The investigation of catalytic ozonation and integrated catalytic ozonation/biological processes for the removal of phenol from saline wastewaters

Gholamreza Moussavi *, Ali Khavanin, Rahimeh Alizadeh

Department of Environmental and Occupational Health Engineering, Tarbiat Modarres University, Tehran, Iran

ARTICLE INFO

ABSTRACT

The effectiveness of the catalytic ozonation process (COP) with a GAC catalyst was assessed based on the degradation and COD removal of phenol from the saline wastewater, as compared with the single ozonation process (SOP). The COP attained a much higher level of phenol degradation compared to the SOP. The influence of several variables was investigated, including pH of solution, NaCl concentration, and dosage of GAC, for their effects on COP phenol degradation in a synthetic saline wastewater. The maximum degradation of phenol was achieved at pH 8 and 20 g/L GAC. NaCl had no adverse effect on phenol removal at ranges between 0.5 and 50 g/L. The activated carbon acted mostly as a catalyst for ozone decomposition, and the subsequent generation of hydroxyl radicals. Furthermore, the GAC preserved its catalytic properties after 5 times reuse. The capability of a biological process to treat COP effluent was also investigated. Results showed that a 10 min reaction time in COP under optimum conditions reduces the concentrations of phenol and COD to an acceptable level for efficient post-treating in a suspended growth bioreactor at a short aeration time of 4 h. Thus, the integration of COP with a biological process is proven to be a technically and economically effective method for treating saline wastewaters containing recalcitrant compounds.

1. Introduction

Several industries including petroleum refineries, petrochemical plants, olive oil mills, pesticide manufacturing, and oil field activities generate saline waste streams containing significant amounts of phenol and its derivatives [1–3]. Since phenol is classified as a toxic and priority hazardous compound [4], it is required to be degraded prior to discharging contaminated streams to the environment. When treating such wastewaters, two challenges must be dealt with high salt content and the recalcitrant nature of phenol. Therefore, treating saline phenol wastewaters is an environmental challenge, and many efforts throughout the world are focusing on finding an effective process either as a pretreatment for biological processes or a single treatment option.

In recent years, advanced oxidation processes (AOPs) in which highly reactive radicals (particularly •OH) are generated have been increasingly applied for the degradation of various classes of organic compounds. Among them, considerable attention has recently been paid to investigating the catalytic ozonation process (COP) as a new AOP. Indeed, COP is among the recently developed

and most promising AOPs; in this process, a catalyst is applied to enhance the ozone decomposition, thereby forming highly reactive and non-selective hydroxyl radicals [5]. These radicals are capable of oxidizing the toxic and/or refractory organic compound(s) into final inorganic products at rates ranging from 10^6 to 10^9 L/M s [6], and sometimes of converting them to less toxic and more biodegradable intermediates [7].

COPs are often classified as homogenous and heterogeneous processes [8–10]. Due to their simplicity of operation, capability to function at ambient temperature and pressure, low cost, potential for catalyst separation, and thus lack of secondary pollution, the heterogeneous COP is the most promising method among recently developed AOPs for treating industrial wastewaters containing refractory compounds [11–14].

Numerous catalysts, including activated carbon, metal ions, metal oxides, natural and synthetic materials have been applied in COPs for oxidizing various organic molecules. Two of the key characteristics of any catalyst in a COP that affects process performance are stability and durability [15]. One of the most frequently applied and promising catalysts in COPs for removal of various refractory compounds is activated carbon [16]. Integrating ozonation and activated carbon adsorption enables the exploration of both processes' advantages and synergies, while also overcoming their individual defects. Degradation of an organic compound in

* Corresponding author. Tel.: +98 21 82883827; fax: +98 21 82883825.
E-mail address: moussavi@modares.ac.ir (G. Moussavi).

a COP with activated carbon involves two mechanisms: catalyzing ozone decomposition and thereby generating oxidative radicals (mainly •OH), and/or adsorbing on the catalyst surface with subsequent oxidation [11,17].

Liotta et al. [15] reviewed the heterogeneous catalytic oxidation of phenolic compounds. Many researchers have investigated the degradation of phenol in aqueous solutions using COP in the presence of different catalysts [18–28], reporting it as an attractive and appealing process for treating such wastewaters. Based on our best literature review efforts, except for a few reports available on using AOPs for removal of phenol from saline wastewaters [29–31], no investigation could be found on COP treatment of saline wastewaters containing high phenol concentrations. Azevedo et al. [29] investigated the degradation of phenol in saline solution using a TiO$_2$-photocatalytic process, and observed a significant inhibitory effect for 50 g/L of NaCl on the phenol degradation. It was also reported that the time required for effective removal of phenol increased with increasing NaCl content. They [30] repeated their experiments on saline phenol wastewater treatment via single ozonation and found that salinity could inhibit the oxidation rate, indicating that ozonation is inefficient for processing high salinity contaminated streams. The effectiveness of Fenton and photo-Fenton processes on phenol removal from a saline effluent was studied by Maciel et al. [31]. Their results indicated that although both processes were effective for phenol degradation, the high salt concentration inhibited the oxidation reaction considerably, so that only a 50% removal of TOC was obtained in the photo-Fenton process in the presence of 50 g/L NaCl, even after 100 min reaction time.

The primary objective of the present study was to explore the COP with the use of activated carbon, as it is one of the most recently investigated and promising AOPs, for removing phenol from saline wastewaters. Effects of solution pH, catalyst quantity, salt concentration, and phenol concentration were investigated on the COP performance. The efficiency of COP in treating defined wastewater was evaluated in terms of phenol degradation and chemical oxygen demand (COD), as measured by percent reduction. The potential for catalyst reuse was also assessed. Post-treatment of the COP effluent at the highest investigated phenol concentration was attempted, under optimum experimental conditions, in a suspended growth biological process.

