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Synthesis of polymer-supported copper complexes and their evaluation in catalytic phenol oxidation

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ABSTRACT

Polymer-supported metal complexes have been used as catalysts for the catalytic wet hydrogen peroxide oxidation (CWPO) of phenol. The synthesis of six catalysts derived from three polymer-supports (a polybenzimidazole resin and two poly(styrene-divinylbenzene) resins) and two Cu(II) salts. The catalytic oxidation of phenol with initial phenol concentration of 1 g L^{-1} was performed in a 200 mL batch stirred tank reactor at 30 °C and atmospheric pressure. Under these conditions, phenol conversion and total organic carbon conversion were evaluated. The highest phenol conversion was 93% obtained for poly(DVB-co-VBC) functionalised with iminodiacetic acid (IMDA) and loaded with copper acetylacetonate, however metal leaching was very unsatisfactory. If metal leaching was taken into consideration, it was found that polybenzimidazole loaded with copper sulphate appeared to be the most stable yielding 54% of mineralisation and 0.75 TOC/phenol conversion efficiency with simultaneously low release of metal during the oxidation.

1. Introduction

Most of the effluents from the chemical, petrochemical, textile, pharmaceutical, etc. industries contain toxic and non-biodegradable compounds. Hence, a variety of oxidation processes have been considered for mineralisation of these recalcitrant compounds. An important group are the advanced oxidation processes (AOP), where the catalytic wet hydrogen peroxide oxidation (CWPO) appears to be economical and also efficient under mild conditions [1,2]. For instance, Fenton or modified Fenton processes belong to the AOP group and have been employed in industrial applications such as dye manufacture, pulp waste bleaching, industrial wastewater or water treatments [3,4]. An important variable in oxidation processes is the use of catalysts to enhance the formation of hydroxyl radicals coming from the decomposition of the hydrogen peroxide. The use of homogeneous catalysts such as transition metal ions is well known [5–7], but their application is limited due to the release of these metal ions along with the products and hence secondary contamination by metals. On the other hand, use of heterogeneous catalysts avoids elevated metal contamination, but their apparent efficiency depends on the catalytic activity, which is negated by the leaching of the active species [1].

Suitable bonds between the support and the metallic ions are crucial for the effective performance of the catalyst, and a potentially important group of catalysts is based on polymer–metal complexes, whose advantage is derived from the use of functionalised macromolecules that bind metal ions tightly without losing their catalytic properties and provide easy separation from the oxidation media [8–10]. The use of polymers such as polybenzimidazole (PBI) resin [10] and functionalised poly(styrene-divinylbenzene) resin (poly(DVB-co-VBC)) [11] has been previously studied. In both cases the effectiveness of each polymer–metal complex as catalysts in different processes has been demonstrated. Olason and Sherrington [10] worked with complexes of Cu, Mn, Fe, Ru and Ti supported on PBI for the heterogeneous catalytic aerobic oxidation of cyclohexene. From this group of catalysts PBI-Cu yielded a conversion of 86% when tert-butylhydroperoxide was the oxidant in inert atmosphere. Moreover, Mbeleck et al. [11] studied alkene epoxidation catalysts, such as PBI-Mo and poly(styrene-divinylbenzene) resin functionalised with 2-aminomethylpyridine (AMP), followed by Mo(VI) loading (P-AMP-Mo). This yielded a stable and long-live polymer-supported complex capable of catalysing up to ten times an epoxidation reaction, obtaining 100% of conversion. The applicability of polymer-supported Cu(II) complexes as catalysts in the degradation of phenol is innovative. So that, the synthesis of catalysts using either PBI, poly(DVB-co-VBC) functionalised with AMP or poly(DVB-co-VBC) functionalised with iminodiacetic acid

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Table 1
Elemental analysis of resins under study.

