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Catalytic wet peroxide oxidation of phenol from industrial wastewater on activated carbon

Jaildes Marques Britto [a], Sérgio Botelho de Oliveira [a,b], Denilson Rabelo [c], Maria do Carmo Rangel [a,*]

[a] Instituto de Química, Universidade Federal da Bahia, Campus Universitário de Ondina, Federação, 40 290-170 Salvador, Bahia, Brazil
[b] Centro Federal de Educação Tecnológica de Goiás, Rua 75, 46, Setor Central, 74055-110 Goiânia, Goiás, Brazil
[c] Instituto de Química, Universidade Federal de Goiás, Caixa Postal 131, 74 001-970 Goiânia, Goiás, Brazil

Abstract

A heterogeneous catalyst obtained from copper adsorption by an ionic exchange resin, followed by carbonization, is presented as a promising option for phenol abatement in industrial wastewater. The catalyst was characterized before and after the catalytic tests by SEM-EDS. The performance of the catalyst in industrial wastewater, with 60 mg L^{-1} phenol, was compared with a model stream (1000 mg L^{-1} phenol). Successive reactions were also carried out in order to study the catalyst deactivation. The reaction was performed at 38 °C, 1 atm, pH 6.5, using a phenol to hydrogen peroxide molar ratio of 14. The catalyst was able to remove all phenol compounds present in both streams. The catalyst did not show any deactivation in the industrial stream, but deactivated in the model stream, a fact that can be assigned to the copper leaching, as inferred by SEM-EDS. In the model stream, the high phenol concentration caused a high production of organic acids, generated by parallel reactions, which led to copper leaching. The industrial stream did not show deactivation since the amount of these acids was too low to leach copper.

Keywords: Catalytic oxidation; Copper; Phenol; Wastewater

1. Introduction

The increasing consciousness of environment preservation and recuperation has made the requirements of the environmental legislation even more restrictive. Therefore, the treatment and the destination of industrial wastewater containing toxic organic pollutants have become a serious concern worldwide. The industrial wastewater generated by the production of resins, petroleum refinery and petrochemicals often contains high toxic compounds like phenol, sulfate and ammoniac ions in large concentration. The phenol toxicity in aquatic environment has been studied [1] and it is well established that even in low concentration this compound affects the nervous and circulation systems, reducing the blood cells [2,3]. Phenolic compounds can also produce carcinogenic compounds, like chlorophenol and polichlorophenol, during the chlorination process of drinking water [4]. In addition, even in extremely low concentration such as 0.002 mg L^{-1}, phenols change the organoleptic properties of water, causing operational problems in breweries, distilleries and in the bottling of mineral water [1]. In the aquatic environment, these compounds can cause the death of fish and other aquatic species, changing the ecological equilibrium [5].

The need of the re-establishment of the contaminated areas and of avoiding future contaminations, required by a strict environmental legislation, has created demands for the statement of clean technologies strategies. They have to improve the current process and to develop closed industrial systems of purification and water recycling [6,7].

Phenol is typically removed from wastewater by the thermal oxidation process and/or biological process, like the activated sludge process [8,9]. However, these processes have some drawbacks, such as the difficulty of biological material recovery, the need of a large treatment area, the high energetic cost of processing and the restrictions concerning the concentration of the pollutants to be treated [10]. A more convenient alternative is the catalytic oxidation that has shown considerable advance in the last 10 years, converting organic

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* Corresponding author. Tel.: +55 71 237 5784; fax: +55 71 235 5166.
E-mail address: mcarmov@ufba.br (M.d.C. Rangel).

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pollutants into inorganic carbon or into products that can be eliminated by the biological residual treatment. The processes of catalytic oxidation using ozone, oxygen, hydrogen peroxide or the combination of them have shown to be extremely effective in the abatement of phenols [10].

