Activated carbon cloth: a potential adsorbing/oxidizing catalyst for phenolic wastewater

Rashmi Chand, Raul Molina, Ian Johnson, Anna Hans and David H Bremner

ABSTRACT

An investigation into the use of activated carbon cloth (ACC) as a potential adsorbent and/or catalyst for oxidation processes is reported. The extent of increase/decrease of oxidation/adsorption of phenol, as measured by total organic carbon content (%), is explained by considering the effects of the oxidants such as ozone and hydrogen peroxide on the activated carbon cloth. Results also show that acid pH enhances the catalytic decomposition of H₂O₂ to hydroxyl radicals, increasing TOC removal from 16 to 55% as a result of oxidation of phenol in addition to adsorption on the ACC surface. Furthermore when using ACC catalysis under optimized conditions, the maximum extent of TOC elimination is approximately 70% with three 15 min doses of ozone at pH 9.

Key words | activated carbon cloth, hydrogen peroxide, hydroxyl radicals, ozone

INTRODUCTION

Until recently, industrial effluents were treated by traditional techniques such as filtration, reverse osmosis, flocculation, coagulation, precipitation and incineration. In these approaches, the pollutants are transferred from a liquid phase to a solid phase and for many years activated carbon (AC) has been the reagent of choice for adsorption of various toxic pollutants particularly as air pollution control devices and there are many reports on the adsorption of toxic pollutants on the surface of AC (see Takaoka et al. 2007).

Granular Activated Carbon (GAC) either as adsorbent alone or in combination with an Advanced Oxidation Process (AOP) have been commonly used in water and wastewater treatment in order to remove toxic pollutants (Lin & Lai 2000; Bremner & Burgess 2004; Bremner et al. 2006; Zhang et al. 2006). On the other hand, on an industrial scale, the use of fibrous activated carbon in the form of cloth (ACC) or felt (ACF) has received enormous attention as an adsorbent for purifying water as well as air (Brasquet et al. 1999; Le Cloirec et al. 1996, 1997).

Since the main objective of this current study was to assess the effect of activated carbon cloths (ACC), pH, temperature and different oxidizing agents, i.e., H₂O₂ and O₃, in conjunction with ACCs for phenol removal via adsorption/oxidation, previous findings and observations with H₂O₂/O₃/AC, in particular, have been taken into

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account and are discussed here to present a background for this study.

Hydrogen peroxide (H₂O₂) in conjunction with AC tends to modify the surface properties of AC for adsorption and its catalytic properties for degradation. However, most of the work has concentrated on granular activated carbons (GAC) but there are few reports describing ACC or ACF in conjunction with O₃/H₂O₂ at room temperature (Lei et al. 2007). The oxidation of organic compounds in an aqueous medium using H₂O₂ catalysed by AC has been investigated and an interesting feature emerges wherein the AC acts as adsorbent as well as catalyst/promoter for the oxidation of organic contaminants (Lücking et al. 1998; Ince & Apikyan 2000).

Likewise, based on findings by Jans & Hoigne (1998), the activity of AC for the transformation of ozone (O₃) into HO⁻ radicals, including various operational parameters such as carbon/O₃ dose, carbon type and treatment time was also quantified (Sánchez-Polo et al. 2005). These authors concluded that in the case of O₃ (and H₂O₂) AC does not really act as a catalyst but rather as a conventional initiator or promoter for the O₃ transformation into HO⁻ radicals.

This integrated technology in wastewater treatment presents strong synergistic effects, especially in the mineralization of organic compounds (Sánchez-Polo et al. 2005; Sánchez-Polo & Rivera-Utrilla 2005, 2006). Adsorption–ozonation–regeneration studies (Lin & Lai 2000) suggest that GAC possesses excellent surface adsorption ability, where the pollutants gradually oxidize and the GAC is regenerated at the same time. Whereas, in catalytic ozonation (Sánchez-Polo & Rivera-Utrilla 2003), GAC initiates radical-type chain reactions in the aqueous media and the oxidation process is catalyzed by the GAC.

**Reaction mechanisms**

The following reaction mechanisms (Table 1) presented in the literature for activated carbon in conjunction with O₃ and H₂O₂ can be utilized to discuss the hydroxyl radical contribution in the adsorption/oxidation properties of the ACC in this study. References to specific reactions (i)–(xi) in relation to the results obtained will be further considered in the Results and Discussion section.

From the literature presented, it can be seen that many studies related to GACs in conjunction with strong oxidants reveal the catalytic efficacy and industrial potential of ACs to treat toxic wastewaters. Hence, the main aim of this research was to investigate the potential use of activated carbon cloth (ACC) for removal of toxic phenol from wastewaters via adsorption and/or chemical oxidation.