Polymer	C	H	N	Cl	Conversion (%)
Polybenzimidazole (PBI)	73.72	4.51	15.73	0.63	
Poly(styrene-divinylbenzene) (P)	74.95	6.45	0.02	17.18	
P-2-Aminomethylpyridine (P-AMP)	82.49	6.93	6.13	3.34	81
P-Iminodiacetic acid (P-IMDA)	74.25	6.76	2.60	2.20	88

(IMDA) as supports was to be undertaken by loading Cu(II) as the catalytic metal.

The aim of this work is the evaluation of a new group of polymer-supported metal complexes, from their synthesis through to their application in the catalytic oxidation of phenol. Catalytic activity, deactivation and kinetics will be used to evaluate the effectiveness of the catalysts.

2. Methodology

2.1. Materials

For the preparation of the catalyst: polybenzimidazole (PBI) was supplied by the Celanese Co. and NaOH was from Sigma–Aldrich. Polyvinylalcohol (Mowiol 40-88), sodium chloride, 2-ethyl-1-hexanol and toluene were used as supplied by the Aldrich Chemical Co. Azobisisobutyronitrile (AIBN) from the BDH Co. was recrystallised from methanol before use. Divinylbenzene (DVB) (80% grade) from the BDH Laboratory and vinyl benzyl chloride (mixed of *m*- and *p*- isomers) (VBC) from Sigma–Aldrich were each freed of inhibitors by passing down columns of silica. 2-Aminomethylpyridine (AMP), iminodiacetic acid (IMDA) and ethanol were used as supplied by Sigma–Aldrich. Copper acetylacetonate ($Cu(acac)_2$), and copper sulphate ($CuSO_4$) were used as provided by the Aldrich Chemical Co. For the catalytic wet hydrogen peroxide oxidation, phenol was purchased from Panreac with purity higher than 99%. Hydrogen peroxide 30% (w/v) (100 vol.) PA was provided by Panreac. Millipore milli-Q deionised water was used to prepare all solutions.

2.2. Catalyst preparation

2.2.1. Polybenzimidazole resin (PBI)

The supplied PBI beads were cleaned, and for this purpose PBI was gently added to a solution of 1 M NaOH and poured into a plastic bottle. The bottle was hermetically closed and the cleaning process was carried out by continuously agitating the mixture on a roller bed overnight. Afterwards the beads were washed until the residual water had neutral pH and they were extracted overnight with acetone in a Soxhlet system before being dried overnight in a vacuum oven at 40 °C.

2.2.2. Synthesis of poly(DVB-co-VBC) macroporous (P)

This polymer was prepared by the suspension polymerisation method [8] with a VBC loading of 88-wt%. An organic phase, an aqueous phase and a free radical initiator formed the polymerisation system. The mixture of VBC and DVB monomers and the porogen (2-ethyl-1-hexanol) with a porogen/monomers mixture volume ratio of 1/1 formed the organic phase. The aqueous phase contained 0.75 wt% polyvinyl alcohol (PvOH) and 3.3 wt% NaCl, in 20/1 volume ratio relative to the organic phase, i.e. 5 wt% of VBC and DVB mixture [10]. Finally, the amount of initiator AIBN was proportional to the mixture of monomers, that is 1 wt% of VBC and DVB mixture [11].

2.2.3. Functionalisation of poly(DVB-co-VBC) (P)

The functionalisation of P was performed by using a reflux system, where the DVB-co-VBC resin was reacted either with an excess of 2-aminomethylpyridine (AMP) or iminodiacetic acid (IMDA) at the resin/ligand molar rate of 1/4 in ethanol. The reaction was run for a period of 48 h, and then the functional polymer was washed with acetone/water and methanol/water before an overnight extraction with acetone.

