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Degradation and COD removal of catechol in wastewater using the catalytic ozonation process combined with the cyclic rotating-bed biological reactor

Ali Ahmad Aghapour [a, b], Gholamreza Moussavi [a, *], Kamyar Yaghmaeian [c]

[a] Department of Environmental Health Engineering, Faculty of Medical Sciences, Tarbiat Modares University, Tehran, Iran
[b] Department of Environmental Health Engineering, School of Public Health, Urmia University of Medical Sciences, Urmia, Iran
[c] Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

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ABSTRACT

The effect of ozonation catalyzed with MgO/granular activated carbon (MgO/GAC) composite as a pre-treatment process on the performance of cyclic rotating-bed biological reactor (CRBR) for the catechol removal from wastewater has been investigated. CRBR with acclimated biomasses could efficiently remove catechol and its related COD from wastewater at organic loading rate (OLR) of 7.82 kg COD/m^3.d (HRT of 9 h). Then, OLR increased to 15.64 kg COD/m^3.d (HRT of 4.5 h) and CRBR failed. Catalytic ozonation process (COP) used as a pre-treatment and could improve the performance of the failed CRBR. The overall removal efficiency of the combined process attained respective steady states of 91% and 79% for degradation and COD removal of catechol. Therefore, the combined process is more effective in degradation and COD removal of catechol; it is also a viable alternative for upgrading industrial wastewater treatment plant.

1. Introduction

Catechol is commonly found in industrial effluents from various industries such as pharmaceutical, petroleum, petrochemical, pesticides, photographic developer, lubricating oils, polymerization inhibitors, anti-oxidants, coal conversion processes, crude wood tar, drainage water from bituminous shale, and in the effluent of coal-tar chemical productions (Lofrano et al., 2009; Subramanyam and Mishra, 2007). Catechol has also been detected in coal carbonization and gasification wastewaters ranging from few to several thousand mg/L (Subramanyam and Mishra, 2007). Catechol removal from wastewaters has been investigated by physical, chemical, and biological processes such as adsorption (Kumar et al., 2003), photocatalysis (Li et al., 2003; Mandal et al., 2004), Fenton and photo-Fenton (Lofrano et al., 2009), single ozonation process (SOP) (Hsu et al., 2003; Li et al., 2003), ozonation catalyzed with MgO/granular activated carbon (MgO/GAC) composites (Moussavi et al., 2014), anaerobic bioreactors including upflow fixed film–fixed bed bioreactor (Latkar et al., 2003) and upflow anaerobic sludge blanket (Subramanyam and Mishra, 2007), sequencing continuous-inflow reactor (SCR) (Aghapour et al., 2013a) and cyclic rotating-bed biological reactor (CRBR) (Aghapour et al., 2013b).

For biodegradable organic contaminants, the biological processes are the environmental friendly and low-cost technologies (García-Peña et al., 2012; Moussavi and Heidarizad, 2011; Moussavi and Mahmoudi, 2009). We reported the catechol degradation and COD removal of 98.7% and 97.9%, respectively, in a CRBR operated at an organic loading rate (OLR) of 7.82 kg COD/m^3.d and concluded that the CRBR is an efficient, compact, easy-to-operate, cost-effective, and high-rate bioprocess for removal of toxic and inhibitory pollutants from wastewater (Aghapour et al., 2013b). Nonetheless, catechol has toxic and inhibitory effects on the biological processes in high loading rates (Iaconi, 2012; Kargi and Konya, 2007; Subramanyam and Mishra, 2007). It has been reported that the pre-treating the toxic phenolic compounds in an COP resulted in the partial degradation of these toxic compounds and thus in the reduction of the organic load applied on the biological post-treatment process (Moussavi et al., 2009a,b, 2010). It in turn led to improving the efficiency of the biological process and thus of the overall efficiency (Dai et al., 2014; García-Peña et al., 2012; Moussavi et al., 2009; Sangave et al., 2007).

* Corresponding author.
E-mail address: moussavi@modares.ac.ir (G. Moussavi).

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In the other words, the complete mineralization of toxic organic pollutants using single chemical oxidation processes requires extensive operation conditions and thus is usually expensive (Moussavi et al., 2010) but the combination of chemical oxidation with a biological process can minimize the operating costs (Iaconi, 2012; Moussavi et al., 2010; Oller et al., 2010). In the combined process, chemical oxidation is a pre-treatment process used to reduce toxic and inhibitory effect of catechol and to increase the biodegradability of wastewater which improves the efficiency of the biological process and the overall efficiency of the catechol removal (Dai et al., 2014; García-Peña et al., 2012; Moussavi et al., 2009a,b; Sangave et al., 2007).

