytic membrane reactor

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ABSTRACT

The one-step conversion of benzene to phenol in a photocatalytic membrane reactor (PMR) coupling simultaneous reaction and product separation by means a membrane contactor is reported.

The effects of parameters such as pH of aqueous TiO_2 suspensions, initial amount of benzene and catalyst concentration were investigated in the batch tests. L–L extraction experiments and transport tests, using benzene as organic extractant, showed a phenol distribution coefficient of 2.1 and an extraction percentage of $24 \pm 2\%$, assuring, also, a constant feed of substrate in the reactive environment. Phenol production and separation was carried out in the PMR investigating the influence of pH and catalyst concentration on the performance of the system. Despite a negligible difference on the phenol flux in the benzene phase (1.16 ± 0.11 mmol h^{-1} m^{-2}), a better control of formation and extraction of oxidation intermediates at pH of 3.1 was obtained. To enhance the performance of the system, photocatalytic experiments with dissolved ions (Fe^{3+}, Cu^{2+} and V^{3+}) were carried out. The results showed a positive effect in presence of iron(III) ion with a phenol flux in the organic phase almost two times greater than those measured without salts.

1. Introduction

Traditional processes for making chemicals are today unsustainable in terms of resources and environmental impact. In this context the application of innovative scientific solutions to solve these problems is the main aim of the Green Chemistry, as reported by several authors [1–4]. "Green" characteristics make photocatalysis an attractive process, such as use of safer photocatalysts, e.g. TiO_2 which is a component of pharmaceuticals and toothpastes; use of mild oxidants (molecular oxygen); possibility to work with mild conditions running reactions closer to room temperature and pressure; request of very few auxiliary additives; no production of harmful chemicals.

These potentialities are further improved when a photocatalytic route is coupled to a membrane separation technique. Photocatalytic membrane reactors (PMRs), in fact, allow a continuous one-step process in which the low catalyst and solvent amounts, the minimization of purification steps and a better control of the equilibrium reactions can be achieved, avoiding large amounts of waste products generally formed during a multistep process. Besides, a continuous reactor can be much smaller than the corresponding batch reactor and the use of an appropriate membrane can allow to remove continuously higher purity products.

Due to the highly unselective reactions involved in the photocatalytic processes, the application of these technologies was addressed mainly to the removal of hazardous compounds in liquid and gas phases. However, selecting or modifying some photocatalytic parameters, such as the semiconductor surface or the wavelength, it is possible to control the reaction route obtaining a better selectivity towards some products and, on this respect, in the last years, many efforts have been devoted with the aim to modify the classical semiconductor materials or synthesize new photocatalysts [5,6].

On the contrary, regards to the reactor configuration, as observed by Choi [7], few studies have been performed for the design of efficient photoreactors for commercial exploitation [8]. In particular, one of the main drawbacks concerns the recovery of the catalyst and/or the separation of products from the reactive environment.

Several immobilized systems in which the catalyst was coated on the walls of the reactor, supported on a solid substrate or deposited around the case of the light source, were proposed [9–11]. Nevertheless, as widely demonstrated in literature [12–14], the suspended systems seem to be more efficient than those based on immobilized catalysts.

Another important aspect which limited practical application of photocatalytic processes is the selective separation of products or/and intermediates from the reactive environment. Although separation systems such as distillation or precipitation can be useful to separate the final mixture, these techniques, involving further treatment steps, do not allow to operate in continuous mode.

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A very promising approach to overcome these photocatalytic drawbacks is the use of PMRs in which a synergic effect can be obtained combining the advantages of classical photoreactors (catalyst in suspension) and those of membrane techniques (one-step separation) [15–17].

In these systems, the choice of the membrane module configuration is mainly determined by the type of photocatalytic reaction and the membrane can assume many roles in the system, as catalyst recovery, separation of the products, rejection of the substrate, etc.

Besides, when the photocatalytic process was used as a synthetic pathway the use of an appropriate membrane [18,19] can allow the selective separation of the product minimizing its secondary oxidation reactions which lead to undesirable by-products. Although these potentialities, the research in the field of PMRs remains still insufficient.

In this context, aim of our studies was to demonstrate the possibility to use a membrane photoreactor for organic syntheses, developing a hybrid system in which the selective photocatalytic reaction and the separation of the product of interest occur in one step.