The catalytic oxidation using hydrogen peroxide is a more efficient process as compared to catalytic oxidation using air, since hydrogen peroxide is a stronger oxidant [11]. In liquid phase and low temperatures, these processes are promising alternatives to treat industrial wastewater with low energetic cost and in environmental friendly conditions. In this context, the development of active, economical and stable catalysts, which can be efficient in the organic compounds degradation in aqueous solution, is a scientific and technological challenge. Therefore, several catalysts have been considered and evaluated. Among them, transition and noble metals supported on oxides or zeolites have shown activity, mainly in the abatement of phenol and phenolic compounds [12,13], especially the nickel and copper oxide-based catalysts [12–14].

With the aim of developing catalyst to the abatement of low concentrations of phenolic compounds, the performance of an activated carbon-supported copper catalyst, prepared from sulfonated styrene-divinylbenzene resin, was evaluated in a previous work [15]. In the present work, the performance of this catalyst was investigated in phenol oxidation, using an industrial stream. The efficiency of the catalyst was followed during successive reaction cycles and an industrial stream was compared with a model one.

2. Experimental

2.1. Catalyst preparation and characterization

The preparation and characterization of the catalyst were described in a previous work [15]. Before and after each evaluation test, the samples were characterized by scanning electron microscopy (SEM), carried out in Jeol model JSM6360LV equipment, operating at 20 kV and provided with an EDS system of Noran System Six. In the acquisition of data, the Point and Shoot mode was used, in which a reference image was acquired and the acquisition points of the spectrum were chosen. They were automatically processed as a function of acquisition time (2–5 min in each point). In the samples preparation, the powder was fixed on a carbon support and covered with carbon or gold.

2.2. Catalysts evaluation

In a previous work [15] the detailed analysis of the data obtained, from the factorial design matrix, allowed the selection of the best conditions for the reaction: 38 °C, pH 6.5 and phenol to hydrogen peroxide molar ratio of 14. These conditions were selected because they corresponded to the minimum energetic consumption (low temperature) and also to the molar ratio close to the stoichiometric ratio, aiming a reduction of the oxidant cost.

The phenol oxidation reactions were carried out in a glass reactor of 150 $\mathrm{cm^3}$, operating at atmospheric pressure and 38 °C. The reaction system was kept under nitrogen flow (100 $\mathrm{mL\,min^{-1}}$) and under stirring (600 rpm), during the experiments. As the model system, 100 $\mathrm{cm^3}$ of a phenol solution (1000 $\mathrm{mg\,L^{-1}}$) were used. The catalyst (1 $\mathrm{g\,L^{-1}}$) was added to the reaction system in the beginning of each run, which took 6 h. The pH value was adjusted by the addition of an ortophosphoric acid solution (0.05 $\mathrm{Eqg\,L^{-1}}$) and monitored during the reaction time, using a WTM model 539 equipment. All the solutions were prepared using deionized water (resistivity $>18\ \Omega$ cm). The reactor temperature was controlled using an Etica Scientifical Instruments model 521.2D thermostatic bath. After temperature stabilization and pH correction, the reaction solution was analyzed to confirm the low phenol adsorption on the catalyst. The hydrogen peroxide (30%, v/v) amount needed for the complete oxidation was then introduced to the reaction system.

The experimental tests were performed in three cycles using a model and also an industrial wastewater stream, in order to monitor the catalyst deactivation in both cases. The first cycle was carried out in duplicate to provide enough amount of catalyst for performing the following tests.

The industrial stream used in this work was collected in a naphtha cracking unit of a petrochemical plant. In this process, the presence of phenolic compounds is detected in the condensed water from the steam injected in the system, which is mixed with pyrolysis gasoline, a subproduct of the reaction. Some gasoline components (including phenol) are solubilized in the water used to cool the naphtha feed. The water, coming from the naphtha reactor, goes to a separator vessel containing hydrocarbons (in ppm amounts), where is reutilized in the process to produce dilution steam. A small amount of this stream is drained to the contaminated wastewater whose concentration is around 70 $\mathrm{mg\,L^{-1}}$ of phenol. This was the effluent sample used in this work. The drainage is needed to avoid the high concentration of solids in the separator vessel, which is in a closed cycle. The contaminated stream, nevertheless, can violate the phenol standard whose legislation defines the maximum value of 0.5 $\mathrm{g\,L^{-1}}$ in the industrial wastewater emission.