Ozonation is often used as a chemical oxidation step in drinking water and wastewater treatment facilities for disinfection, removal of organic micropollutants, color removal and taste and odor control (Wenk et al., 2013; Zeng et al., 2014). Also, ozonation process has a high synergistic effect with the biological process (Ariunbaatar et al., 2014; García-Peña et al., 2012) and thereby a considerable attention has been recently paid on the combination of ozonation with the biological process has drawn (García-Peña et al., 2012; Zhang et al., 2014). Nevertheless, the main critical defects of single ozonation are low solubility of ozone in water, high production costs and low reaction rates (Moussavi et al., 2010; Sangave et al., 2007; Zeng et al., 2014).

The best method of choice to overcome these defects is to use a catalyst in the ozonation process creating a catalytic ozonation process (COP) (Hsu et al., 2003; Li et al., 2006; Zeng et al., 2014). Due to their unique features, the catalytic ozonation process (COP) is one of the recently accepted and attractive types of advanced oxidation processes in which the very powerful radical species, mainly $^{\bullet}OH$, are generated from the interaction between ozone and a solid material (Li et al., 2006; Merayo et al., 2013; Moussavi et al., 2010; Roshani et al., 2014; Schweigert et al., 2001; Wenk et al., 2013). MgO has the destructive adsorbance, high surface reactivity, high adsorption capacity, high specific surface area and surface basic sites (Moussavi et al., 2009a,b). Therefore, it has been used as an efficient heterogeneous catalyst in the ozonation process of different class of organic compounds. The optimum conditions for degradation of 1000 mg/L catechol in the COP with MgO loaded on granular activated carbon (MgO/GAC) as catalyst was at pH of 8, MgO/GAC concentration of 10 g/L and reaction time of 20 min (Moussavi et al., 2014).

Although the COP and CRBR techniques have been individually used for removal of catechol in wastewater, no report could be found on the combination of COP with CRBR. Therefore, the novelty and main purpose of the present study is the investigation of the combined MgO/GAC-COP with the CRBR for removal of high catechol loading rate. The performance of the COP-CRBR system in removal of catechol was evaluated in terms of degradation and COD removal percentages.

2. Materials and method

2.1. Experimental setup and conditions

Fig. 1 depicts the schematic of the laboratory-scale COP/CRBR experimental setup used in this study. The COP reactor was made of a plexy-glass column with a diameter of 20 cm and a total height of 50 cm having a working volume of 10 L. The ozone generated in a generator (ARDA, Model AEGCOG-2A) was entered to the COP reactor through a sintered-glass diffuser installed at the bottom of the reactor. The rate of air flow was regulated while passing through the ozone generator to maintain the desired ozone dose. Ozone in the off-gas stream of the reactor was destroyed using a concentrated KI solution. The CRBR setup and operation was described in detailed elsewhere (Moussavi et al., 2013).

The COP reactor was operated in batch mode using the MgO/GAC as the catalyst. The preparation method and the characteristics of the MgO/GAC is presented in detail elsewhere (Moussavi et al., 2014). In each batch, the synthetic wastewater (containing 1000 mg/L catechol) was fed to the COP and the reactor was operated under optimum operational conditions. The optimum operational conditions of MgO/GAC-COP for the catechol degradation and mineralization were pH of 8, ozone dosage of 2.1 mg/min, MgO/GAC concentration of 10 g/L and reaction time of 20 min (Moussavi et al., 2014). At the end of the specific batch, the catalyst was separated from the solution by filtration and the filtrate was transferred to the inlet tank of the CRBR after regulating the pH (by adding normal NaOH solution) and addition of nutrients. The nutrient solution composed of 5 g/L K_2HPO_4, 15 g/L KH_2PO_4, 120 g/L NH_4Cl and 12 g/L $(NH_4)_2HPO_4$. The synthetic wastewater was prepared daily by diluting aliquots of a 15 g/L catechol stock solution with tap water. The stock solution of catechol (15 g/L) was prepared by dissolving known amount of catechol (Merck Co.) in the distilled water. It was then preserved in a refrigerator (at dark and 4 °C). The wastewater pretreated in the COP was then fed continuously (after modifying its composition) at the desired flow rate to the CRBR with polyurethane foam as the biofilm media. The each operational cycle in the CRBR lasted for 6 h consisted of aeration (4 h), sedimentation (1.5 h) and decant (0.5 h). The phases and conditions of the CRBR operation are presented in Table 1.