2.2.4. Metal loading

PBI and P resins were loaded with Cu to be evaluated as the catalyst in the phenol oxidation. Cu was used because it offers important catalytic properties for the catalytic wet oxidation of phenol. Each metal loading reaction was carried out in a three-necked 100 mL round-bottomed flask, which was fitted with a reflux condenser and overhead mechanical stirrer [10]. The reaction was performed with a ligand/metal molar ratio of 1/2, which was calculated from the known ligand loading of each polymer deduced from the microanalytical data of the polymers (Table 1). The metal loading was carried out with an appropriate solvent, under an inert atmosphere and temperature not higher than the boiling point of the solvent for four days. Afterwards, each polymer-supported metal complex was exhaustively extracted overnight with the suitable solvent in a Soxhlet system. Finally, the polymer complexes were dried overnight at 40 °C under vacuum. Some details of the metal loading process are presented in Table 2, where the six catalyst configurations synthesised are listed combining polymer-supports and metal sources. The different sources of Cu(II), indicated by the abbreviations Cua and Cus, specify the use of acetylacetonate and sulphate salts respectively for the metal loading.

2.3. Oxidation process

The oxidation experiments were conducted in a stirred tank reactor of 200 mL. The initial phenol concentration was always $1\,g\,L^{-1}$, the temperature was 30 °C and the pressure was 1 atm. Hydrogen peroxide was used as oxidant at the stoichiometric phenol/peroxide (Ph/H_2O_2) molar ratio of 1/14. The amount of catalyst for the heterogeneous catalytic oxidation was calculated to provide a Cu(II) concentration of $50\,mg\,L^{-1}$ with respect to the reaction volume. The catalyst weight (W_{CAT}) (g) is calculated from a mass

Table 2
Abbreviation, metal loading conditions and metal ligand content of the polymer-supported metal complexes.

Catalyst	Polymer	Metal salt	Reac. solvent	Extrac. solvent	Metal/ligand ratio
PBI-Cua	PBI	$Cu(acac)_2$	Ethanol	CH_2Cl_2	0.1/1
P-A-Cua	P-AMP	$Cu(acac)_2$	Toluene anh.	Acetone	0.5/1
P-I-Cua	P-IMDA	$Cu(acac)_2$	Toluene anh.	Acetone	0.3/1
PBI-Cus	PBI	$CuSO_4$	Ethanol	CH_2Cl_2	0.5/1
P-A-Cus	P-AMP	$CuSO_4$	Water	Water	0.8/1
P-I-Cus	P-IMDA	$CuSO_4$	Water	Water	0.2/1

balance in the catalyst and is represented by Eq. (1). This equation relates the required amount of metal (W_M) (g) for the CWPO with the metal content of the catalyst (M_C), i.e. g Cu(II) g_{support}^{-1}.

$$W_{CAT} = W_M\left(1 + \frac{1}{M_C}\right) \tag{1}$$

The pH was monitored during the reaction time using an electronic pHmeter. A buffer solution of NaOH, H_3PO_4 and K_2HPO_4 was used to control the pH when phenol intermediates were evaluated.

The reaction progress was monitored from the start by withdrawing 6 mL samples (11 samples) over 240 min. Phenol and TOC conversion were calculated for each sample after sample analyses.

2.4. *Analytical procedure*

2.4.1. *Polymer analysis*

Metal analyses were carried out on a Perkin-Elmer Analyst 200 spectrophotometer. Each sample of catalyst, was ground to a fine powder, digested with 15 mL of aqua regia for a three-day period, after digestion, the liquid was filtered and diluted to 100 mL with distilled water. Finally the samples were analysed by standard methods employing an atomic adsorption spectrophotometer.

Elemental microanalysis was carried out by the microanalytical laboratory staff of the Department of Pure and Applied Chemistry at the University of Strathclyde, with a Perkin-Elmer 2400 Series II Analyser.

2.4.2. *Oxidation analysis*

Phenol conversion was calculated by measuring the phenol concentration using HPLC (Agilent Technologies, model 1100) with a C18 reverse phase column (Agilent Technologies, Hypersil ODS), the method used is fully described elsewhere [12]. The total organic carbon (TOC) values were collected from a TOC Analyser (Analytic Jena, model NC 2100). Samples were acidified with 50 μL HCl 2N, then they were bubbled with synthetic air for 3 min to eliminate any possible inorganic carbon content and finally injected. Leaching of the catalyst was determined by Atomic Absorption Spectrometry (Perkin-Elmer, model 3110) at 325 nm with a specific lamp for the element of Cu.