The reaction was monitored by taking samples at intervals of 2 h. The phenol and the products concentrations were determined by gas chromatography, using a Varian model CP 3900 equipment, with a capillary column HP (50%/50% phenyl/silicon methyl) and a flame ionized detector. The phenol oxidation products were also identified by a Varian model HPLC Pro Star equipment, with a Varian C-18 column and an ultraviolet detector, using a mobile phase based in ammonium dehydrogenate phosphate acid.

The chemical oxygen demand (COD) was determined using a Hach reactor model Box 389. The carbon dioxide was measured by the volumetric methodology of Standard Methods for The Examination of Water and Wastewater, 4500-$\mathrm{CO_2}$C method [16], in where free inorganic carbon reacts with carbonate or sodium hydrate to form sodium bicarbonate. The end of reaction was indicated by a pH value of 8.3.

The leaching of copper was evaluated by determining the copper concentration in the reaction solution, using an atomic absorption spectrophotometer equipment (Varian model Spectra AA- 220 FS).

3. Results and discussion

3.1. Model stream evaluation

When the reaction was carried out using the model stream, in the absence of catalyst, a low conversion (less than 30% molar) was noted after 6 h; also, the phenol adsorption capacity was very low (around 2% molar).

However, using the optimized condition, a complete phenol conversion (100% molar) and COD reduction of around 80% in the stream were noted. The COD indicates the extension of the oxidation reaction and represents the phenol amount that was converted into carbon dioxide and water. It is a more important answer parameter than the phenol conversion, which measures the contaminant abatement without considering the products. The COD shown by the model system was attributed to the reaction products as well as to the intermediate compounds produced in the phenol oxidation (organic acids) that did not contribute significantly to increase the total COD.

The oxalic and acetic organic acids, the main products observed, present low toxicity. It was also found catechol and hydroquinone, as reaction products from phenol oxidation using the model stream system. These large molecules are more toxic as compared to organic acids, however they were present in a low concentration (<50 mg/L) and did not increase the medium toxicity.

The carbon-supported copper catalyst showed a similar performance as compared to a reference catalyst, described in the literature [5,11,17] using the hydrogen peroxide as oxidant, which led to total phenol conversion. Additionally it was detected, in the present work, a lower concentration of heavy and toxic compounds as hydroquinone, benzoquinone and catechol as reaction products when compared to other catalytic system as Fenton catalyst or Fe-Clay based catalysts [5,11].

3.2. Industrial wastewater evaluation

The industrial wastewater, from the steam dilution of the naphtha cracking plant of a petrochemical industry, presented the main characteristics shown in Tables 1 and 2. The industrial wastewater showed a change of COD as a function of the soluble organic compounds presence, while the phenol concentration in the industrial wastewater depended on the kind of naphtha.

Table 3
Comparison between the performance of catalyst in the model stream and in the industrial stream with the oxidant and in the absence or in the presence of the catalyst

Sample	Phenol conversion (%mol) without catalyst	Phenol conversion (%mol) with catalyst	Phenol absorption capacity (%mol)
Model stream	30	99.9	2
Industrial stream	5	100	0

The application of the experimental conditions, selected from the experimental design of the model stream, to the industrial system resulted in a total phenol conversion, while the COD abatement was 35%. The original sample showed 292 mg L^{-1} of COD and after the treatment, it showed the value of 182 mg L^{-1}. The COD reduction was equivalent to the whole phenol amount present in the stream. The residual COD value is inherent to the complexity of the industrial wastewater. Therefore, the value of 35% of the chemical organic demand is significant and corresponds to the total removal of phenol. The oxalic and maleic acids were identified as the principal products of the reaction and were considered intermediate compounds during the phenol mineralization. These products do not contribute to increase the toxicity or COD of the system. Benzoquinone and catechol were only detected as trace amounts (<2 mg/L) in the wastewater stream.