2. Materials and methods

2.1. Chemical and materials

All reagents and chemicals used throughout the study, including phenol and NaCl and those used in phenol and COD analysis, were of analytical grade. All solutions were prepared using distilled water. All glassware was acid-washed, distilled water-rinsed, and dried before each experiment. A commercial granular activated carbon (GAC) supplied by Merck Co. was used in this study as the catalyst, which was grinded into at an average size of 0.5 mm before use. The GAC was washed first with distilled water and then dried at 100 °C for 24 h prior to use in the experiments.

2.2. Experimental reactor and procedure

2.2.1. Single and catalytic ozonation processes

The catalytic ozonation reactor was a glass sparger with 250 mL total volume fitted with other components, including an ozone generator, a sintered glass diffuser to distribute the ozone air stream to the solution, an air pump, an ozone off-gas destruction system, valves, and tubing. Several experimental runs were defined for investigating phenol removal from saline wastewater, with the objectives and conditions given in Table 1. All experiments were performed in batches, with a constant volume solution of 200 mL at 24 ± 2 °C. Ozone was generated by feeding air into a generator (ARDA, Model AEGCOG-5S) with 5 g O$_3$/h capacity. The dose of ozone was kept constant at 0.25 g/h throughout the experiment. The ozone in the off-gas stream of the reactor was destroyed in a concentrated KI solution.

2.2.2. Biodegradability assessment of COP effluent

In order to assess the biodegradability of the COP effluent investigated in the present work, a series of biological batch tests were performed on the COP effluent resulting from the operating conditions given in Table 1. In each test of this phase, 150 mL of filtered solution from the COP effluent was poured into a sparger equipped for aeration. The solution was initially conditioned with pH and nutrient levels suitable for microbial metabolism. Then 50 mL of thickened and acclimated activated sludge (1% solids), taken from a bench scale SBR was added to the reactor and aerated for a given time. After the prescribed aeration time, the mixture was filtered and analyzed for remaining phenol and COD. The investigated aeration times were at ranges between 0.5 and 4.5 h.

2.3. Analysis

pHzpc of GAC was measured by the procedure detailed by Lopez-Ramon et al. [32]. In order to evaluate the effectiveness of catalytic ozonation in phenol and COD removal, samples were taken from each experiment at the beginning and end of the reaction. Samples were then analyzed for phenol and COD. The phenol concentration was determined by the colorimetric 4-aminoantipyren procedure [33], using a Unico-UV 2100 UV/vis Spectrophotometer to measure

Table 1
Experimental phases and conditions.

Phase	Experiment	Conditions				
		C_{phenol} (mg/L)	C_{NaCl} (g/L)	C_{GAC} (g/L)	pH	RT (min)
1	Effect of pH	1200	20	7.5[a]	2–12[b]	5–60
2	Synergistic effect of GAC on ozonation	1200	20	20[a,c]	8[d]	2.5–60
3	Effect of radical scavenger (0.6 g t-butanol)	1200	20	20	8	2.5–60
4	Effect of GAC dosage	1200	20	0–25	8	2.5–60
5	Effect of NaCl concentration	1200	0–50	20[a]	8	30
6	Phenol and COD removal under optimum conditions	1200	20	20	8	2.5–60
7	Catalyst durability	1200	20	20	8	15
8	Biodegradability of the COP effluent (experimental conditions of COP)	1200	20	20	8	10

(C_{phenol} = phenol concentration; C_{NaCl} = NaCl concentration; C_{GAC} = GAC concentration).
[a] The same experiments were carried out for SOP (without GAC).
[b] The investigated pHs in SOP were 2, 8 and 10.
[c] The same experiment was performed for phenol adsorption on GAC (without ozone).
[d] Optimum pH in which the maximum phenol removal was obtained in COP.
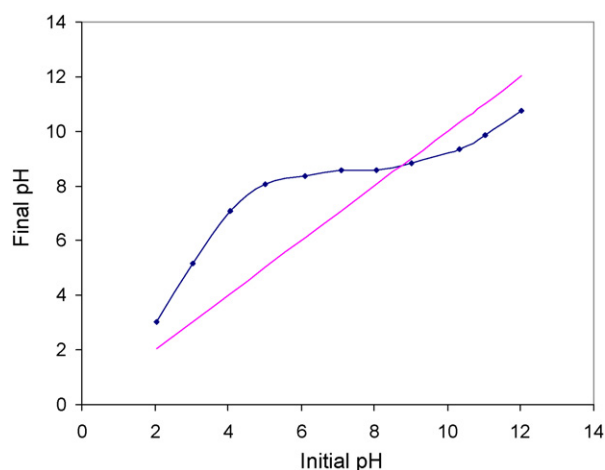
Fig. 1. pH drift for estimating pHzpc of GAC.

Fig. 3. Effect of initial pH on phenol removal from saline wastewater in the SOP.

maximum transmission/absorbance at wavelength of 500 nm. COD was measured with a standard potassium dichromate oxidation method [33], and the pH was determined using an electrode (Sense Ion 378, Hack). The ozone concentration in the inlet gas stream was quantified by iodometric titration [33].

3. Results and discussion

At the beginning of the experiment, the main characteristic of the catalyst, pHzpc, was determined. The pH-drift experiment results presented in Fig. 1 show a pHzpc value of 8.9 for the GAC; this characteristic affects ozone decomposition [34], and thereby the process performance.