3. Results and discussion

3.1. *Functionalisation of P*

The functionalisation of P was achieved using AMP and IMDA as potential metal ligands. Table 1 shows the microanalytical data for C, H, N and Cl contained in each polymer. The percent amination of CH_2Cl was determined using appropriate elemental microanalytical data after amination, which show a fall in Cl% and a rise in N%, indicating the exchange of $–CH_2Cl$ with $–NH_2$. The results demonstrated that functionalisation with both AMP or IMDA was successful with conversions above 80%, indicating the presence of high loading of ligands capable of coordinating to Cu(II).

3.2. *Phenol oxidation—blank experiment*

Most of heterogeneous catalytic processes involve an adsorption step where a part of the substrate is adsorbed onto the catalytic surface. For this reason, a series of blank experiments were carried out in which the oxidation was performed using either polybenzimidazole (PBI) resin or functionalised poly(styrene-divinylbenzene) resins (P-AMP and P-IMDA) without any metal content as catalyst (Table 3). At 30 °C and atmospheric pressure, the oxidation of phenol is not expected to occur without the presence of catalyst, so it is assumed that these metal-free polymers undergo a classical phenol adsorption process.

Table 3
Phenol adsorption capacity of polymeric supports and weight of the amount of polymer-supported Cu(II) catalysts.

Polymer	q (mg g^{-1})	Cua[a] complex (g)	Cus[b] complex (g)
PBI	65.6	0.387	0.092
P-AMP	73.1	0.211	0.142
P-IMDA	84.8	0.373	0.120

[a] Cua: copper acetate as Cu(II) source for the metal loading.
[b] Cus: copper sulphate as Cu(II) source for the metal loading.

Phenol isotherms showed an immediate phenol adsorption over the polymer during the first 5 min of contact, after which phenol concentration in the liquid phase remained constant for 2-h period.

Table 3 lists the phenol adsorption capacity of PBI, P-AMP and P-IMDA and the mass of catalyst used in each experimental run based on an equivalent Cu(II) content of 50 mg L^{-1}. The percent of phenol absorbed onto each catalyst can be calculated from Eq. (2) using the data collected at Table 3.

$$\%_{\text{ads}} = \left(\frac{q \cdot \text{weight}_{\text{complex}} \times 100}{[\text{Ph}]_0\, V}\right) \tag{2}$$

Surprisingly, all the catalysts show a very low phenol adsorption capacity, which is not more than 16% in the best of the cases. Anyway, apparent phenol “conversion” by adsorption during reaction was avoided by pre-treating the catalyst before reaction (addition of hydrogen peroxide) for half an hour with phenol. After this initial contact of the catalyst and substrate (phenol), the catalyst was ready to be used in the oxidation experiments.

3.3. *CWPO of phenol with polymer-supported Cu(II) complexes*

Employing the oxidation procedure described in the Section 2, the group of polymer-supported Cu(II) complexes was used as catalysts for the oxidation of phenol. The substrate was buffered to pH 6 and oxidation was carried out at 40 °C and atmospheric pressure. During the catalytic testing, a qualitative signal of the reaction progress was a colour change in the reaction media, which evidenced the formation of coloured compounds like quinones. Fig. 1 shows the progress of phenol conversion when polymer-supported Cu(II) catalysts were used. It is noticeable that P-I-Cua achieved a final phenol conversion of 93% after 4 h, with the rest of catalysts displaying lower phenol conversions as follows: PBI-Cus (72%) > P-A-Cus (67%) > P-I-Cus (43%) > PBI-Cua (29%) > P-A-Cua (13%). Catalysts also exhibited characteristic trends with reaction time, such as PBI-Cua and P-A-Cua, which showed their highest