In particular, this work reports the results obtained in a photocatalytic membrane contactor (PMC), using TiO_2 as suspended catalyst, for the one-step synthesis of phenol and its simultaneous separation. The study of this reaction, through the photocatalytic approach, is interesting both as model reaction and an industrial point of view [20,21]. In this system the separation is performed using benzene as both reactant and extraction solvent and a polypropylene membrane to separate the organic phase from the aqueous environment according to our previous works [22,23].

Particular attention was addressed to some aspects related to the photocatalytic reaction (catalyst concentration, initial amount of substrate, pH) and to the membrane module (breakthrough pressure, extraction efficiency) which affect the synthesis and separation of phenol and oxidation by-products. These results were then used to run the PMC in the photooxidation of benzene to phenol and its extraction from the reactive environment. Some preliminary results on the use of metal salts ($FeCl_3$, $CuCl_2$ and VCl_3) in solution to enhance the photocatalytic efficiency and the extraction of phenol are also reported [24–27].

2. Experimental

2.1. Materials

TiO_2 Degussa P25 type (specific surface area = 44 $m^2 g^{-1}$, crystallographic phase ca. 80% anatase and 20% rutile, band gap 3.2 eV) was used as photocatalyst. TiO_2 X500 (100% anatase, band gap 3.2 eV) and TiO_2 C380 (100% anatase, band gap 3.2 eV), from TitanPE technology (Shanghai) were also tested as photocatalysts.

Benzene (C_6H_6, purity 99.8%) from Carlo Erba Reagenti was used both as substrate and as organic 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%), catechol $C_6H_6O_2$, purity 99.5%) from Sigma–Aldrich were used for analytical calibrations.

Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) from Fluka, copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$) and vanadium(III) chloride (VCl_3) from Aldrich were used in the photocatalytic tests with dissolved ions.

Hydrophobic polypropylene porous membrane (Accurel, manufactured by Membrana, thickness 142 μm; pore size 0.2 μm; porosity 70%) was used in the membrane reactor.

Sodium hydroxide (NaOH, purity 98%) from Sigma, hydrochloric acid 37% (w/w) (HCl) from Riedel-de Haen and sulphuric acid (H_2SO_4) from Carlo Erba were used to correct the pH of aqueous phases.

2.2. Methods

The identification of the oxidation products was performed analysing the solutions by gas chromatograph mass spectrometer (GC–MS QP2010S) from Shimadzu.

Phenol and oxidation by-products concentrations 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. The mobile phase consisted of an acetonitrile/water/acetic acid solution 50/49/1 (v/v) fed to a flow-rate of 1.0 mL min^{-1}. The column pressure was 110 bar and the injection volume was 20 μL.

All the aqueous samples were filtered by means of a low-adsorbing hydrophilic polypropylene membrane (Pall Corporation, mean pore size 0.2 μm) before carrying out the analyses.

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.

The UV light intensity I was measured by a UVX Digital Radiometer (from UVP).

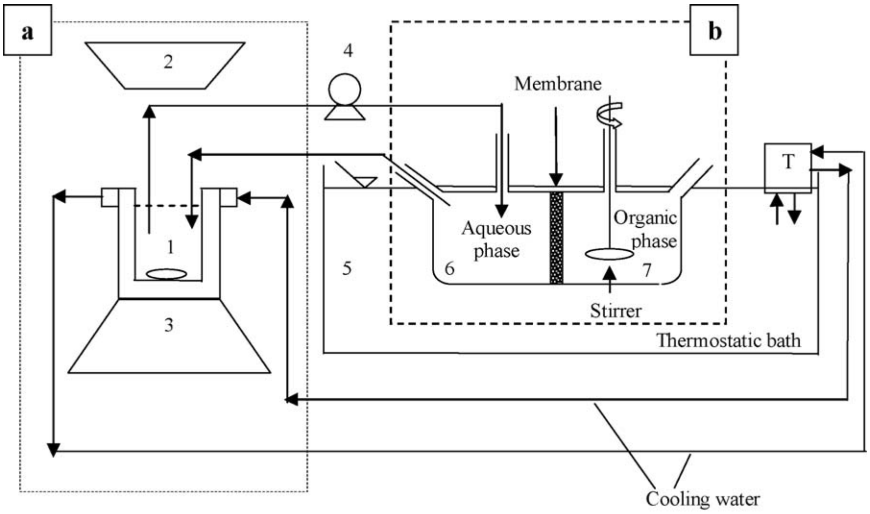

Fig. 1. System set-up: photocatalytic reactor (a) coupled with the membrane contactor (b); (1: batch reactor, 2: UV lamp, 3: magnetic stirrer, 4: peristaltic pump).