3.1. Single and catalytic ozonation processes

3.1.1. Effect of initial pH and the mechanism of degradation

The pH affects the way that ozone reacts to oxidize organic molecules in a liquid. Therefore, the effect of initial solution pH (ranging from 2 to 12) was investigated on the phenol degradation in COP under the conditions defined in Table 1. Fig. 2 presents the results in terms of phenol removal. As seen, the effect of pH on COP performance is more pronounced for reaction times less than 30 min. The highest removal percent by COP was measured for pH 8, where greater than 88% of phenol was degraded in the first 10 min of reaction time. The degradation increased to 96% when the reaction was extended to 60 min. Therefore, the pH of 8 was selected as optimum for the next experimental runs. For comparison purposes,
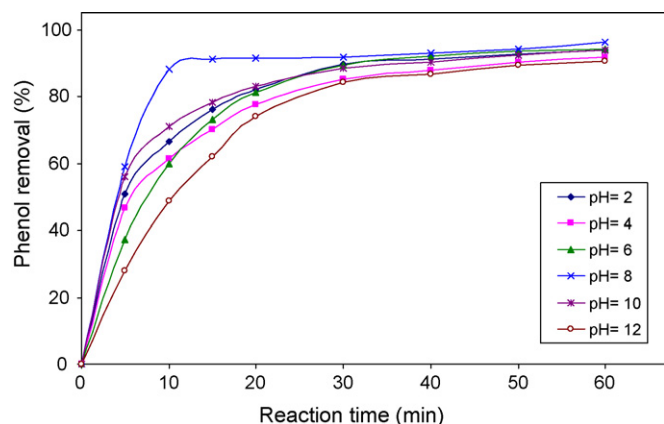

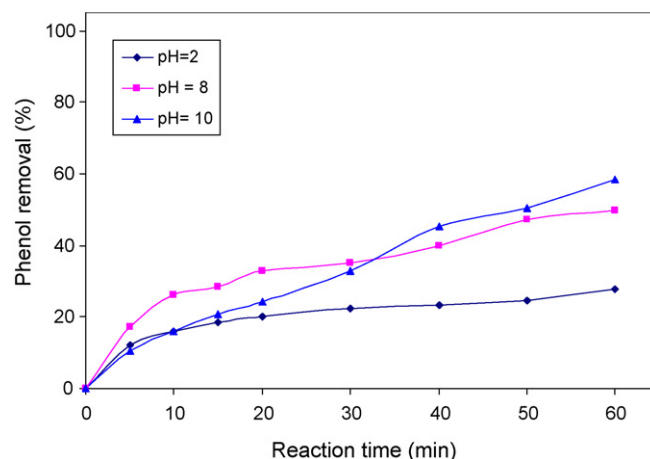Fig. 2. Effect of initial pH on phenol removal from saline wastewater in the COP.

degradation of phenol in SOP was also investigated at pH values of 2 and 10 as optimum for direct and indirect radical oxidation, respectively, as well as pH 8 as the optimum obtained in the COP. As is observed in Fig. 3, only 26% and 49% of phenol was removed at 10 and 60 min reaction times in SOP at pH 8, respectively. In order to better illustrate the effect of pH, the kinetic of phenol degradation was assessed for both COP and SOP. The resulting information is summarized in Table 2, which indicates that oxidation of phenol in both processes under the selected condition was of second order. As Table 2 shows the phenol degradation in the COP increased with increasing pH to attain the maximum value at the weakly alkaline pH of 8, which are several orders of magnitude faster than that in an SOP under identical conditions.

The improvement of phenol degradation rate with increasing pH up to the moderate alkaline value of 8 might be due to acceleration of ozone mass transfer and ozone decomposition rates with pH [17,35]; this in turn leads to the formation of highly reactive radicals, mainly $^{\bullet}OH$ [36]. The greater the pH, up to the optimum value, the higher would be the produced $^{\bullet}OH$ and thus the higher the degradation rate. In the other words, low degradation of phenol in COP under acidic pH is presumed to be due to the lack of OH^- available for significant dissociation of ozone. This precludes the production of enough $^{\bullet}OH$, and/or causes the generation of radicals that are less reactive than $^{\bullet}OH$ on the GAC surface [37,38].

The solution pH had a negative effect on phenol degradation at values 10 and higher; i.e. the degradation rate of phenol was reduced under strong alkaline conditions (Table 2). This finding can be better interpreted by taking into consideration both the speciation of phenol (pKa) and the surface charge of the GAC, with respect to solution pH and catalyst pHzpc. Since the pHzpc of GAC is 8.9, a negative charge is developed on its surface at this pH (10) and above. Phenol, on the other hand, is mostly dissociated to phenolate anions (pKa = 9.9) at these basic conditions [39]. There-

Table 2
Kinetic information of phenol removal as a function of pH in the COP and SOP.

pH	2	4	6	8	10	12
COP						
Order	2	2	2	2	2	2
Constant (L/mM min)	0.024	0.016	0.021	0.032	0.019	0.014
R^2	0.988	0.998	0.994	0.941	0.972	0.99
SOP						
Order	2	–	–	2	2	–
Constant (L/mM min)	0.0005	–	–	0.0014	0.0021	–
R^2	0.681	–	–	0.921	0.982	–
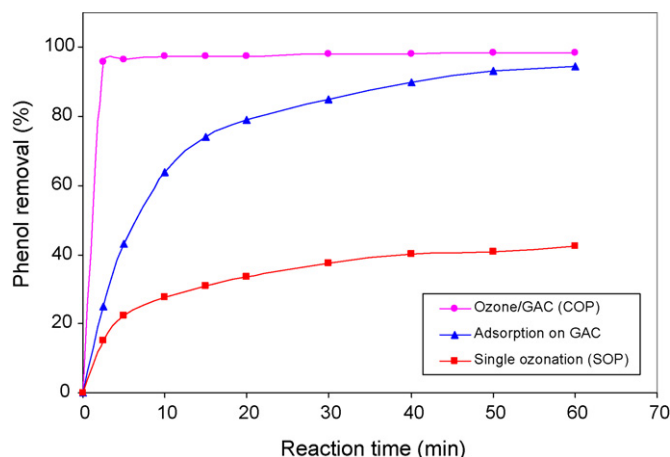
Fig. 4. Synergistic effect of GAC (20 g/L) on ozonation process.

Fig. 5. Effect of *t*-buanol radical scavenger on phenol removal in the COP.

fore, the affinity of catalysts for phenolate under strong alkaline conditions is restricted, and the surface catalyst reactions would probably be inhibited, leading to the reduction in phenol degradation rate.