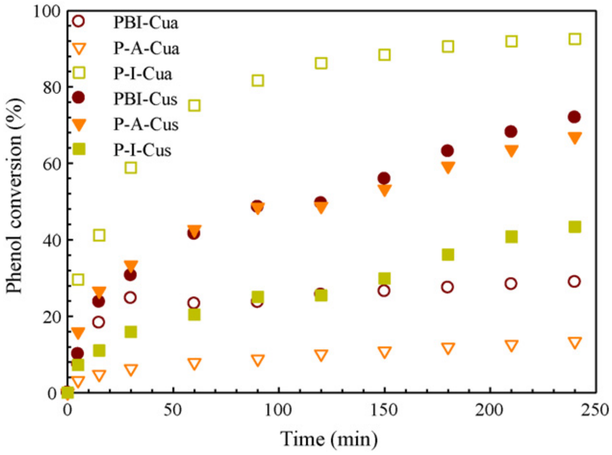

Fig. 1. Phenol conversion using polymer-supported Cu(II) complexes. [Phenol] = 1 g L^{-1}, phenol/H_2O_2 ratio = 1:14, pH = 6, T = 40 °C, pressure = 1 atm.

Table 4
Phenol and TOC conversion, leaching, deactivation and efficiency of the catalytic oxidation of phenol using polymer-supported Cu(II) complexes as catalysts.

	PBI-Cua	P-A-Cua	P-I-Cua	PBI-Cus	P-A-Cus	P-I-Cus
X_{Phenol} (%)	29	13	92	72	67	43
X_{TOC} (%)	20	9	43	54	15	32
X_{TOC}/X_{Phenol}	0.69	0.69	0.47	0.75	0.22	0.74
Leaching (mg L^{-1})	0.1	1.4	6.2	2.7	5.1	0.4
Deactivation (%)	0.1	3.0	13.0	6.0	10.1	1.0

catalytic capacity for the phenol oxidation after 30 min. This fact suggests a surface contamination of PBI-Cua and P-A-Cua caused by the adsorption of phenol intermediates onto the catalytic surface. This would create difficulties for the interaction of Cu(II) with OH$^\bullet$ radicals appeared because the interaction of Cu(II) with the media would be hindered. As a result, phenol conversions rose to only 29 and 13%, respectively. It was also observed that P-I-Cua, PBI-Cus, P-A-Cus and P-I-Cus promoted a steady continuous increase of phenol conversion with the time. During this phase the possibility of catalyst contamination by adsorption of phenol oxidation intermediates is expected to be low because Cu(II) continuously promotes the reaction of H_2O_2 with both phenol and partial oxidation products. After 3 h of reaction, PBI-Cus and P-A-Cus had similar phenol conversions, 72 and 67% respectively, however none of these catalysts can be taken as suitable for real cases until their efficiencies are evaluated. Table 4 lists the phenol and TOC conversions, catalytic leaching and deactivation, and mineralisation efficiency, this latter being calculated from the relation of TOC/phenol conversions. The best TOC conversion results were obtained with PBI-Cus with 54% of conversion and P-I-Cua with 43%. However, considering that P-I-Cua presented higher phenol conversion than PBI-Cus, it was found an effective mineralisation of 75% for PBI-Cus. The mineralisation obtained with the P-I-Cua catalyst indicates that 47% of phenol was evolved to CO_2 while the other 53% was in form of phenol oxidation intermediates, which are probably easy to further decompose or oxidise. In contrast, P-A-Cus had the lowest mineralisation efficiency, i.e. 0.22, although its 67% of phenol conversion suggests that P-A-Cus provides good catalytic activity in the first step of the reaction where phenol oxidation intermediates were produced, but then its catalytic activity decreased. P-A-Cua, PBI-Cua and P-I-Cus yielded an average TOC/phenol conversion of 0.7, but their respective phenol conversions were lower than 40%, and this is not too much suitable for an industrial pre-treatment process. On the whole, P-I-Cua provided better phenol conversion results than the rest of the Cu(II) catalysts, although PBI-Cus provided noteworthy results when mineralisation is the main goal.

