

REMOVAL OF PHENOL AND COD VIA CATALYTIC TREATMENT USING ACTIVATED CARBON AND ALUMINA WITH OZONE

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RINGKASAN : Kajian terhadap penyingkiran fenol dan COD (chemical oxygen demand) dalam larutan telah dijalankan menggunakan teknik pengozonan, penyerapan serta pengozonan bermangkin dengan karbon teraktif dan alumina. Ujikaji penyerapan dan pengozonan bermangkin dijalankan menggunakan larutan fenol dengan kepekatan 100 ppm pada suhu 30°C. Keputusan yang diperolehi menunjukkan bahawa karbon teraktif adalah pejerap yang terbaik dengan keupayaan menyingkir sebanyak 71.2% dan 75.4% kandungan fenol dan COD dalam masa dua jam berbanding alumina yang tidak menghasilkan penyingkiran yang nyata. Penambahan ozon ke dalam larutan pula berjaya meningkatkan kadar penyingkiran dengan 100% dan 95.1% fenol berjaya disingkirkan oleh karbon teraktif dan alumina. Penyingkiran COD pula adalah lebih berkesan menggunakan ozon dan karbon teraktif yang berjaya menyingkirkan sebanyak 93.4% kandungan COD dalam larutan yang sama berbanding penyingkiran sebanyak 57.9% yang diperolehi oleh alumina. Maka, ozon dan karbon teraktif adalah kombinasi yang sesuai digunakan sebagai alternatif untuk merawat air sisa yang mengandungi fenol secara berkesan.

ABSTRACT : The removal of aqueous phenol and COD (chemical oxygen demand) was examined by ozonation, adsorption and catalytic ozonation with granular activated carbon (GAC) and alumina. Adsorption and catalytic ozonation tests were performed on 100 ppm phenol at 30°C. Results of the experiments indicated that GAC removed up to 71.2% of phenol and 75.4% of COD in two hours via adsorption, and is potentially a promising adsorbent to remove phenol compared to alumina, which does not remove phenol and COD to any significant extent. Addition of ozone into the system resulted in larger phenol removal with 100% and 95.1% removal achieved by GAC and alumina respectively. However, the COD removal achieved by ozonation with GAC was more complete with 93.4% removal compared to alumina with 57.9% removal. Therefore, combination of ozone with GAC is potentially a suitable alternative to treat wastewater containing phenol.

KEYWORDS : Ozonation, catalytic ozonation, phenol, alumina, activated carbon

INTRODUCTION

Activated carbon (AC) is a favourably used material to remove contaminants from water and gas stream due to its flexibility in production by various material and reasonable cost (Yehaskel, 1978). It provides large surface area and non-polar surfaces to adsorb wide range of materials in sufficiently large amount. Typical uses include removing odours and volatile organic compounds (VOCs) and as filter in water purification system (McGuire and Suffet, 1980; Perrish, 1981).

During the adsorption process, the AC will become saturated after all the active sites are taken up by the pollutant molecules. High temperature steam is required to degrade the adsorbed compounds and regenerate the AC. However, the main problems associated with the use of activated carbon are the costly regeneration step and loss in its activity after regeneration (Jankowska *et al.*, 1991; Chiang *et al.*, 1997). Due to this, Lin and Wang (2003) have proposed that treatment of industrial wastewater can be carried out using activated carbon in combination with ozone. Their study revealed that with the addition of ozone, the treatment efficiency is not only doubled, but the granular AC (GAC) was regenerated *in situ* during the ozonation period with very minor loss in activity.

Alumina is the most common oxide (besides MnO_2 and TiO_2) used as catalyst or support in the catalytic ozonation of aqueous organics. It possesses high activity to enhance the oxidation capacity of ozone on organic compounds (Volk *et al.*, 1997; Legube and Leitner, 1999; Gracia *et al.*, 2000).

Taking into account the importance of these materials and the vast application of ozone in wastewater treatment, this study attempts to combine the adsorptive properties of activated carbon and catalytic properties of alumina with ozone to treat phenol in solution. It is anticipated that combination of ozone with either GAC or alumina will reduce the consumption of ozone and lower the cost for the generation of ozone as well as the regeneration of GAC. It provides a cost effective solution to overcome the limitation induced by conventional biological treatment on industrial waste stream containing toxic compounds.