2.3. Apparatus

The preliminary tests and the batch photooxidation experiments were carried out in the system described in Fig. 1a, excluding the membrane zone.

This part of the system set-up is constituted by a batch reactor (1) equipped with a Pyrex glass jacket surrounding it which allows to maintain the system at a temperature of 25 °C.

Above the reactor is placed a 500 W medium pressure Hg lamp (Helios Italquartz) emitting a light intensity in the UV–vis range (maximum centred at $\lambda = 366$ nm with the emission profile between 240 and 440 nm) equal to 6.0 mW cm^{-2} (2). The reactive solution, magnetically stirred (3), was constituted by 500 mL of ultrapure water containing the suspended catalyst and the substrate to oxidize.

When the membrane module was used, the photocatalytic experiments were performed in the whole system reported in Fig. 1. It was made by coupling the membrane contactor module to the batch photocatalytic reactor by means of a peristaltic pump (4) that withdraws the solution from the photocatalytic zone to the separation zone. The retentate comes back in the photoreactor by gravity.

The permeation module, immersed in a thermostatic bath (5), is constituted by two compartment cells (each one with a volume of 130 mL) separated by a flat sheet polypropylene membrane with an exposed membrane surface area of 28.3 cm^2. The first compartment (6) contains the aqueous phase coming from the photoreactor where the reaction was carried out, while the second one (7) contains an organic stripping solution, constituted by benzene, mechanically stirred by a motor. Samples were periodically withdrawn from the two phases and analysed.

3. Results and discussion

3.1. Photocatalytic oxidation in the batch reactor

By means of photolysis tests and "dark" reactions, on benzene solutions in absence of the catalyst or UV light, respectively, no oxidation products were detected. They were, instead, found when the oxidation reaction proceeded via a photocatalyzed mechanism.

To investigate the influence of pH, catalyst concentration and presence of O_2 on the conversion of benzene to phenol in the photocatalytic system some photooxidation experiments in the batch reactor were performed. The tests were carried out in the reactor of Fig. 1a (without the membrane) adding to 500 mL of ultrapure water the catalyst and benzene and varying one parameter for each run.

One important drawback observed in the open batch reactor was to maintain a useful concentration of benzene in solution because of its tendency to rapidly vaporize. For this reason it was established to work in presence of an excess of substrate that permitted to maintain its concentration in the reactive ambient until the end of a run. On this basis, photooxidation tests were carried out using three different initial volumes of benzene, 1 mL (which corresponded to the amount equal to its solubility in water, 1.77 g L^{-1}), 5 and 10 mL.

The obtained results (Table 1) showed an oxidation rate quite the same in the first 100 min ($r_{\text{Phenol (100)}}$), but it was lower with 1 mL of substrate. This finding can be explained considering the concentration of benzene in solution which resulted of about 350 ± 50 mg L^{-1} with 5 and 10 mL vs 40 ± 10 mg L^{-1} with 1 mL after 3 h. The phenol production, therefore, did not depend on the undissolved substrate but from the little solubilised amount, evidencing the need to use a system that provides continuously benzene in order to maintain a constant concentration in the aqueous ambient.

Table 1
Comparison of the results obtained in the batch experiments.

Operative parameter	$r_{\text{Phenol (100)}}$ mg L^{-1} min^{-1}	$C_{\text{Phenol (240)}}$ mg L^{-1}
Initial substrate amount (mL)		
1 mL (1.77 g L^{-1})	0.102	10.9
5 mL	0.126	15.46
10 mL	0.126	17.09
TiO_2 concentration (g L^{-1})		
0.01	0.060	9.23
0.1	0.126	15.46
0.5	0.139	17.79
1	0.185	21.39
pH		
11	0.128	20.23
5.5	0.126	15.46
3.1	0.094	14.45
3.1 (H_2SO_4)	0.122	18.65
O_2 bubbled	0.121	15.32

Several studies showed that the photocatalytic reaction rate depends on the catalyst concentration, though it was observed that above a certain value the reaction rate becomes independent on the catalyst mass [28]. Indeed, for high amounts of catalyst, aggregation of particles, increase of opacity and light scattering decrease the photocatalytic efficiency. Therefore, an optimal catalyst concentration value is necessary for controlling the performance of the system.