For the SOP, the degradation rate increased with increasing pH. This can be justified by the fact that the decomposition of ozone increases with increasing pH, resulting in the formation of highly reactive •OH [40,41] with much higher oxidation potential than ozone molecules. Nonetheless, the phenol removal was remarkably faster in the COP than the SOP regardless of the conditions, verifying the positive effect of coupling ozonation and GAC to degrade toxic compounds such as phenol.

Another point worth emphasizing in Table 2 is the noticeable degradation rate of phenol attained in the COP at the acidic pH of 2, compared to the SOP. It can be clearly seen that adding GAC to the ozonation reactor had a strong positive effect on phenol degradation. Due to the fact that ozone reacts directly with organic molecules at acidic pHs [42], this increased degradation can be attributed to the increased contact surface between ozone and phenol molecules for reaction. To further elucidate the role of GAC in the COP, an experiment was carried out under conditions similar to phase 1 (Table 1, pH 8) in which a GAC saturated with phenol was used instead of a fresh one. The phenol removal percentages did not deviate significantly from those obtained with the fresh GAC at the same experimental conditions. This suggests the catalytic role is the dominant reaction in the COP rather than adsorption–oxidation one [43], and indicates a synergistic effect of GAC with ozonation in degrading the phenol. Fig. 4 compares the removal of phenol in COP, SOP and single GAC (adsorption) systems under the same phenol and NaCl concentrations, pH 8, and 20 g/L GAC dosage (no GAC in SOP). A synergistic effect is observed in combining ozonation and GAC, especially in the initial reaction stages. For example, phenol removal percent in COP at reaction times of 2.5 and 5 min was 56% and 32% greater than sum of removals in single ozonation and GAC adsorption systems, respectively, indicating a significant synergistic effect in the COP. No synergistic effect was observed at reaction times over 10 min. Lei et al. [17] also found a 36% synergistic effect for COD removal in the combined ozonation and activated carbon process at alkaline pH. Another reason for this effect is the in situ regeneration of saturated GAC by molecular ozone and generated radicals [22,26]. As such, it can be inferred that GAC can be reused; this will be presented in more detail later in the text. The high removal percent of phenol in the COP can be attributed to the capability of GAC to decompose ozone and thereby enhance •OH generation [34,44,45]. Other researchers [e.g. 20,21] have also observed the synergistic effect of activated carbon and ozonation

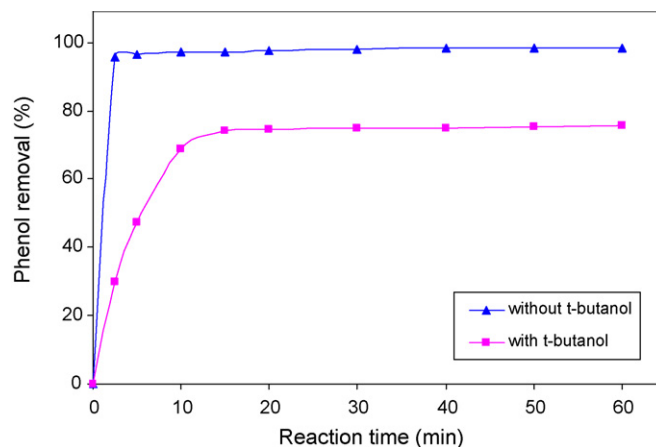in phenol removal, but in non-saline liquid. Effects of salinity will be discussed later in this text.

Table 2 further illustrates that COP performed better than direct oxidation with ozone (at pH 2) and even than ozonation at high pH, where •OH are generated; this confirms that GAC can significantly promote •OH formation to a concentration higher than those generated with ozonation at high pH, as would be found in an AOP. These findings strongly suggest the predominance of indirect radical-type degradation mechanisms in COP, both at the GAC surface (heterogeneous) and in bulk solution (homogenous) [16,45]. Some degree of oxidation with non-decomposed ozone, however, might also be occurring both at the surface and in bulk solution [45]. It is also possible that the adsorption on GAC could cause a higher concentration of phenol and ozone/radicals on surface of GAC, therefore enhance the phenol degradation. The predominance of radical degradation of phenol in the COP was confirmed by the radical scavenger experiment defined in Table 1. Fig. 5 shows the phenol removal via COP with and without *t*-butanol as a function of reaction time, clearly exhibiting that adding *t*-butanol noticeably suppressed the oxidation and thus diminished the degradation of phenol, particularly in initial reaction times. For instance, the removal percent was reduced from around 99% to 74% in the presence of *t*-butanol for a 60 min reaction time. In other words, the radical scavenger reduced the reaction rate constant from 0.032 to 0.0032 L/mM min, representing a 10-fold reduction in degradation rate. Since *t*-butanol is a known •OH scavenger that has very low reactivity with ozone molecules [27], this result verifies that •OH was the dominant radical species working in the reactor [12], and thus that indirect radical oxidation has been the predominant phenol degradation mechanism in saline liquid in the GAC catalyzed ozonation process.

It can therefore be concluded from these findings that the COP with GAC is an efficient and feasible method for removing phenol from saline wastewaters at weakly basic pH.

3.1.2. Effect of GAC dosage

The removal of phenol was studied for ozonation process in the presence of different dosage of GAC ranging from 0 to 25 g/L (Table 1). Fig. 6 presents the removal of phenol as a function of GAC dosage, showing a significant enhancing effect of GAC on the ozonation process, particularly for shorter reaction times. For instance, at a reaction time of 5 min the removal of phenol increased from 22% in the absence of GAC to 50% in the presence of 0.5 g (2.5 g/L) of GAC (Fig. 6), reiterating the catalytic effect of GAC on ozonation. The phenol degradation increased thereafter with increasing GAC dosage up to 20 g/L, where a 97% removal of phenol was achieved during the first 5 min of reaction. The removal of phenol increased
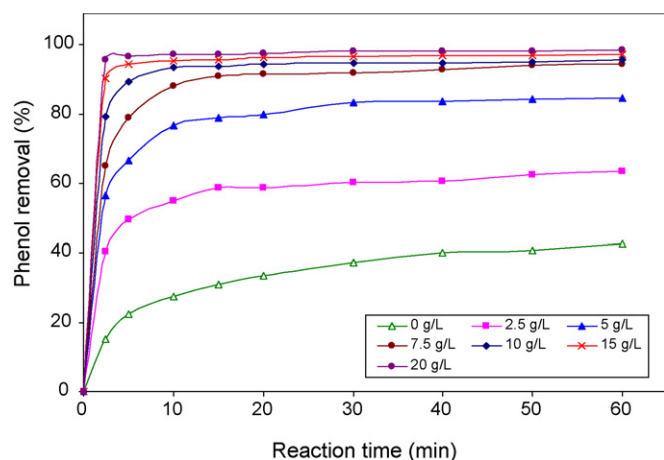
Fig. 6. Effect of GAC dosage on phenol removal in the COP.