The objective of this paper is to study the effectiveness of phenol treatment by ozone, alumina and catalytic ozonation with GAC and alumina by determining the level of phenol and COD removal from the solution.

METHODOLOGY

Liquefied phenol (phenol solution 80% w/w in water) was obtained from BDH Chemicals, England. The characteristic of the activated carbon and alumina used in this research are listed in Table 1.

Table 1. Type and characteristic of catalyst used

Catalyst	Supplier	Size (mm)	Surface area (m ² /g)
Granular activated carbon	KD Technology Sdn. Bhd. (Palm shell base)	0.6 - 2.32	1020
γ -Al ₂ O ₃	Merck	-	120 - 150

Adsorption of phenol onto the catalyst was carried out using the method adapted from Ernst *et al.* (2004). The ozonation tests were conducted in a semi-continuous system (Figure 1) for two hours. Ozonated air with an ozone concentration of 4.0 mg/L was generated using purified air by an ozone generator (Triogen 2B Lab Ozone Generator). The gas produced was then diffused at 1 L/min into 350 ml of 100 ppm phenol solution (300 ± 10 mg/L of COD) containing one gram of the catalyst. Temperature was set at 30°C. The mixture was agitated at 400 rpm. The surplus ozone was retained by two bubblers, containing saturated calcium hydroxide and 2% potassium iodide (KI) solution. In the adsorption and catalytic ozonation tests, 10 ml of sample was withdrawn within certain intervals for analysis purpose. The samples were filtered prior to analysis.

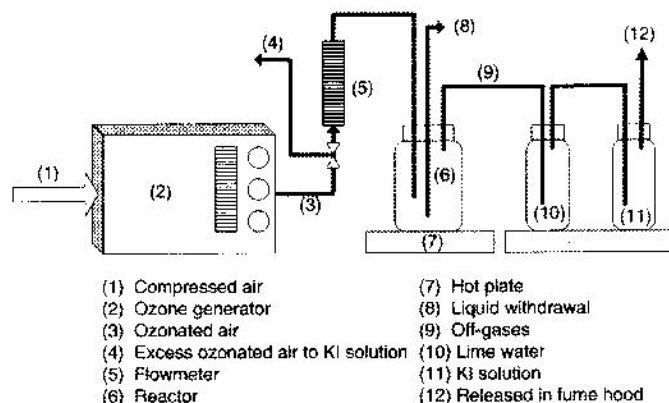


Figure 1. Semi-continuous catalytic ozonation experimental set-up

A Waters high performance liquid chromatograph (HPLC) equipped with Waters 486 UV detector, Waters 600 Controller, Waters 717 plus autosampler and an integrator (Millenium Software) was used to analyse the phenol content in the samples. The column used was a reverse phase SGE Wakosil-II 5 μ m (15 cm x 0.46 cm). A mixture of 40% acetonitrile and 60% water was chosen as the optimal mobile phase for phenol. The wavelength of the UV absorbance used was 254 nm. COD of the samples was determined using Hach method 8000 with Hach DR2000 spectrophotometer.

RESULTS AND DISCUSSION

Adsorption of Phenol

The results obtained from phenol adsorption by GAC and alumina are shown in Figure 2. GAC possess reasonably large surface area and non-polar surfaces for successful removal of organic contaminants from solution (Jankowska *et al.*, 1991). Based on the figure, the rate of phenol removed by GAC adsorption was fairly rapid for the first few minutes and started to slow down after 60 min. Adsorption occurs due to van der Waals forces, which reduce in adsorption rate with increase adsorption of phenols (Perrish, 1981), leveling off close to 120 min. The efficiency of removal of phenol and COD was at 71.2% and 74.5%, respectively at 120 min. The removal rate decreased continuously as expected. Study on phenol adsorption using AC conducted by Cooney and Xi (1994), showed AC had the capacity to adsorb about 500 ppm of phenol in 40 days before saturation. Therefore, it is assumed that the concentration of phenol in this study can be totally removed via adsorption by GAC within 64 hours. Apparently no phenol removal was observed using alumina and the COD removal detected from the solution was also very low (assumed to be within sampling error). This is presumably due to the conspicuously small surface area of alumina compared to GAC and its polar surface (Roostaei and Tezel, 2004) which suppressed its adsorption capacity. Therefore, alumina is not inherently a good adsorbent to remove phenol from aqueous solution.