A set of experiments, employing a benzene amount of 5 mL, were carried out to investigate the effect of the suspended catalyst on the phenol production using TiO_2 in a concentration range of 0.01–1 g L^{-1}.

Observing the rate values (see Table 1) it can be noticed that the reaction rates increased with increasing TiO_2 concentration. Besides, from Fig. 2a it was observed that for the catalyst amounts equal to 0.1, 0.5 and 1 g L^{-1}, the phenol concentration reached a maximum value and then decreased owing to a consecutive reaction of phenol. In Fig. 2b the results of phenol production in terms of the optical thickness of the photoreactor, τ, are also reported. This dimensionless parameter was calculated as $\tau = \mu\delta c$, where μ is the absorption coefficient, δ is the thickness of the reaction space (0.125 m) and c is the photocatalyst concentration (kg m^{-3}) [29]. The value of μ is a function of the catalyst concentration and the extinction coefficient ($\sigma + k$) that for TiO_2 Degussa P25 is 1296 m^2 kg^{-1} [30]. The obtained data show that

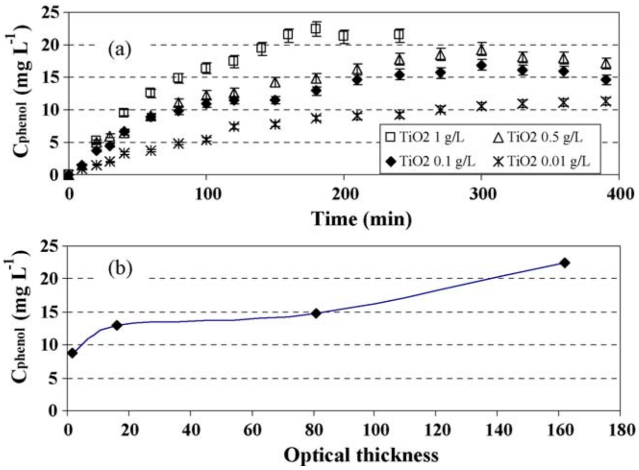

Fig. 2. Phenol concentrations vs the time (a) and the optical thickness at a run time of 180 min (b) at different catalyst amount (pH 5.5, $I = 6.0$ mW cm^{-2}, $T = 25$ °C).

working at high optical thickness an increase in the phenol concentration is observed. Nevertheless, in order to couple a membrane with the photocatalytic system, a low catalyst concentration permit to reduce the fouling phenomena and give better working of the pump.

The pH is another important parameter which influences the photocatalytic process leading to the formation of different reaction products because of the acid–base character of TiO_2.

This effect was studied by adding to the aqueous suspension of TiO_2 and benzene at initial pH 5.5, a diluted solution of HCl or NaOH.

Although the obtained results showed a similar initial oxidation rate, a significant increase of phenol concentration at alkaline pH (Table 1) was observed after the second hour, reaching a productivity ($0.023\ g_{Ph}\ g_{cat}{}^{-1}\ h^{-1}$) at 360 min almost two times greater than the acidic pH ($0.014\ g_{Ph}\ g_{cat}{}^{-1}\ h^{-1}$). This evidence can be explained by considering a lower phenol adsorption on the catalyst surface, as reported in literature by Bekkouche et al. [31], with a consequent decrease of its photodegradation.

Moreover, using sulphuric acid to reduce the pH, it was observed that the oxidation was also influenced by the type of anions in solution. In particular, sulphate ion increased the initial rate and the productivity but it reduced the selectivity of the process, leading to the formation of several oxidation by-products that were revealed as intermediate peaks to the HPLC chromatograms.