Fig. 8. COD and phenol removal in the COP under the optimum operation conditions.

to greater than 99% when the reaction was extended to 60 min. The increase of phenol degradation with increasing GAC dosage is related to the increase of catalyst surface area and of active sites available for ozone decomposition; these increases therefore enable enhanced generation of reactive radicals, mainly •OH [6,35,43,44,46], resulting in improvement of the phenol removal efficiency. Further increases of GAC to 25 g/L, however, did not affect the percentage of phenol degraded. Although the optimum dosage of catalyst in a COP depends heavily on the type of catalyst, the target compound, the reaction conditions, and desired performance, the value of 20 g/L was determined as the optimum dosage for GAC in the present work, and was thus used in all remaining experiments. Although achieved under different experimental conditions and in the absence of NaCl, these results are commensurate with Qu et al. [26] who also showed an increase in phenol removal with the increase of activated carbon in the COP, up to an optimum value.

3.1.3. Effect of NaCl concentration

The influence of NaCl concentrations between 0 and 50 g/L was compared on COP and SOP performance in phenol removal under the conditions designated in Table 1, and the results are presented in Fig. 7. It is clear from Fig. 7 that the NaCl affects the performance of COP and SOP differently with respect to phenol removal.

For the COP, only 63% of the phenol was removed in the absence of NaCl. Interestingly, the removal efficiency of phenol in COP improved to 97.5% with the increase of NaCl concentration to 0.5 g/L. Further increasing the NaCl concentration led to a slight increase
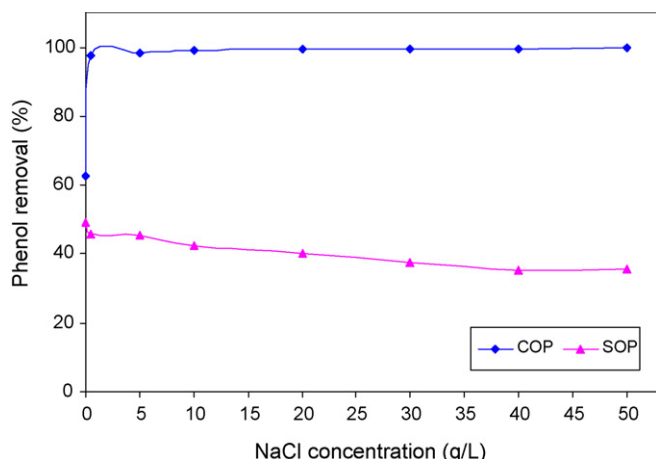

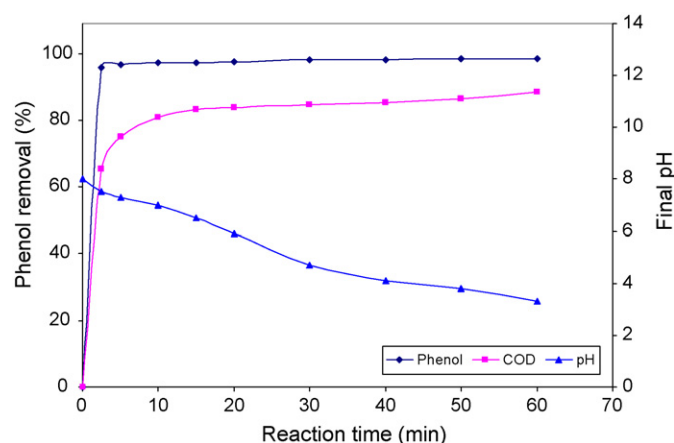**Fig. 7.** Effect of NaCl concentration on phenol removal in the COP and SOP.

in phenol degradation; a removal efficiency greater than 99% was achieved for phenol at 50 g/L NaCl. This is opposed to the findings of some other researchers who worked on phenol removal from saline liquids using AOPs other than COP [29–31], who have reported that high chloride concentrations had a strong inhibitory effect on phenol degradation. However, Bacardit et al. [47] observed that the presence of chloride ions did not affect the performance of the photo-Fenton process in the mineralization of 200 mg/L 4-chlorophenol. Therefore, it can be deduced from above that the effect of chloride anions on an AOP depends on the type of the process as well as on the compound(s) being targeted for degradation.

For the SOP, as indicated in Fig. 7, the removal efficiency of phenol decreased slightly with the introduction of NaCl; it reduced from 49% in absence of NaCl to around 35.5% in the presence of 50 g/L NaCl. This part of the present study is consistent with Azevedo et al. [30], who investigated single ozonation for phenol removal from saline wastewater and found that high NaCl concentrations inhibited the degradation rate. The negative effect of NaCl on the single ozonation process can be attributed to the reduction of ozone decomposition and/or the scavenging of •OH by chloride ions [30,48].

Based on above results, it is seen that coupling GAC with ozonation eliminated the adverse effects of NaCl on single ozonation; however, the exact mechanism of this interaction is still unclear. In other words, it is very clear that NaCl, even in high concentrations, not only increased the percentage of phenol degradation in a COP, but also enhanced the degradation rate. Thus it can be seen as a technically viable and promising surrogate technology for treating saline wastewaters.