These results are very promising, since the phenol content is considered the main restriction to dispose industrial wastewaters in the environment. In addition, the phenol removal from this stream can allow its reutilization in the water refrigeration cycle of the industrial unit, eliminating the generation of the industrial wastewater.

3.3. Comparison between the model stream and the industrial wastewater

The catalytic tests performed with the industrial stream, in the absence of the oxidant, confirmed the low catalyst

Table 1
Properties of industrial wastewater stream

Flow rate ($m^3 h^{-1}$)	Temperature (° C)	pH	COD (mg L^{-1})	Oils and grease (mg L^{-1})
20–35	28–44	5–8	130–300	Free

Table 2
Main contaminants in the industrial wastewater

Phosphate (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)	NH_3 (mg/L)	BTX (mg/L)	Phenol (mg/L)
0.2–7.0	1–5	0.3–4.3	3–27	0.01–0.1	40–70

B, benzene; *T*, toluene; *X*, xylene.

Table 4
Surface atomic composition of fresh catalyst, related to the regions labeled in Fig. 3

Sample point	Carbon (% molar)	Oxygen (% molar)	Sulfur (% molar)	Copper (% molar)
Point 1 (cluster)	35.84	48.23	8.42	7.36
Point 2 (pellets)	72.24	22.42	4.00	1.26

adsorption capacity, as observed with the model stream. In another experiment, the wastewater reacted with hydrogen peroxide in the absence of catalyst and a low conversion was noted. Table 3 shows these results.

Fig. 1 shows the comparison between the catalyst performance on the model system (1000 mg L^{-1} in phenol) and on the industrial stream (60 mg L^{-1} in phenol), in successive tests. It can be noted a progressive decrease of activity in the successive cycles of the model stream. On the other hand, the catalyst did not show a deactivation in the industrial stream, in spite of the complex composition of the industrial wastewater. This performance can be associated to the copper leaching from the catalyst surface. A previous work [15] had shown that a high phenol concentration led to a high copper leaching and this was assigned to organic acids (reaction products) that removed superficial copper sites and then caused the catalyst deactivation. In fact, the stream with low phenol concentration, such as the industrial wastewater, led to lower copper leaching (10 mg L^{-1}) as compared to the model stream (31 mg L^{-1}).

The experiments of electron scanning microscopy performed on the fresh catalyst showed that there was no significant rupture in the sample spheres, during the preparation steps, as shown in Fig. 2. One can see white deposits on the surface of the dark pellets. The EDS analysis showed differences in the composition between the deposits and the pellets, as shown in Table 4. These values correspond to average ones obtained from the regions displayed in Fig. 3, whose respective EDS spectra are shown in Fig. 4. It can be observed

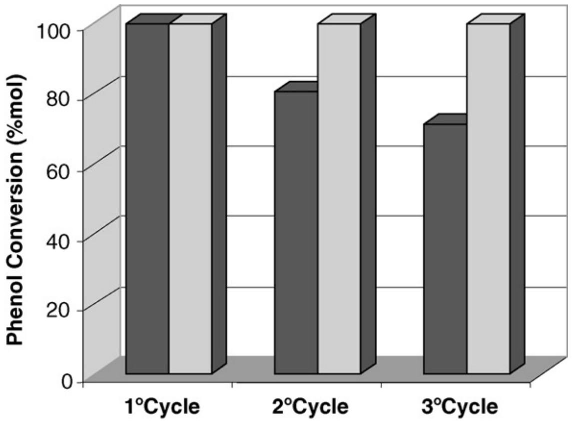

Fig. 1. Comparison of the catalyst performance in the model (■) and in the industrial stream (▒).