Finally, in order to verify if in our system the oxygen guaranteed from the air contacting the surface represents the limiting reagent in the oxidation reactions, a set of experiments were performed in the same conditions previously described (pH 5.5, $TiO_2 = 0.1\ g\ L^{-1}$, $C_6H_6 = 5$ mL, $I = 6.0\ mW\ cm^{-2}$) and bubbling oxygen at 0.2 bar during the run. In a photocatalytic system, molecular oxygen acts as electrons acceptor avoiding the charge recombination that leads to a reduction of the photocatalytic efficiency. Besides, its reduction leads to superoxide ions which give other reactive radicals involved in the oxidation reactions. The trends of phenol concentration with and without added oxygen were similar with an initial rate of phenol production of 0.121 vs 0.126 $mg\ L^{-1}\ min^{-1}$, respectively. Although the oxygen from the air did not represent the limiting reagent, a more rapid decrease of benzene concentration in the reactive environment was observed when the oxygen was bubbled, probably due to a stripping effect. This behaviour was confirmed by the results of tests on benzene solutions in which the benzene disappearance led to a concentration, at 240 min, of 35.1 and 108.8 $mg\ L^{-1}$ with and without bubbling O_2 respectively.

The photocatalytic conversion of benzene to phenol was also studied using other types of titanium dioxide powder. In particular two different TiO_2 photocatalysts, X500 and C380, constituted by only anatase, at concentration of 0.1 $g\ L^{-1}$ and pH 3.1 were tested in the batch reactor. Comparing the preliminary results in terms of productivity after 360 min it was observed that the Degussa P25 type was the best catalyst, with a productivity two times greater than those obtained with the other two photocatalysts (0.014 vs $0.006\ g_{Ph}\ g_{cat}{}^{-1}\ h^{-1}$). This different reactivity is under study, after the complete characterization of these catalysts concerning surface area, light absorption and other reaction parameters.

3.2. PMC characterization

The permeation module used in this work was a liquid–liquid membrane contactor (MC) in which two phases, the reactive aqueous solution and the organic substrate (benzene), were separated by a flat sheet hydrophobic polypropylene membrane.

In this system the separation performance of phenol is determined by its distribution coefficient ($K_D = C_{org}/C_{aq}$) in the two phases. Thus, in order to verify the optimal pH value for the aqueous solution, L–L extraction tests were carried out at three different pH. As expected, the pH plays an important role in the separation due to the acidic character of phenol. At alkaline pH, in fact, phenol is in the anionic form which results less soluble in the organic solvent, negligible differences were observed, instead, in a pH range of 3–6.

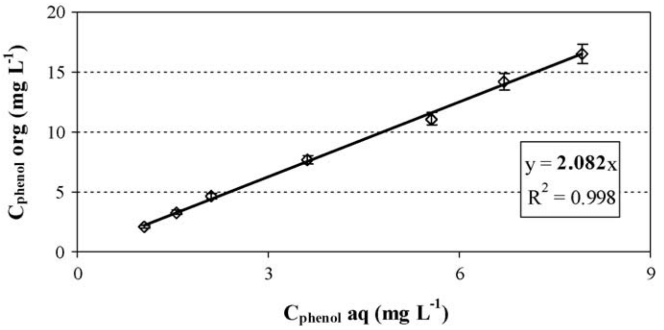

Fig. 3. Phenol extraction isotherm at 25 °C between aqueous and benzene phases.

The distribution coefficient was calculated using different volume ratios of aqueous and organic phases (with a constant initial concentration of phenol in the aqueous phase) [32]. 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 (Fig. 3) was a straight line passing from zero with the slope corresponding to the distribution coefficient of phenol between the two phases. Its value was $K_D = 2.082$ with a $R^2 = 0.998$ showing a good correlation.

Concerning the aqueous/benzene system, a low extraction percentage $E\% = (n_{Phenol\ org}/n_{Phenol\ tot}) \times 100$ of 68.04% and a low distribution coefficient was measured at acidic pH with respect to other extraction systems reported in literature [32,33]. Thus the benzene solubility in water was exploited for assuring a constant restocking of the substrate to the reactive environment avoiding, also, the presence of other organic solvents.