Previous reports have stated that any heterogeneous catalytic systems can become a new problem when the metal release is high [13–15], in addition to the progressive catalytic deactivation. Therefore, oxidation results have to be considered together with the metal release during the reaction period in order to control the contamination of the treated effluent by Cu(II). The leaching is caused by hydrogen peroxide bond attack and acidification of the reaction media [16,17]. In the present case, the influence of carboxylic acids on leaching was neglected because the reaction media was buffered; so leaching must be mainly ascribed to desorption of weakly linked copper. Table 4 lists the Cu(II) leaching data for the group of catalysts. The highest Cu(II) release was 6.2 mg L^{-1}, which exceeds by 1.2 mg L^{-1} the permissible metal content of wastewater treatment plants. However, this excess could easily be removed by precipitation, filtration or adsorption before feeding the effluent into a subsequent process. Knowing that P-I-Cua and PBI-Cus yielded promising phenol and TOC conversions, it is important to know the activity of the leached Cu(II) in the homogeneous phase. Data and trends from a previous catalytic phenol oxidation report [12] were employed here. Thus, Cu(II) leaching from P-I-Cua (6.2 mg L^{-1}) promoted approximately 32% phenol conversion and represented 13% of catalyst deactivation, while Cu(II) leaching from PBI-Cus (2.7 mg L^{-1}) yielded 21% phenol conversion with 6% catalytic deactivation. It is important to emphasise that none of the other catalysts, apart from P-A-Cus, gave more than 2 mg L^{-1} of Cu(II) release, indicating that the oxidation was almost completely catalysed in heterogeneous phase.

Overall P-I-Cua and PBI-Cus could be selected as suitable catalysts for the phenol CWPO, principally because they showed promising results in terms of phenol and TOC conversions and also because their Cu(II) desorption or polymer degradation did not represent insurmountable contamination problems.

Recycling experiments were made for two periods of 2 h each (results not shown) where their catalytic activity was reduced in 50% for the second run, possibly caused by adsorption of phenol intermediates. On the other hand, when the catalysts were used in periods more than 2 h, e.g. 4 h, the catalysts with important catalytic activity did not suffer contamination by adsorption of phenol intermediates. Hence, it seems that the loading of Cu(II) on PBI and P-I gives heterogeneous catalysts that conserve the catalytic activity of Cu(II) ions, so these heterogeneous catalysts are suitable for continuous processes.

3.4. Kinetics and mechanisms

The kinetic evaluation that was undertaken was applied to the experimental data obtained from the CWPO of phenol. The literature reports that the catalytic oxidation of phenol in a homogeneous phase follows a first order rate law [18,19]. Thus, the kinetic behaviour analysis was firstly evaluated using this model.

Calculations of the kinetic rate constants are made for all the groups of polymer-supported Cu(II) catalysts (Table 5). The rate constant for P-A-Cua was the lowest in the Cu(II) group of catalysts; this value reflected the lowest phenol conversion and probably reproduced the lack of interaction between Cu(II) and hydrogen peroxide.

The kinetic constant for P-I-Cua is the highest in the group of catalysts, which suggests that P-I-Cua had a better availability of Cu(II) ions to promote the catalytic oxidation of phenol. Additionally, an evaluation of phenol intermediates was made when using P-I-Cua and PBI-Cus catalysts bearing in mind that the production of intermediates during phenol oxidation represents the first step in achieving the mineralisation of phenol. The evolution of carbonaceous products when P-I-Cua was the catalyst is shown in Fig. 2. Five organic oxidation intermediates (catechol, fumaric acid, malonic acid, formic acid and succinic acid) were detected. In the first 30 min the production of 36% of catechol was recorded,

Table 5
Kinetic rate constants for phenol oxidation using polymer-supported Cu(II) complexes as catalysts.