**METHODS**

**ACC and H₂O₂ reactions**

The experiments involving ACC and hydrogen peroxide were performed in a conical flask (500 mL) submerged in a shaker bath operating at 200 strokes min⁻¹.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Reaction mechanisms discussed in the literature for activated carbon in conjunction with the use of O₃ and H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Khalil et al. 2001)</td>
<td>AC−OH + H⁺ OOH⁻ → AC−OOH + H₂O AC−OOH + H₂O₂ → AC−OH + H₂O + O₂</td>
</tr>
<tr>
<td>(Kimura et al. 1996)</td>
<td>AC + H₂O₂ → AC⁺ + HO⁻ + OH⁻ (ii) AC⁺ + H₂O₂ → AC + HO₂⁻ + H⁺ (iii)</td>
</tr>
<tr>
<td>(Beltran et al. 2006)</td>
<td>G + O₃ → Int + H₂O₂ (iv) Int + O₂ → Ket + Ox + H₂O₂ (v) H₂O₂ → HO₂⁻ + H⁺ (vi) HO₂⁻ + O₃ → HO₂⁺ + O₃⁻ (vii)</td>
</tr>
<tr>
<td>(G, gallic acid; Int, Intermediates; Ox, oxalic acid and Ket, ketomalonic acid)</td>
<td>Many steps HO⁻ (viii) HO⁻ (viii) H₂O₂ or HO₂⁻ (ix) CO₂ + H₂O (x) (xi)</td>
</tr>
</tbody>
</table>
In a typical experiment, a solution of phenol in water (2.5 mM; 200 mL) was placed in the shaker bath. Two pieces of ACC (0.085 g each; equivalent to 0.85 g L\(^{-1}\) of ACC in the solution) and hydrogen peroxide (1.19 g L\(^{-1}\); corresponding to the theoretical stoichiometric amount for a complete mineralization of 2.5 mM phenolic aqueous solution, according to Equation (1)) was then added to the flask, thus starting the experimental run.

\[ \text{C}_6\text{H}_6\text{O} + 14\text{H}_2\text{O}_2 \rightarrow 6\text{CO}_2 + 17\text{H}_2\text{O} \] (1)

Three different pH values were investigated in this study—pH 3 and 9 were obtained by adding appropriate amounts of H\(_2\)SO\(_4\) (0.05 M) and NaOH (0.1 M), respectively, to the initial solution; and pH 5.5, which corresponds to the natural pH of the initial phenolic aqueous solution. Each experimental run was repeated three times.

Samples were withdrawn from the reaction after 1, 2 and 3 h and the total organic content (TOC) was determined using a combustion/non dispersive infrared gas analyzer (1020A; O-I Analytical). Phenol removal was determined by use of a GC-MS chromatograph model (QP2010S; Shimadzu) and the hydrogen peroxide concentration was measured by iodometric titration.

**ACC and O\(_3\) reactions**

The experiments involving ACC and ozone were performed in a round bottom flask submerged in a shaker bath operating at 200 strokes min\(^{-1}\) at room temperature. The effects of phenol removal through direct ozonation were studied at the natural pH of 2.5 mM aqueous phenol (pH 5.5) and at the modified conditions of pH 3 and 9 respectively. Oxidation was evaluated based on the decreasing TOC/TIC and pH values. Ozone was produced by reaction of an oxygen gas feed in a corona discharge ozone generator (Triogen). An O\(_2\) flow rate of 5 L min\(^{-1}\) was selected for all the ozonation experiments and provided an overall concentration of ozone in the reaction medium of 5.6 to 6.3 mg L\(^{-1}\), measured by the indigo colorimetric. Direct ozonation was carried out in one of two ways: either the reaction medium was ozonized for 15 minutes just before the reaction was started or a step-wise ozonation process was used wherein the reaction solution was ozonized for 15 minutes prior to starting the reaction and then it was ozonized again for 15 minutes after different reaction times. This study was carried out in order to determine if enhanced phenol removal was observed, depending on the ozonation process.

**RESULTS AND DISCUSSION**

Elimination of phenol in the presence of hydrogen peroxide and activated carbon cloth

Figure 1a shows the extent of TOC removal after 3 hours of treatment in the presence and absence of hydrogen peroxide and ACC. The adsorption of several organic compounds (phenolic compounds, dyes, etc.) onto the surface of activated carbon is highly influenced by the pH of the bulk solution, since its surface charge density depends on the solution pH (Moreno-Castilla et al. 1995; Lazslo & Szucs 2001). This factor determines the surface charge of the activated carbon, as well as the ionisation of the organic solute. Thus, three different pHs were selected for study: pH 3, 5.5 (corresponding to the natural pH of 2.5 mM phenol in aqueous solution) and 9. On the other hand, experiments in the absence of the oxidant allow determination of the extent of the phenol adsorption on the ACC surface.