3.1.4. COD removal in COP under optimum conditions

The performance of a COP in removal of COD from a saline phenol-containing wastewater was evaluated at optimum pH and GAC conditions (Table 1) to determine the effectiveness of the process for degradation of the organic intermediates of the reaction. Fig. 8 displays the degradation and COD removal of phenol in the COP. As illustrated, 81% of COD was removed by 10 min of the reaction; this value increased to 88% after 60 min reaction time. According to Fig. 8, the removal of COD is slightly lower than that of phenol, in particular in the early minutes of the reaction (i.e. reaction times under 15 min). This phenomenon can be explained because prior to complete oxidation, and particularly in first minutes of the reaction, phenol is converted to some organic intermediates, including catechol, benzoquinone, and acetic and formic acids [49]. The phenol is thus considered removed, but the intermediates still contribute to the COD. The higher the degree of oxidation, the simpler are the acidic intermediates formed and thus
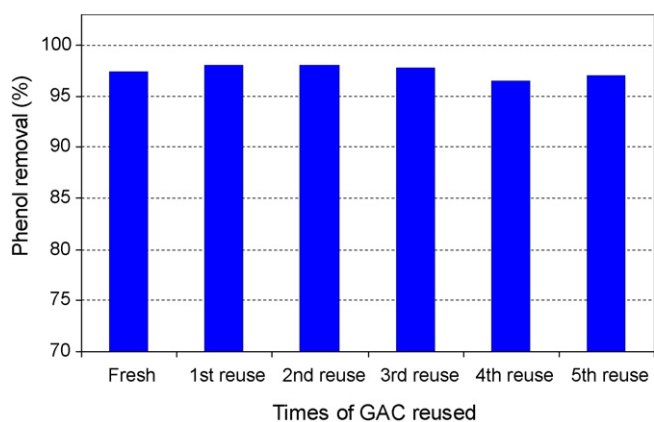
Fig. 9. Effect of GAC reuse times on phenol removal in the COP.

Fig. 10. Time-evolution profile of phenol and COD concentrations in the integrated catalytic ozonation/biological process.

the more pH decreases, and/or the more simple intermediates are mineralized, thereby reducing COD. The quick drop of solution pH versus the reaction time (Fig. 8) confirms the formation of acidic intermediates during the oxidation of phenol. Another point in Fig. 8 is that as the reaction proceeds, the difference between phenol and COD removal percentages becomes smaller. This is likely because the intermediates are more efficiently oxidized in the COP than the parent compound is. Since COD is a gross measurement of the organic content in the sample, any reduction of this parameter denotes the degree of mineralization of the compounds. Overall, it is inferred that the COP with activated carbon induced a high degree degradation and mineralization of phenol in saline media, where other processes such as TiO_2-photocatalytic [29], single ozonation [30], and Fenton and photo-Fenton [31] have been reported inefficient.

3.2. Durability of the catalyst

An important characteristic of a catalyst, from practical point of view, is its deactivation or potential reuse. To evaluate the capability of the GAC used in the present COP for reuse, an experimental phase was defined (Table 1) and carried out. To do this, the catalyst was reused 5 times under identical conditions, except that the catalyst was being reused from the previous experiment without any modifications. The phenol removal efficiency was determined after each experiment, and results are plotted in Fig. 9. As indicated, the GAC preserved its catalytic properties after reuse. This can be explained either by the predominance of catalytic reactions rather than adsorption–oxidation reactions in the COP, as mentioned above, or to the in situ regeneration of GAC [22,26]. A closer look at Fig. 9 reveals that the phenol removal has been slightly improved after reuse, probably due to the modification of surface chemical properties (functional groups) and the increase of BET and pore volumes [26]. Hence, COP with GAC is a stable method for treating saline wastewaters containing organic compounds.

3.3. Biodegradability assessment of the COP effluent

Although COP in the presence of activated carbon was able to degrade almost all the phenol and remove a significant of COD (80%) from phenol saline wastewater after 60 min reaction time, this rather long time requirement would impose high costs on the treatment system. A viable option is the partial oxidation of toxic phenol in the COP, to be completed by treatment in a following biological process. This exploits the advantages of both processes, shortening the time required to attain high effluent quality at the lowest cost. The effluent of COP obtained after 10 min reaction in COP under the conditions selected in Table 1 was used for biodegrada-
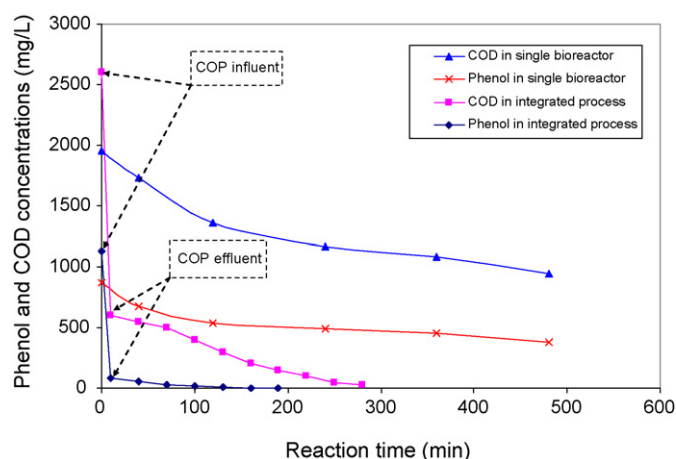
tion tests. The reaction time of 10 min in COP was selected because at this time, the concentration of phenol and its associated COD at those conditions had been reduced to below 100 and 600 mg/L, respectively (Fig. 10), making it suitable for treatment in a biological process.