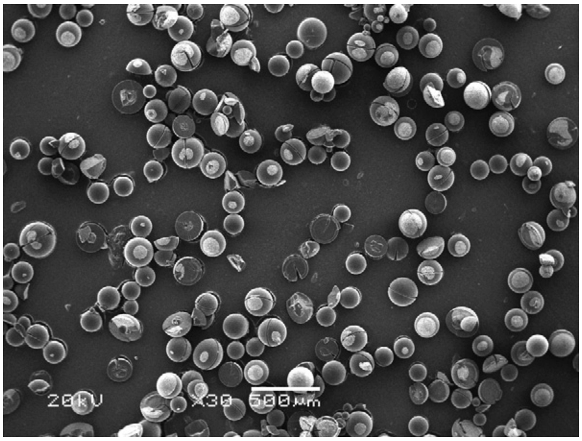

Fig. 2. SEM image of the fresh catalyst.

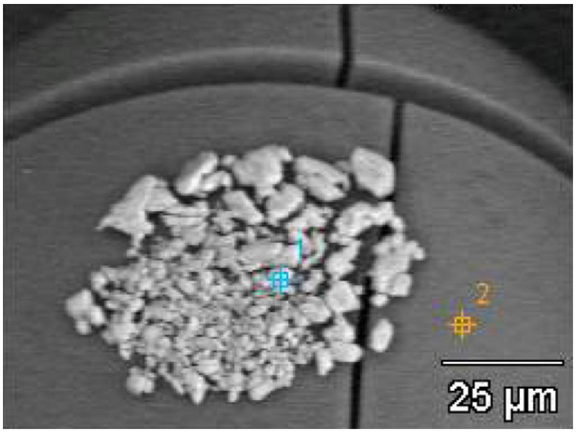

Fig. 3. SEM image of the deposits observed on the pellets surface of the fresh catalyst. The numbers label the regions whose compositions are shown in Table 3.

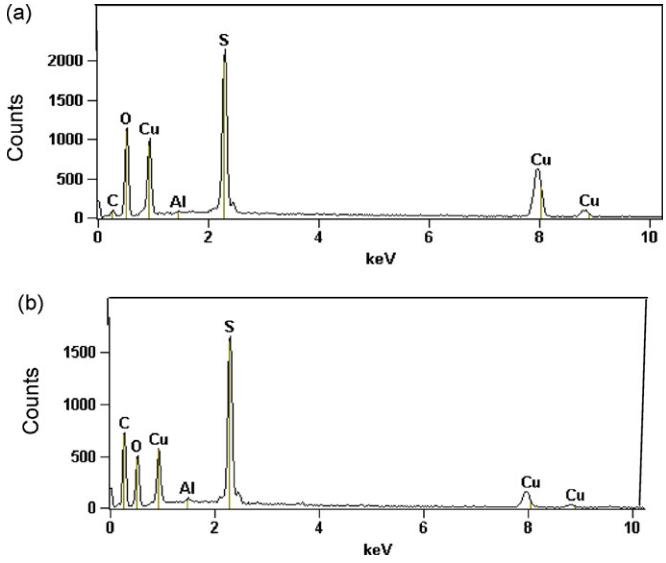

Fig. 4. EDS spectrum of the fresh catalyst in different regions labeled in Fig. 3. (a) Point 1 (cluster) and (b) Point 2 (pellet).

Table 5
Surface atomic composition of fresh catalyst, correspondent to the showing points on Fig. 6

Sample points	Carbon (%molar)	Oxygen (%molar)	Sulfur (%molar)	Copper (%molar)
Point 1 (sphere)	81.02	16.22	2.15	0.54
Point 2 (cluster)	79.28	18.48	1.61	0.55
Point 3 (pellet)	80.89	16.60	1.99	0.47
Point 4 (cluster)	76.64	20.70	1.85	0.55

that the white deposits have the highest copper and oxygen concentration, confirming that the copper ions were absorbed on the sulfonated polymer forming copper oxides. The sulfur presence in the catalyst was related with the sulfonation level. The higher concentration of this element in the white regions, as compared to the black pellets, showed that the sulfonation was not regularly distributed on the polymer surface. This was a consequence of a heterogeneous reticulation of the polymeric matrix, providing less reticulated regions and thus more sensitive to sulfonation (Fig. 5).