TOC removal of around 50% is obtained with the addition of hydrogen peroxide to the aqueous phenol solution in presence of ACC regardless of pH. These values are higher than those obtained in the absence of hydrogen peroxide, when the adsorption of the organic pollutant over the ACC surface is the major process. It has been previously stated that activated carbon can decompose H\(_2\)O\(_2\) by a mechanism involving the exchange of a hydrogen peroxide anion with a surface hydroxyl group, followed by the decomposition of another H\(_2\)O\(_2\) molecule to result in the production water and oxygen (Equations (2)–(3); Khalil et al. 2001).

\[ \text{AC–OH} + \text{H}^+\text{OOH}^- \rightarrow \text{AC–OOH} + \text{H}_2\text{O} \] (2)

\[ \text{AC–OOH} + \text{H}_2\text{O}_2 \rightarrow \text{AC–OH} + \text{H}_2\text{O} + \text{O}_2 \] (3)

Additionally, AC can also behave as an electron-transfer catalyst following a Haber-Weiss mechanism (similar to the
Fenton catalyst) and involving the production of free radicals (Equations (4)–(5); Kimura et al. 1996).

\[
AC + H_2O_2 \rightarrow AC^+ + HO^- + OH^-
\]  

(4)

\[
AC^+ + H_2O_2 \rightarrow AC + HO_2^- + H^+
\]  

(5)

All of the above can be applied to ACC and, in summary, the combined use of ACC and hydrogen peroxide enhances TOC diminution by promoting the generation of hydroxyl radicals and influences the overall oxidation process. It is remarkable that the benefits of hydrogen peroxide are particularly striking at acid pH, whereas TOC removal is less pronounced at higher pH. This influence of the initial pH has been reported in the literature (Georgi & Kopinke 2005; Fan et al. 2006), where an optimum pH of 2–3 was found for the oxidation of different organic compounds and dyes with AC/H₂O₂ systems. This was ascribed to the combination of a number of factors including non-effective decomposition of H₂O₂ caused by an increase in pH. It has been reported in literature that the decomposition of H₂O₂ towards, predominately, O₂ occurs at pH 5 and 7 when heterogeneous catalysts, such as Fe/C, Fe-ZSM-5 zeolite or pillared clays (Fajerwerg et al. 2000; Guo & Al Dahhan 2003; Zazo et al. 2006) are employed. On the other hand, additional explanations can be obtained by considering the higher redox potential of H₂O₂ with decreasing the pH, as well as possible changes in properties of the ACC surface (Georgi & Kopinke 2005). Thus the adsorption of H₂O₂ on AC is favoured at high pHs, changing the concentration of carboxylic acids on the surface by oxidation (Figueiredo et al. 1999; Orfao et al. 2006).

Likewise, it is remarkable that the outstanding enhancement of TOC removal at the initial pH of 3 is accompanied by lower consumption of hydrogen peroxide, whereas at pH 9 the decomposition of hydrogen peroxide is maximum (Figure 1b). In this way, the increased adsorption of H₂O₂ seen at high pH promotes scavenging reactions between HO⁻ previously formed and another H₂O₂ molecule, producing H₂O, H⁺ and O₂⁻ (relatively stable at high pH), which can decompose more adsorbed hydrogen peroxide in a chain reaction (Equations (6)–(8); Khalil et al. 2001).

\[
H_2O_2 + HO^- \rightarrow H_2O + HOO^-
\]  

(6)

\[
HOO^- \rightarrow H^+ + O_2^-
\]  

(7)

\[
H_2O_2 + O_2 \rightarrow HO^- + HO^+ + O_2
\]  

(8)

A slight decrease in the pH during the process when an initial pH of 9 is employed was observed, which supports
Equations (6)–(8) though there is no change seen at the other pH values employed.

Summarizing, these results indicate that ACC catalyzes the decomposition of \( \text{H}_2\text{O}_2 \) producing active hydroxyl radicals at acidic pH, but at higher pH the hydrogen peroxide decomposition is less effective towards \( \text{HO}^\cdot \) generation. This is in agreement with the literature relating to the role of the chemical nature of the AC surface in the catalytic decomposition of \( \text{H}_2\text{O}_2 \) (Khalil et al. 2001).