The time evolution of phenol and COD concentration during the integrated COP and biodegradation process compared to that of single bioreactor are demonstrated in Fig. 10. As observed, the phenol concentration in the bioreactor of integrated process was completely removed after 3 h aeration. The COD concentration reduced to below 30 mg/L after 4.5 h aeration in the combined system. This reveals that the COP can efficiently pre-treat saline wastewater containing a considerable concentration of phenol in a short reaction time, after which the effluent is not too toxic to be completely post-treated in a suspended bioreactor. In a single bioreactor where raw wastewater even with lower concentration was directly added, however, the concentrations of phenol and COD after 8 h aeration reached around 385 and 960 mg/L, respectively (Fig. 10), requiring more aeration time to achieve the quality obtained in the integrated COP and biological process. These findings show that integration of COP with a bioreactor is an efficient and viable technology for cost-effectively treating saline wastewater containing toxic compounds like phenol with a short retention time.

4. Conclusions

The capability of a COP in the presence of GAC and integrated catalytic ozonation/biological process was investigated for their ability to remove phenol from a synthetic saline wastewater. The effects of several operational variables on COP performance were evaluated first to determine the optimal experimental conditions. It was shown that the COP could decrease the concentrations of phenol and COD from about 1150 and 2600 mg/L, respectively, to lower than 100 and 600 mg/L after 10 min of reaction time. This effluent was then efficiently post-treated in a bioreactor, where in a relatively short retention time the phenol was completely removed and COD lowered to below 30 mg/L. It is thus concluded that the integrated catalytic ozonation/biological process is a promising and economically viable technology for the treatment of saline wastewater containing phenol.

References

[1] S.H. Lin, C.T. Shyu, M.C. Sun, Saline wastewater treatment by electrochemical method, Water Res. 32 (1998) 1059–1066.

[2] N. Azbar, A. Bayram, A. Filibeli, A. Muezzinoglu, F. Sengul, A. Ozer, A review of waste management options in olive oil production, Crit. Rev. Environ. Sci. Technol. 34 (2004) 209–247.

[3] X. Zhao, Y. Wang, Z. Ye, A.G.L. Borthwick, J. Ni, Oil field wastewater treatment in biological aerated filter by immobilized microorganisms, Process Biochem. 41 (2006) 1475–1483.

[4] ATSDR, 2005. CERCLA priority list of hazardous substances. Available at: http://www.atsdr.cdc.gov/cercla/05list.html (accessed 20.10.2007).

[5] H. Jung, H. Park, J. Kim, J.-H. Lee, H.-G. Hur, N.V. Myung, H. Choi, Preparation of biotic and abiotic iron oxide nanoparticles (IOnPs) and their properties and applications in heterogeneous catalytic oxidation, Environ. Sci. Technol. 41 (2007) 4741–4747.

[6] J. Rivera-Utrilla, M. Sánchez-Polo, Ozonation of 1,3,6-naphthalenetrisulphonic acid catalysed by activated carbon in aqueous phase, Appl. Catal. B: Environ. 39 (2002) 319–329.

[7] R. Thiruvenkatachari, T.O. Kwon, J.C. Jun, S. Balaji, M. Matheswaran, I.S. Moon, Application of several advanced oxidation processes for the destruction of terephthalic acid (TPA), J. Hazard. Mater. 142 (2007) 308–314.

[8] Y. Dong, K. He, B. Zhao, Y. Yin, L. Yin, A. Zhang, Catalytic ozonation of azo dye active brilliant red X-3B in water with natural mineral brucite, Catal. Commun. 8 (2007) 1599–1603.

[9] F. Erol, T.A. Özbelge, Catalytic ozonation with non-polar bonded alumina phases for treatment of aqueous dye solutions in a semi-batch reactor, Chem. Eng. J. 139 (2008) 272–283.

[10] M.H. Khan, J.Y. Jung, Ozonation catalyzed by homogeneous and heterogeneous catalysts for degradation of DEHP in aqueous phase, Chemosphere 72 (2008) 690–696.

[11] B. Legube, V.L.N. Karpel, Catalytic ozonation: a promising advanced oxidation technology for water treatment, Catal. Today 53 (1999) 61–72.

[12] C. Hu, S. Xing, J. Qu, H. He, Catalytic ozonation of herbicide 2,4-D over cobalt oxide supported on mesoporous zirconia, J. Phys. Chem. 112 (2008) 5978–5983.

[13] Y.-F. Zeng, Z.-L. Liu, Z.-Z. Qin, Heterogeneous catalytic degradation of phenolic substrates: catalysts activity, J. Hazard. Mater. 162 (2009) 588–606.

[14] L. Zhao, J. Ma, Z. Sun, X. Zhai, Mechanism of influence of initial pH on the degradation of nitrobenzene in aqueous solution by ceramic honeycomb catalytic ozonation, Environ. Sci. Technol. 42 (2008) 4002–4007.

[15] L.F. Liotta, M. Gruttadauria, G. Di Carlo, G. Perrini, V. Librando, Heterogeneous catalytic degradation of phenolic substrates: catalysts activity, J. Hazard. Mater. 162 (2009) 588–606.

[16] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Catalytic ozonation of sulfonated aromatic compounds in the presence of activated carbon, Appl. Catal. B: Environ. (2008) 150–159.

[17] L. Lei, L. Gu, X. Zhang, Y. Su, Catalytic oxidation of highly concentrated real industrial wastewater by integrated ozone and activated carbon, Appl. Catal. A: Gen. 327 (2007) 287–294.

[18] N. Al-Hayek, B. Legube, M. Dore, Catalytic ozonation (Fe III/Al$_2$O$_3$) of phenol and its ozonation by-products, Environ. Technol. Lett. 10 (1989) 415–426.

[19] J. Villaseñor, P. Reyes, G. Pecchi, Catalytic and photocatalytic ozonation of phenol on MnO$_2$ supported catalysts, Catal. Today 76 (2002) 121–131.

[20] F.J. Beltrán, F.J. Rivas, R. Montero-De-Espinosa, Mineralization improvement of phenol aqueous solutions through heterogeneous catalytic ozonation, J. Chem. Technol. Biotechnol. 78 (2003) 1225–1233.

[21] S.H. Lin, C.H. Wang, Adsorption and catalytic oxidation of phenol in a new ozone reactor, Environ. Technol. 24 (2003) 1031–1039.