The concentration of catechol in the filtered (Whatman filter with a 0.45 l m pore size) effluent samples was determined by an Agilent 1200 high performance liquid chromatography (HPLC). The evaluation was carried out with a reversed-phase Nucleodur C18 Column (250 mm × 4.6 mm, 5 μm) and UV–visible detector (Agilent 1200 DAD) at 275 nm. The mobile phase was methanol/water (55:45%), flow rate of 1 mL/min and temperature of 23 °C (Aghapour et al., 2013a,b; Moussavi et al., 2014). The mineralization of catechol was determined by the reduction in the COD level measured as described in the standard methods (APHA, 1998). Also, the ozone concentration in the gas injected to the COP was determined by the standard KI method (APHA, 1998).

3. Results and discussion

3.1. Performance of CRBR

Fig. 2 shows the performance of the CRBR in degradation and COD removal of catechol at operational conditions given in Table 1. As observed in zone A of Fig. 2, the average pseudo steady-state removal of catechol and COD in the CRBR operated at the catechol (COD) concentration of 1560 mg/L (2930 mg/L) and HRT of 9 h (corresponding to the OLR of 7.82 kg COD/m^3.d) 98.4% and 97.9%, respectively.

When the HRT was reduced from 9 h to 4.5 h, the catechol degradation and COD removal efficiencies dropped sharply and decreased to below 58% and 37%, respectively, only 6 d after switching (zone B in Fig. 2). The sudden decrease in degradation and COD removal of catechol after the reduction of HRT can be attributed to the inhibitory effect of catechol on the microbial metabolism as a result of the increase in the volumetric loading rate (from 7.82 to 15.64 kg COD/m^3.d) applied to the bioreactor (Aghapour et al., 2013b; Allsop et al., 1993; Sarfaraz et al., 2004). It indicates that the catechol-loading rate applied to the CRBR was over the tolerable limit, thus the metabolic process of microbial degradation was strongly inhibited (Aghapour et al., 2013b). Therefore, it was decided to combine the CRBR with COP to recover the bioreactor and improve its performance.

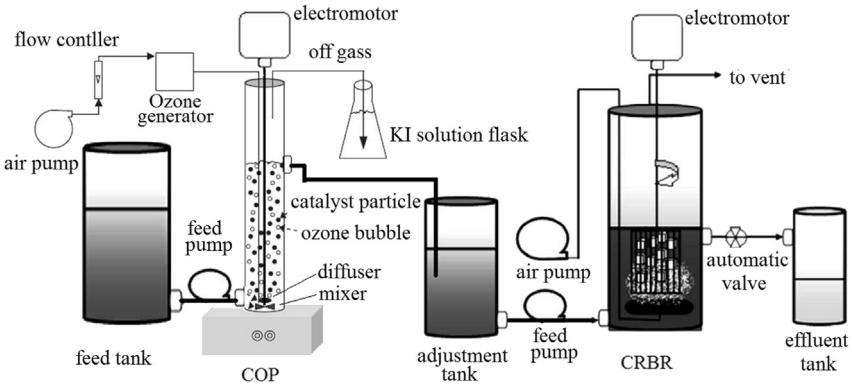

Fig. 1. Experimental setup of the combined COP-CRBR system.

3.2. Performance of SOP and MgO/GAC-COP

The performance of SOP in the degradation and COD removal of catechol was investigated as a function of inlet concentration and the results are depicted in Fig. 3. As observed in Fig. 3, the removal of catechol and its related COD decreased in both SOP and COP with the increase of initial catechol degradation. For the highest catechol concentration (1560 mg/L), the SOP attained a degradation and COD removal of 9.5% and around 2%, respectively. Therefore, the SOP is not a suitable process for pretreatment of catechol in concentration of 1560 mg/L.

According to results given in Fig. 4, the COP achieved a much greater performance in catechol degradation and mineralization (COD removal) as compared with the SOP. For instance, at an initial catechol concentration of 1560 mg/L, catechol and COD removal of 51% and 39%, respectively, could be achieved in the COP under the selected conditions. Therefore, COP as a stand-alone system is not able to complete the removal of high concentrations of catechol from the wastewater and the effluent quality was not acceptable in terms of environmental standards for disposal to the environment. However, the COP might be an efficient process for degradation of high concentration of catechol and thus can be used as a pretreatment for the biological systems when treating the toxic

Table 1
Experimental phases and conditions of the CRBR as single and combined system.