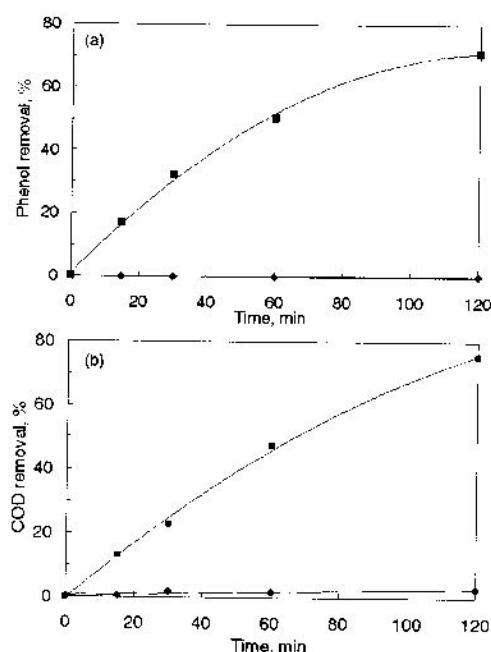


Figure 2. Profile of (a) phenol and (b) COD removal via adsorption at different time intervals. Catalyst : (■) GAC and (◆) alumina

Catalytic Ozonation of Phenol

The results attained from catalytic ozonation of phenol with GAC and alumina are shown in Figure 3. In the ozonation test, phenol removal was rapid in the first 20 min. Then the rate of its removal decreased and reached a maximum value of 63.1% after 120 min. Removal of phenol with combination of ozone and GAC or alumina respectively was significantly enhanced compared to ozone only. Removal efficiency of phenol removal by ozonation in the presence of GAC or alumina were similar. In the first few minutes, alumina gave higher phenol removal than GAC, but the reverse occurred at the beginning of the 40th min. Research conducted by Cooper and Burch (1999) and Ernst *et al.* (2004) suggested that presence of hydroxyl group on the surface of alumina was responsible for ozone decomposition to form hydroxyl radical, a powerful oxidant that reacted non-selectively with organic compounds at a higher rate than ozone. Figure 4 shows that ozone adsorbed on the catalyst surface reacts with the surface hydroxyl groups. The active oxygen atom produced reacts with the hydroxyl groups to form O_2H^- anions, which subsequently react rapidly with ozone to produce O_2H radicals. This radical subsequently reacts with another ozone molecule to generate the O_3^- radical that decomposes into oxygen and free hydroxyl (OH) radical which can oxidise organic matter in the solution. Therefore, it is anticipated that the significant improvement observed in phenol removal during ozonation with alumina compared to its adsorption was attributed to the above

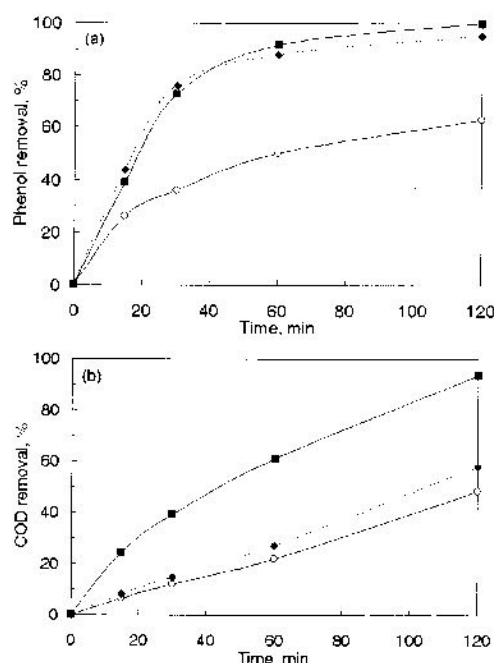


Figure 3. Profile of (a) phenol and (b) COD removal at different ozonation time. Catalyst : (O) without catalyst, (■) GAC and (◆) alumina