Catalyst	k (min^{-1})	R^2
PBI-Cua	9.3×10^{-3}	0.93
P-A-Cua	4.4×10^{-4}	0.95
P-I-Cua	9.5×10^{-3}	0.93
PBI-Cus	4.5×10^{-3}	0.98
P-A-Cus	3.6×10^{-3}	0.97
P-I-Cus	2.0×10^{-3}	0.98

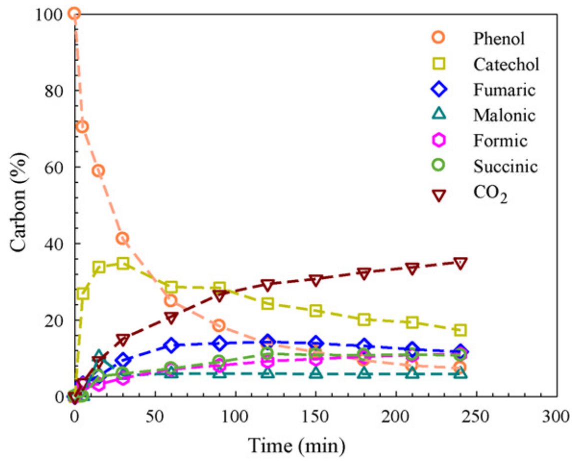

Fig. 2. Carbon percent formation in phenol oxidation. [Phenol] = 1 g L^{-1}, P-I-Cua catalysts: 0.373 g equivalent to 50 mg L^{-1}. Phenol/H_2O_2 molar ratio: 1/14 (stoichiometric) at 40 °C, pH 6 and atmospheric pressure.

while acid production was low during this period. Later, malonic, formic and succinic acids were produced from the oxidation of catechol, which were subsequently oxidised to finally produce CO_2. For instance after 90 min the level of catechol (28%) decreases to produce fumaric acid (14%), also seems to produce malonic (6%), formic (8%) and succinic (9%) acids. The carbon distribution of the CWPO of phenol using PBI-Cus catalyst was also evaluated and the same behaviour can be seen (evolution not shown). It seems therefore that the oxidation process follows the main reaction pathway reported by Devlin and Harris [20], where phenol is oxidised to produce catechol, at the same time the reaction mixture develops a brown colour. Further oxidation produces carboxylic acids such as fumaric, malonic, formic and succinic acids and these do not represent toxicity or inhibitory effects [21]. Indeed, it has been reported that these acids are biodegradable so their environmental impact is nil [22]. In general, the main aim of pre-treatments for phenol mineralisation is to destroy the aromatic benzene ring in order to produce easily degradable intermediates for wastewater treatment plant to deal with. For this reason, the results obtained in the present work, with phenol degradation beyond 50%, suggests that further work with polymer-supported metal complexes as catalysts for pre-treatments like CWPO of phenol would be extremely valuable.

4. Conclusions

After testing this group of polymer-supported metal complex catalysts it can be concluded that Cu(II) was successfully supported on different types of polymeric materials without losing its catalytic properties in homogeneous phase for CWPO of phenol under mild conditions. The group of catalysts, containing Cu(II) sulphate as metal source, developed higher deactivation than the rest of catalysts. In contrast the group using Cu(II)(acac), apart from P-I-Cua, showed low catalytic deactivation, favourable for the catalytic reuse. In any case and considering an initial phenol concentration of 1 g L^{-1}, it was highlighted that P-I-Cua displayed a permissible leaching degree of 6 mg L^{-1} simultaneously with very high phenol conversion, 93%, and TOC conversion, 43%. It seems therefore that the use of the P-I-Cua catalyst is viable for a continuous process because it can achieve 80% of phenol conversion in just 90 min without signs of metal contamination. However, PBI-Cus better balances a high conversion, 72%, with a deep mineralisation, 54%, and a low metal leaching, 2.7 mg L^{-1}, after 4 h. Moreover, the importance of the metal leaching was demonstrated due to the activity of Cu(II) ions in the homogeneous phase, also contributes the catalytic oxidation. However for all the cases studied, a pseudo first order rate law describes well the reaction under study.

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