In the membrane contactor module the benzene filled the pores of the polypropylene membrane by capillary forces (wetting fluid). To avoid its complete passage into the aqueous reactive ambient (non wetting fluid), the pressure of the aqueous phase on the membrane surface must be maintained slightly higher. Furthermore, to maintain the benzene in the membrane pores, the pressure of the aqueous phase must be kept below a critical value known as wetting or breakthrough pressure (ΔP_b) [34] given by the Laplace equation: $\Delta P_b = (2\gamma \cos\theta)/r$, where γ is the interfacial tension, θ the contact angle and r is the pore radius.

Measuring the contact angle between benzene and the polypropylene membrane (10.292 at time zero) and knowing the interfacial tension benzene/water ($35.0\ mJ\ m^{-2}$) and the membrane pore radius (0.1 μm) the calculated breakthrough pressure was 688.8 kPa. Since the pressure of the aqueous phase on the membrane surface measured for our system was of 0.61–0.40 kPa, the requested condition resulted broadly satisfied.

Moreover, in order to verify the efficiency of the membrane system in terms of flux and extraction degree of phenol, preliminary transport tests were carried out.

The obtained results, reported in Fig. 4, showed that the equilibrium condition (K_D of about 2.0) was reached after 360 min, with a phenol extraction percentage (E%) of 24 ± 2% and a constant benzene concentration in the aqueous phase of about 200 $mg\ L^{-1}$.The flux of phenol ($J_{org\ Ph}$) in the organic phase, measured in the first 180 min, was 1.7 $mmol\ h^{-1}\ m^{-2}$.

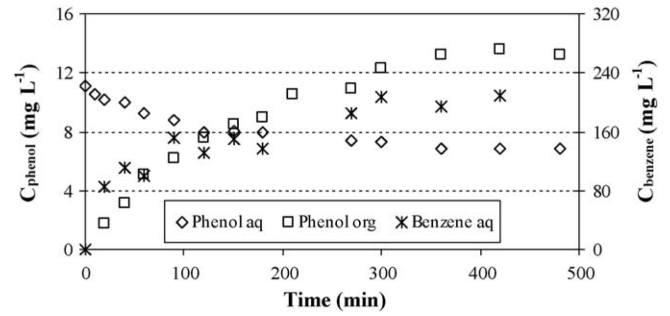

Fig. 4. Concentrations of phenol in aqueous and organic phases and benzene concentration in the aqueous phase during the transport tests.

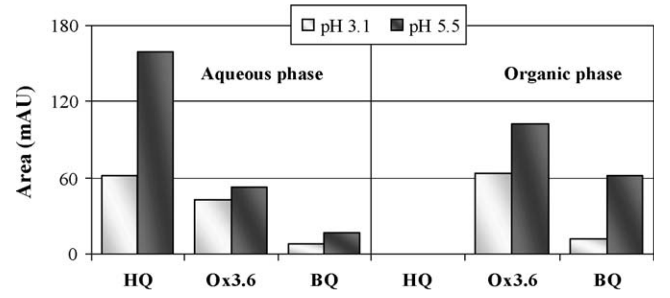

Fig. 5. Area of the intermediates in the aqueous and organic phases at pH 3.1 and 5.5.

These data confirm the possibility to use a membrane contactor for the separation of phenol from the aqueous phase, assuring, also, a constant restock of the substrate in the reactive ambient.

3.3. Photooxidation experiments in the PMC

On the basis of the obtained results, the operative conditions used in the photooxidation tests in the PMC were: 700 mL of aqueous phase at acidic pH with suspended TiO_2 at concentration of 0.1 g L^{-1} and 5 mL of benzene (to guarantee a high initial substrate concentration); 130 mL of organic phase constituted by only benzene; a pressure difference on the membrane surface water side of 0.20–0.40 kPa and a constant restocking of the substrate guaranteed from the solubility of benzene in water.

In these conditions, the influence of pH, catalyst concentration and light intensity on the overall process (synthesis and separation) was studied, considering, also, the effects of these parameters on the presence of intermediate products.

Operating in a continuous mode, the extraction equilibrium condition in these tests was not reached, therefore the distribution of phenol between the two phases was reported at the time t as distribution ratio $R_D = [\text{Phenol}]_{org}/[\text{Phenol}]_{aq}$ and the extraction efficiency was reported for this time in terms of extraction quotient percentage $Q_E\% = (n_{\text{Phenol org}}/n_{\text{Phenol tot}}) \times 100$.