Phase	System	Inlet catechol (mg/L)	Inlet COD (mg/L)	HRT (h)	Overall OLR kg COD/m^3.d
A	CRBR	1560	2933	9	8.72
B	CRBR	1560	2933	4.5	15.64
C	COP + CRBR	1560	2933	0.3 + 4.5	15.64

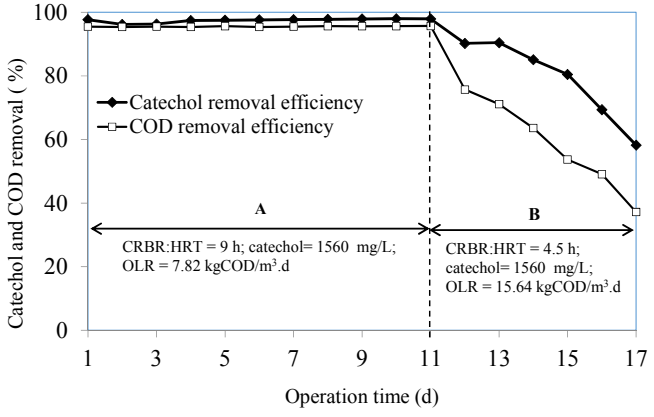

Fig. 2. Profile of the catechol and COD removal efficiencies in the single CRBR (catechol concentration = 1560 mg/L, HRT = 9 h and 4.5 h).

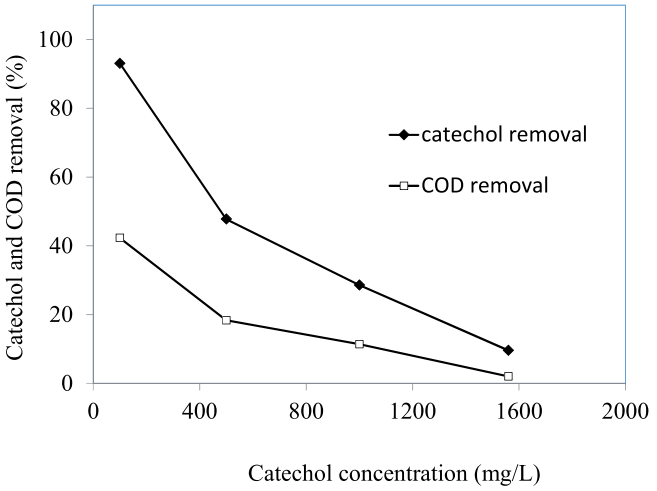

Fig. 3. Profile of the catechol and COD removal efficiencies in the SOP (pH = 8, ozone dosage = 2.1 mg/min, and reaction time = 20 min).

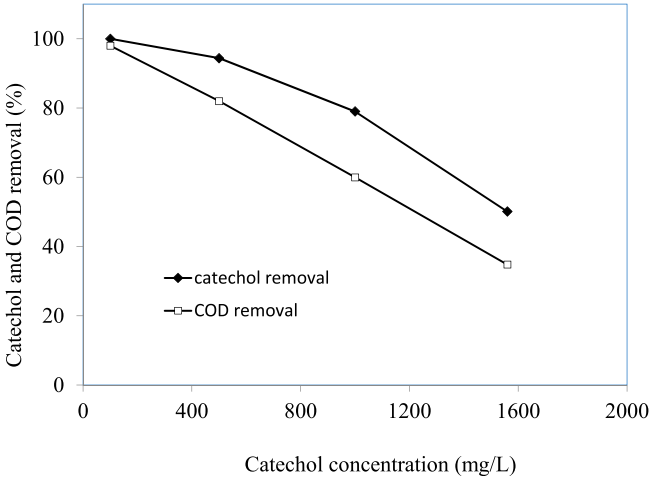

Fig. 4. Profile of the catechol and COD removal efficiencies in the COP (pH = 8, ozone dosage = 2.1 mg/min, MgO/GAC concentration = 10 g/L and reaction time = 20 min).

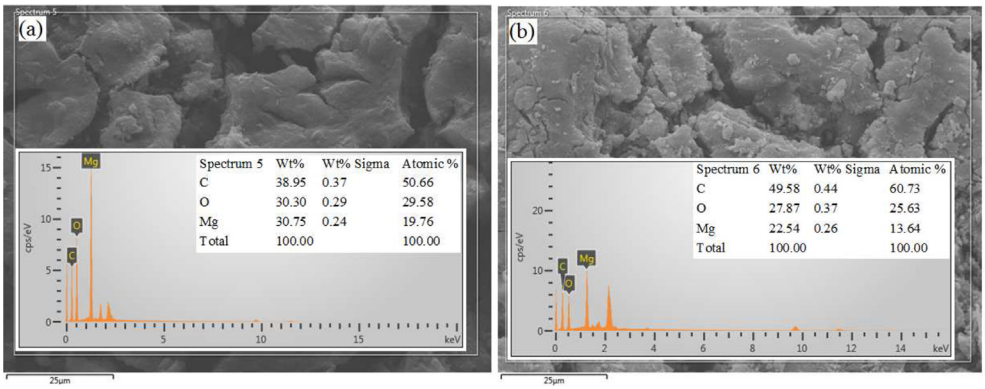

Fig. 5. The SEM image and EDX analysis of fresh (a) and 5-times reused (b) MgO/GAC.

contaminants such as catechol.