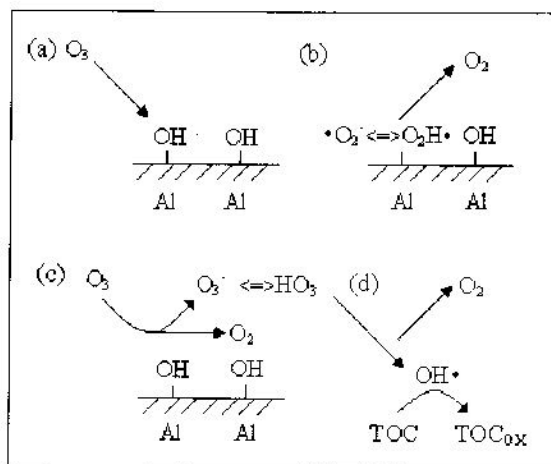


Figure 4. Suggested reaction mechanism during catalytic ozonation with alumina (Ernst *et al.*, 2004)

mentioned factor. GAC on the other hand is a strong adsorbent. It also quickly decomposes ozone to hydroxyl radicals on its surface (Fujita *et al.*, 2004). At the beginning of the reaction, adsorption of phenol onto surface of GAC most probably limited the available surface for ozone decomposition. As the reaction proceeds, adsorption and desorption of reaction products provide accessible sites for further adsorption and decomposition that enabled higher phenol removal than alumina after 40 min of reaction. The maximum phenol removal achieved by GAC and alumina was 100% and 95.1%, respectively at 120 min indicating that both the GAC and alumina behaved as good catalyst to remove phenol in an ozonated system. Ozonation of phenol with GAC resulted in the highest phenol removal compared with treatment using either GAC or ozone only.

The COD removal steadily increased for the combined system of ozone with either GAC or alumina. The GAC gave higher percentage of COD removal than only alumina. A maximum of 93.4% and 57.9% of COD removal was achieved at 120 min by GAC and alumina respectively. GAC possesses superior adsorption capability compared to alumina, which is capable to remove phenol and its oxidation products formed during ozonation. Work carried out by Cooney and Xi (1994), Lin and Wang (2003) and Fujita *et al.* (2004) on application of activated carbon and/or ozone to treat organics observed several effects. These are: (1) activated carbon is a strong adsorbent in the case of phenol, (2) ozone undergoes rapid decomposition to generate highly oxidative radicals when in contact with activated carbon and (3) organics adsorbed by activated carbon can be oxidised by ozone, restoring its porous medium for further adsorption. Therefore, activated carbon initiates the transformation of ozone to hydroxyl radicals, that are not bound to the surface of carbon but are free to react with organics in the aqueous solution (Utrilla and Polo, 2002; Polo and Utrilla, 2003). Consequently, the homogeneous and heterogeneous oxidation by ozonation coupled with adsorption by GAC most probably

attributed to 100% phenol removal and a higher COD removal in the presence of ozone compared to either ozonation or adsorption by GAC. A schematic diagram illustrating the potential above mentioned reactions occurring during ozonation of phenol with GAC is shown in Figure 5. This thus implies that GAC acts not only as an adsorbent but also as a catalyst in promoting ozone oxidation to improve the removal of phenol and COD in wastewater.

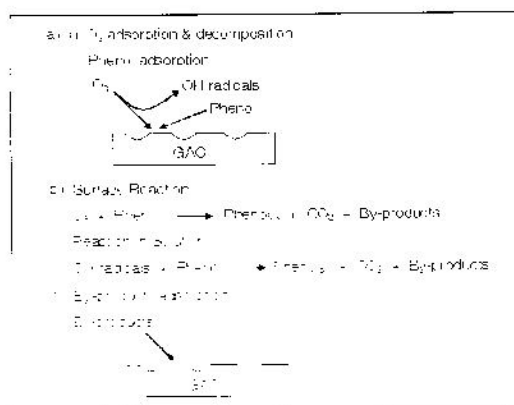


Figure 5. Schematic diagrams of the possible phenomena occurring during catalytic ozonation with GAC

CONCLUSION

GAC can effectively remove 71.2% of phenol and 75.4% of COD by adsorption. Phenol and COD was not significantly removed by alumina indicating its poor potential for use as adsorbent to remove phenol. Presence of ozone enhanced the phenol and COD removal achieved by GAC and alumina. Both the GAC and alumina significantly gave better results than ozone alone with complete (100%) and 95.1% phenol removal respectively, compared to 63.1% removal achieved by ozone. The COD removal also increased with the combined system of ozone with either GAC or alumina. However, the GAC gave higher percentage of COD removal than alumina. A maximum of 93.4% and 57.9% of COD removal was achieved after 120 min by GAC and alumina respectively. Thus, the use of ozone-GAC system can be considered as a potential process to achieve complete removal of phenol and high removal of COD in wastewater.

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