Since it was observed that the pH influences not only the photocatalytic reaction but also the extraction performance in the system, a first set of experiments using acidic aqueous solution (pH 3.1 and 5.5) was performed. Although it was previously reported an increase of phenol production at pH of 10–11, in this work the alkaline environment was not used due to the lower phenol extraction obtained in these conditions.

They were obtained phenol concentrations in the aqueous and organic phases similar in the two conditions, with organic fluxes that reached constant values after 2 h (Table 2).

Although negligible differences on the phenol extraction performance of the system were observed, an important different behaviour towards some intermediates was revealed.

Three main oxidation by-products were detected as HPLC peaks at retention times of 3.0, 3.6 and 3.9 min. By GC–MS measurements on the aqueous and organic phases, hydroquinone (HQ) and *p*-benzoquinone (BQ) were identified in traces as the intermediates at retention times of 3.0 and 3.9, respectively. The other oxidation by-products reported in literature, such as catechol, *o*-benzoquinone, biphenyl, resorcinol, were not found in this system. The peak at 3.6 min was identified as 2,4-hexadienil-1,6-diol, a product which can be hypothesized deriving from the following oxidation reactions that led to the opening of the cyclic structure, though, this intermediate is actually under study.

Table 2
Comparison of the results obtained in the photooxidation experiments in the PMC at pH 3.1 and 5.5.

	$C_{aq\ Ph}$ (mg L^{-1})	$C_{org\ Ph}$ (mg L^{-1})	Q_E%	$J_{org\ Ph}$ (mmol h^{-1} m^{-2})
pH 3.1	16.27	19.04	17.86	1.27
pH 5.5	13.05	17.84	20.25	1.06

As can be observed in Fig. 5, the system permitted to maintain completely the HQ in the aqueous phase, but it was not able to reject the other by-products, which passed in the organic phase due to their greater solubility in benzene. The most acidic pH, however, allowed to obtain a lower formation and extraction of these intermediates. This finding was particularly evident for BQ and HQ and can be explained considering the equilibrium position of the reaction of conversion of HQ to BQ which is switched to the left in acidic conditions.

In the batch tests an increase of phenol concentration increasing the catalyst concentration was observed (see Table 1). However, at a value of 1 g L^{-1}, the high reactivity of the system led, also, to a quick degradation of phenol. The use of an extractive system coupled to the photocatalytic synthesis can allow to solve the problem of the secondary reaction, minimizing the phenol degradation. Therefore, the performance of the PMC was also studied using a catalyst concentration of 1 g L^{-1}. The results obtained in these tests showed an increase in the reaction rates, with a flux of 1.70 mmol h^{-1} m^{-2}. Nevertheless, the lower system productivity obtained after 480 min (0.002 $g_{Ph}\,g_{cat}^{-1}\,h^{-1}$) with respect to that measured with a TiO_2 concentration of 0.1 g L^{-1} (0.017 $g_{Ph}\,g_{cat}^{-1}\,h^{-1}$), led to consider this last catalyst concentration the best operative condition considering also the reduction of fouling and the improved pump operation of the membrane system.

To decrease the system reactivity and to enhance the separation of phenol before its successive oxidation, a test using a lower light intensity with 0.1 g L^{-1} photocatalyst was also performed. As expected, a lower irradiation intensity (4.7 mW cm^{-2}) led to a decrease in phenol production with a $J_{org\ Ph}$ of 0.85 mmol h^{-1} m^{-2} and a productivity of 0.012 $g_{Ph}\,g_{cat}^{-1}\,h^{-1}$ after 8 h, maintaining a Q_E% value (18.66%) similar in both cases which means the same efficiency of the extraction rate of phenol in the aqueous phase.

The advantage in the coupling a membrane to the photocatalysis was evidenced comparing the data obtained in the PMC with those in the batch photoreactor. In the first one an increase of 40% of produced phenol amount (13.9 vs 9.9 mg) was observed.

3.4. Effects of dissolved ions on the PMC performance

As reported by several studies [24,25], dissolved metal ions influence the photocatalytic reactions because, when they are used in their higher oxidation state, they act as photoelectron acceptors preventing the charge–carrier recombination ($M^{n+} + e^- \rightarrow M^{(n-1)+}$). Moreover, the reduced species can react with H_2O_2, formed during

Table 3
Results obtained in the photooxidation experiments in the PMC in presence of dissolved metal ions.