**Elimination of phenol in presence of ozone and activated carbon cloth**

Bulk and step-wise direct ozonation effects were also investigated in this work in order to determine if they had any effect. From **Table 2**, it can be clearly seen that ozonation of phenol under alkaline pH conditions leads to high phenol removal in the presence and absence of the ACC catalyst. More importantly, step-wise ozonation was found to be more beneficial than bulk ozonation as it continuously provides oxidizing radical species to the reaction medium, which in-turn enhances the oxidation and this theory agrees with the literature (Gogate & Pandit 2004a,b) and reactions (iv–xi) presented in **Table 1** (Beltran et al. 2006).

Bulk treatment with 15 min ozone at the start of the reaction (no ACC) resulted in 6, 17 and 20% TOC removal at pH = 3, 5.5 and 9 respectively. Step-wise treatment with 5 min ozonation at 0 min and then 5 min ozone at 1 h and 2 h (no ACC) resulted in 12, 16 and 24% TOC removal at pH = 3, 5.5 and 9 respectively. However, a synergistic effect of the ACC/O\(_3\) system was evident since bulk ozonation for 15 min at the start of the reaction in the presence of ACC (0.85 g L\(^{-1}\)) led to 33–38% TOC removal at all the pHs studied. Similar results were observed in the combined effect of ACC/ozonation on the removal of phenol from aqueous solution and were accounted for by adsorption/oxidation (Sánchez-Polo & Rivera-Utrilla 2003).

Also, step-wise ozonation and a longer period of contact between the phenol, ACC and \( \text{O}_3 \) were studied for enhanced phenol removal and results are presented in **Figure 2**.

It can be seen that step-wise addition of \( \text{O}_3 \) at suitable time intervals over a longer contact period lead to the highest (~70%) phenol removal as a result of the combined effect of adsorption/oxidation. Notable changes in pH were also observed (pH 3 decreased to 2.80; 5.5 to 3.04 and 9 to 3.20) indicating the formation of acid decomposition by-products via oxidation of phenol by radicals produced due to \( \text{O}_3 \) decomposition on the ACC surface. Considerable change in TIC values (2.27–6.33 mg L\(^{-1}\)) were also noticed indicating \( \text{CO}_2 \) formation due to mineralization of the organic compounds.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Time (h)</th>
<th>pH</th>
<th>( t_i )</th>
<th>( t_f )</th>
<th>( \Delta \text{TIC} ) (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step-wise: 5 min ozonation (at 0 min and ( \times 2 ) after every 1 h) (No ACC)</td>
<td>3</td>
<td>3</td>
<td>180.0</td>
<td>157.7</td>
<td>3.04</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>180.0</td>
<td>152.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>180.0</td>
<td>137.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk ozonation: 15 min at the start of the reaction (No ACC)</td>
<td>3</td>
<td>3</td>
<td>180.0</td>
<td>168.4</td>
<td>3.79</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>180.0</td>
<td>149.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>180.0</td>
<td>144.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk ozonation: 15 min at the start of the reaction + (ACC, 0.85 g L(^{-1}))</td>
<td>3</td>
<td>3</td>
<td>180.0</td>
<td>119.9</td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>5.5</td>
<td>180.0</td>
<td>116.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>180.0</td>
<td>112.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Therefore, from studies on the ACC/O₃ system, it can be concluded that optimized conditions of ozonation over a suitable period time with the ACC catalysts could lead to efficient phenol removal. Moreover, the decrease of TOC during ozonation of phenol in the presence of ACC is a result of the combined effect of two parallel systems: catalytic–chemical oxidation and adsorption. Thus, the positive combined effects of treatments for enhanced pollutant removal proposed in this study with ACC/H₂O₂ systems are in line with those suggested through combinations of various AOPs in the literature. Hence, it is seen that the combination of ACC with different AOP's is a promising technology for the degradation toxic pollutants in wastewater, via an adsorption/oxidation mechanism.

CONCLUSIONS

Using ACC catalysis under optimized conditions, the maximum extent of TOC decrease was approximately 70% with three 15 minute doses of ozone at pH 9. Results show that acid pH enhances the catalytic conversion of H₂O₂ into hydroxyl radicals, increasing TOC removal from 16 to 55%, by oxidation of phenol in addition to adsorption on the ACC surface. The benefits of H₂O₂ at pH 5.5 and 9 are hardly significant, due to decomposition of H₂O₂ occurring through other parallel reactions at these pHs.

In-depth knowledge of the chemical/textural properties and behavior of ACC in oxidant-assisted phenol removal could lead to a better understanding and support of the proposed hypothesis of adsorption/chemical oxidation via ACC/O₃/H₂O₂ systems and these studies are currently underway.

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