The spent catalyst after three cycles of reaction using the model stream showed an uniform image, related to a more homogeneous surface composition, as shown in Fig. 6. It means that the copper agglomerates were leached and only the copper species absorbed by sulfonic groups in lower proportion produced clusters strongly bounded to the surface and thus more resistant against leaching.

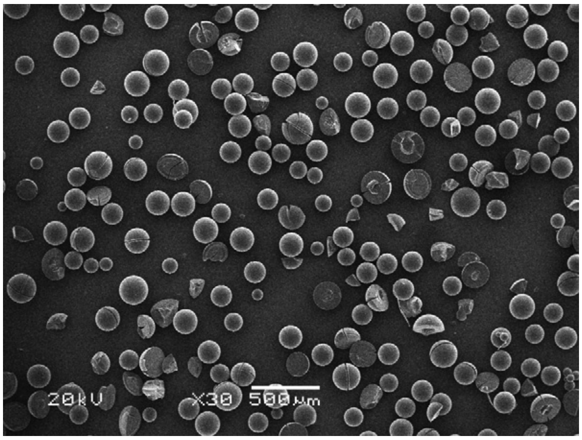

Fig. 5. SEM image of the spent catalyst.

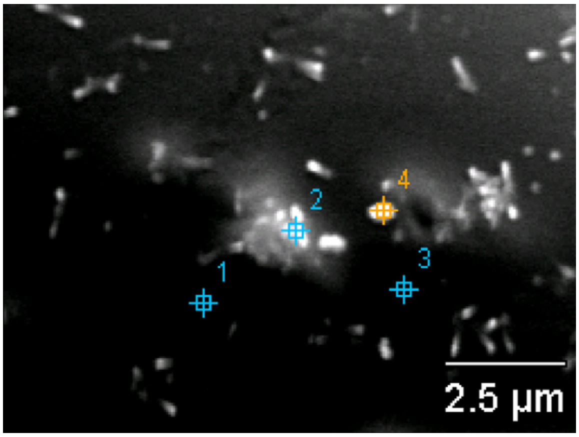

Fig. 6. SEM image of the spent catalyst after three reaction cycles.

Table 5 shows the surface composition of the catalyst after three successive runs and corresponds to the labeled regions in Fig. 6. It can be noted that the surface of the spent catalyst was more homogenous than the fresh catalyst (Fig. 3 and Table 4), regarding the distribution of copper, sulfur and oxygen. It can be noted that the amount of copper, sulfur and oxygen on the surface of the spent catalyst was lower than the amount on the fresh catalyst, confirming the copper leaching.

4. Conclusions

The carbon-supported copper catalyst, obtained from sulfonated styrene-divinylbenzene resin, is an efficient alternative to remove phenol from industrial wastewater, in the presence of hydrogen peroxide. The catalyst shows high performance and stability, when used in an industrial wastewater contaminated with low phenol concentration (60 mL L^{-1}); in this case, all phenol is removed. The catalyst also shows high performance in a model stream with high phenol concentrations (1000 mg L^{-1}), but copper is largely leached. The presence of organic acid from phenol oxidation reaction products is probably the cause of copper leaching from the catalyst surface.

The results obtained in this work are important from the environmental point of view, since phenol concentration is considered the main restriction parameter for discarding industrial wastewater in the environment. In addition, the phenol abatement in industrial wastewater can allow its reutilization in the refrigeration of the water cycle of industrial units, avoiding the waterwaste generation and reducing the environmental impact.

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