	No salt	$FeCl_3$	$CuCl_2$	VCl_3
Produced (mg)	13.86	20.94	7.31	7.74
Extracted (mg)	2.48	4.62	1.26	1.63
R_D	1.17	1.52	1.12	1.44
Q_E%	17.86	22.06	17.19	21.12
Productivity ($g_{Ph}\, g_{cat}^{-1}\, h^{-1}$)	0.0173	0.0262	0.0091	0.0097
$J_{org\ Ph}$ (mmol $h^{-1}\, m^{-2}$)	1.27	2.12	0.64	0.85

the reaction [26,27] to give additional $^{\bullet}OH$ by photo-Fenton reaction ($M^{(n-1)+} + H_2O_2 \rightarrow M^{n+} + {}^{\bullet}OH + OH^-$).

To enhance the performance of the PMC, photocatalytic tests with dissolved metal ions (Fe^{3+}, Cu^{2+} and V^{3+}) at concentration 1 mM were performed investigating their effects on the efficiency and separation performance of the system.

Comparing the achieved results with those obtained with only TiO_2 (Table 3) it can be observed a positive influence in presence of ferric ion but inhibition effects with dissolved Cu^{2+} and V^{3+}. As demonstrated by Brezova et al. [24], the decrease of photocatalyst activity with cupric ions can be explained supposing its reduction into the unreactive form Cu^0 and its deposition on the TiO_2 surface.

Regarding the separation performance, an increase of the phenol extraction percentage with Fe^{3+} and V^{3+} was obtained, while no influence was observed in presence of Cu^{2+}. This aspect was probably due to an enhanced ionic strength of the aqueous phase with $FeCl_3$ and VCl_3 which affects positively the phenol extraction in the organic phase.

Although the lower productivity obtained with vanadium cation, a positive effect in terms of selectivity was observed with the formation of the only intermediates at retention time of 3.6 min as oxidation by-products. This aspect will be studied in the future.

4. Conclusions

The photocatalytic tests in the batch reactor showed that increasing the catalyst concentration the reaction rates increase although with a C_{TiO_2} of 1.0 g L^{-1} a quick degradation of phenol was observed. Alkaline pH allowed to obtain a higher phenol concentration (20.2 vs 15.0 ± 0.5 mg L^{-1} in acidic conditions) due to a lower phenol adsorption on the catalyst surface which reduced its degradation. An initial excess of benzene was necessary to guarantee enough amount of substrate for the reaction, while no influence on the reaction rate was observed bubbling oxygen in the reactive environment.

L–L extraction tests and mass transport experiments showed that use of benzene as organic phase in the role of solvent (other than substrate) allowed the separation of phenol from the aqueous ambient with a K_D which reached a value of 2.1, providing also a constant restocking of substrate (about 200 mg L^{-1}) in the aqueous phase.

The PMC allowed to obtain the phenol production and its separation, although the formation of intermediate oxidation by-products, like benzoquinone, hydroquinone and other oxidized molecules was observed.

The reduction of pH to 3.1 did not influence significantly the system productivity with $J_{org\ Ph}$ of 1.27 mmol $h^{-1}\, m^{-2}$ with respect to 1.06 mmol $h^{-1}\, m^{-2}$ at pH 5.5. Nevertheless, the most acidic condition permitted to control the selectivity towards the intermediates, allowing to obtain a lower formation and extraction of these oxidation by-products.

Despite the enhancement of system reactivity by increasing the catalyst concentration, a little increase of the phenol flux in the organic phase was observed. However, the productivity of the system decreased of one order of magnitude leading to a less interesting operating condition.

Use of dissolved metal ions, like Fe^{3+}, Cu^{2+} and V^{3+}, to improve the system productivity showed an increase in the phenol production only using iron(III) ion, whereas an inhibiting influence with the other two cations was observed. Regards the separation performance of the system, the enhanced ionic strength of the aqueous phase, with $FeCl_3$ and VCl_3 allowed to reach a R_D of 1.52 and 1.54, respectively, in comparison to a value of 1.17 obtained without salts.

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