To evaluate the durability and reusability of the MgO/GAC, the catalyst was reused for 5 consecutive times under identical experimental conditions. The results indicated that the removal of catechol and its COD was almost the same at all repeated 5 runs. It implies that the MgO/GAC is a stable and durable catalyst for using in the ozonation process of toxic contaminants (Moussavi et al., 2009a,b). The scanning electron microscope (SEM) image and the energy-dispersive X-ray spectroscopy (EDX) of the fresh and used (after 5 times reuse) are shown in Fig. 5. It is observed in Fig. 5 that the surface morphology of the catalyst did not considerably change during the reusing process. Also, the EDX results (inset of Fig. 5) indicates that even after 5 times reuse a high amount of Mg is still present on the surface of the catalyst resulted in preserving its catalytic activity.

3.3. Performance of combination of the COP/CRBR

In this phase of the study, the effluent of the COP treating the wastewater containing 1560 mg/L was fed to the CRBR working at HRT of 4.5 h and the operation of the combined treatment system was continued until the pseudo steady state was re-attained in the CRBR. Fig. 6 shows the results of the COP/CRBR combined treatment system. As can be seen in Fig. 6, the performance of the CRBR in the combined system started to increase immediately after feeding the pretreated wastewater and reached to the steady-state level 4 d after the combination. Average steady-state removal of catechol and COD in the combined system (COP + CRBR) was 91% and 79%, respectively.

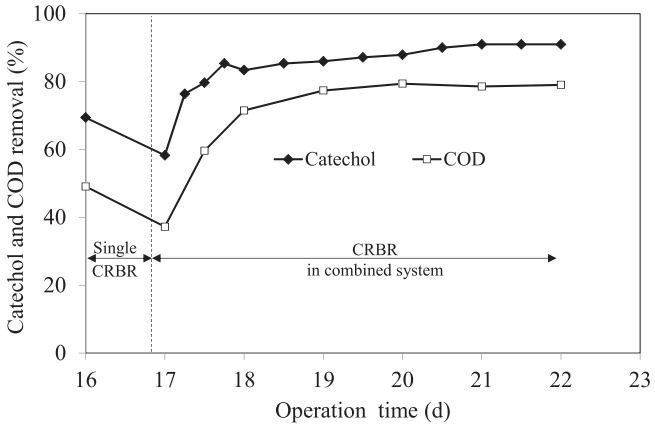

Fig. 6. Profile of the catechol and COD removal efficiencies in the combined COP/CRBR system as compared to the single CRBR (COP: pH = 8, ozone dosage = 2.1 mg/min, MgO/GAC concentration = 10 g/L and reaction time = 20 min; CRBR: catechol concentration = 1560 mg/L, HRT = 4.5 h)).

It can be concluded therefore that the pretreatment of the wastewater containing a high concentration of catechol as the toxic compound in the COP for a relatively short reaction time of 20 min could improve the performance of the failed CRBR. Better performance of the CRBR in the combined system can be attributed to the detoxification of catechol in the COP and the reduction of catechol loaded on the biomass resulted in overcoming the inhibitory conditions. Indeed, the combined system could efficiently treat the catechol-laden wastewater at a high OLR of 15.64 kg COD/m^3.d during a total time of 4.8 h (20 min in the COP and 4.5 h in the CRBR). Accordingly, the COP with MgO/GAC as catalyst is an appropriate pretreatment option for improving the performance of the overloaded biological processes.

4. Conclusion

In this study, the performance of the COP with MgO/GAC as catalyst was examined as the pretreatment process of the high concentration of catechol to be post-treated in the CRBR. The CRBR failed to degrade catechol at a loading rate 8.3 kg/m^3.d (15.64 kg COD/m^3.d); the COP was an efficient process to reduce the catechol loaded on the CRBR by 50% at a reaction time as short as 20 min. Therefore, coupling the COP with the CRBR allows treating catechol (over 90% degradation) at loading rate of twice as much as the single CRBR. In conclusion, the COP is an appropriate pretreatment option for improving the performance of the biological processes treating toxic contaminants.

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