[22] S.H. Lin, C.H. Wang, Ozonation of phenolic wastewater in a gas-induced reactor with a fixed granular activated carbon bed, Ind. Eng. Chem. Res. 42 (2003) 1648–1653.

[23] I. Udrea, C. Bradu, Ozonation of substituted phenols in aqueous solutions over CuO–Al$_2$O$_3$ catalyst, Ozone Sci. Eng. 25 (2003) 335–343.

[24] F.J. Beltrán, F.J. Rivas, O. Gimeno, Comparison between photocatalytic ozonation and other oxidation processes for the removal of phenols from water, J. Chem. Technol. Biotechnol. 80 (2005) 973–984.

[25] M. Matheswaran, S. Balaji, S.J. Chung, I.S. Moon, Studies on cerium oxidation in catalytic ozonation process: a novel approach for organic mineralization, Catal. Commun. 8 (2007) 1497–1501.

[26] X. Qu, J. Zheng, Y. Zhang, Catalytic ozonation of phenolic wastewater with activated carbon fiber in a fluid bed reactor, J. Colloid Interface Sci. 309 (2007) 429–434.

[27] Y. Dong, H. Yang, K. He, X. Wu, A. Zhang, Catalytic activity and stability of Y zeolite for phenol degradation in the presence of ozone, Appl. Catal. B: Environ. 82 (2008) 163–168.

[28] K. He, Y.M. Dong, Z. Li, L. Yin, A.M. Zhang, Y.C. Zheng, Catalytic ozonation of phenol in water with natural brucite and magnesia, J. Hazard. Mater. 159 (2008) 587–592.

[29] E.B. Azevedo, F.R. de Aquino Neto, M. Dezotti, TiO$_2$-photocatalyzed degradation of phenol in saline media: lumped kinetics, intermediates, and acute toxicity, Appl. Catal. B: Environ. 54 (2004) 165–173.

[30] E.B. Azevedo, F.R. de Aquino Neto, M. Dezotti, Lumped kinetics and acute toxicity of intermediates in the ozonation of phenol in saline media, J. Hazard. Mater. B 128 (2006) 182–191.

[31] R. Maciel, G.L. Sant'Anna Jr., M. Dezotti, Phenol removal from high salinity effluents using Fenton's reagent and photo-Fenton reactions, Chemosphere 57 (2004) 711–719.

[32] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carrasco-Marin, On the characterization of acidic and basic surface sites on carbons by various techniques, Carbon 37 (1999) 1215–1221.

[33] APHA, AWWA, WEF, Standard Methods for the Examination of Water and Wastewater, 21st edition, Washington, DC, 2005.

[34] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Activated carbon catalytic ozonation of oxamic and oxalic acids, Appl. Catal. B: Environ. 79 (2008) 237–243.

[35] P.M. Alvárez, J.F. García-Araya, F.J. Beltrán, I. Giráldez, J. Jaramillo, V. Gómez-Serrano, The influence of various factors on aqueous ozone decomposition by granular activated carbons and the development of a mechanistic approach, Carbon 44 (2006) 3102–3112.

[36] Y.-H. Han, K. Ichikawa, H. Utsumi, A kinetic study of enhancing effect by phenolic compounds on the hydroxyl radical generation during ozonation, Water Sci. Technol. 50 (2004) 97–102.

[37] J.P. Kaptijn, The ecoclear process. Results from full-scale installations, Ozone Sci. Eng. 19 (1997) 297–305.

[38] F.P. Logemann, J.H.J. Annee, Water treatment with a fixed bed catalytic ozonation process, Water Sci. Technol. 35 (1997) 353–360.

[39] N. Graham, C.-C. Jiang, X.-Z. Li, J.-Q. Jiang, J. Ma, The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate, Chemosphere 56 (2004) 949–956.

[40] A.R. Freshour, S. Mawhinney, D. Bhattacharyya, Two-phase ozonation of hazardous organics in single and multi component systems, Water Res. 30 (1996) 1949–1958.

[41] S. Esplugas, J. Giménez, S. Contreras, E. Pascual, M. Rodríguez, Comparison of different advanced oxidation processes for phenol degradation, Water Res. 36 (2002) 1034–1042.

[42] J.C. Crittenden, R.R. Trussell, D.W. Hand, K.J. Howe, G. Tchobanoglous, Water Treatment: Principals and Design, 2nd edition, MWH, John Wiley and Sons Inc., 2005.

[43] M. Sánchez-Polo, J. Rivera-Utrilla, Effect of O$_3$/reaction on the catalytic activity of activated carbon during degradation of 1,3,6-naphthalenetrisulphonic acid with ozone, Carbon 41 (2003) 303–307.

[44] U. Jans, J. Hoigné, Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH-radicals, Ozone Sci. Eng. 20 (1998) 67–90.

[45] H. Valdés, C.A. Zaror, Heterogeneous and homogeneous catalytic ozonation of benzothiazole promoted by activated carbon: kinetic approach, Chemosphere 65 (2006) 1131–1136.

[46] P. Peralto-Zamora, A. Kunz, S. Gomez de Morales, R. Pelegrini, P. de Capos Moleiro, J. Reyes, N. Duran, Degradation of reactive dyes. I. A comparative study of ozonation, enzymatic and photochemical processes, Chemosphere 38 (1999) 835–852.

[47] J. Bacardit, J. Sttzner, E. Chamarro, S. Esplugas, Effect of salinity on the photo-Fenton process, Ind. Eng. Chem. Res. 46 (2007) 7615–7619.

[48] E.M. Siedlecka, P. Stepnowski, Decomposition rates of methyl tert-butyl ether and its by-products by the Fenton system in saline wastewaters, Sep. Purif. Technol. 52 (2006) 317–324.

[49] A. Santos, P. Yustos, T. Cordero, S. Gomis, S. Rodríguez, F. García-Ochoa, Catalytic wet oxidation of phenol on active carbon: stability, phenol conversion and mineralization, Catal. Today 102–103 (2005) 213–218.