Industrial wastewater treatment in a new gas-induced ozone reactor

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Abstract

The present work was to investigate industrial wastewater treatment by ozonation in a new gas-induced reactor in conjunction with chemical coagulation pretreatment. The reactor was specifically designed in a fashion that gas induction was created on the liquid surface by the high-speed action of an impeller turbine inside a draft tube to maximize the ozone gas utilization. A new design feature of the present reactor system was a fixed granular activated carbon (GAC) bed packed in a circular compartment between the reactor wall and the shaft tube. The fixed GAC bed provided additional adsorption and catalytic degradation of organic pollutants. Combination of the fixed GAC bed and ozonation results in enhanced oxidation of organic pollutants. In addition to enhanced pollutant oxidation, ozonation was found to provide in situ GAC regeneration that was considered crucial in the present reaction system. Kinetic investigations were also made using a proposed complex kinetic model to elucidate the possible oxidation reaction mechanisms of the present gas-induced ozonation system. As a complementary measure, chemical coagulation pretreatment was found able to achieve up to 50% COD and 85% ADMI removal. Experimental tests were conducted to identify its optimum operating conditions.
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Keywords: Gas-induced ozone reactor; Granular activated carbon; Adsorption; Reaction kinetic model; Chemical coagulation

1. Introduction

Rapid industrial developments in the past several decades in Taiwan have resulted in formation of industrial parks in various parts of this island country. An industrial park comprises a wide variety of manufacturing plants, clustering in a preplanned area. A typical one in northern Taiwan consists of over 450 manufacturing plants, including auto-making, steel

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milling, heavy machinery, pharmaceutical, plastic, food processing, textile, paper-making, heavy electric, electronic, computer peripheral, petrochemical and fine chemicals. Currently, the manufacturing facilities generate approximately 25,000 t per day of wastewater. The bulk of these wastewaters are collectively treated in a common activated sludge treatment plant. However, because of the diversity of manufacturing facilities within the industrial park, the collected wastewater is highly complex and contains many recalcitrant organic compounds, leading to significant daily variation of the wastewater quality. These wastewater characteristics place a considerable strain on the current biological treatment facility. To help alleviate the treatment overload, ozonation may provide a good complement to the activated sludge system.

Ozonation has been a treatment method widely used for tackling various industrial wastewaters [1–3]. Gould and Weber [4], Yamamoto et al. [5], Gurol and Singer [6] and Gurol and Vatistas [7] investigated ozone oxidation of phenolic compounds. Snider and Porter [8], Beszedits [9], Gould and Groff [10], Lin and Lin [11], Lin and Liu [12]and Lin and Lai [13] found efficient color removal of textile wastewater by ozonation. Ozonation was also employed to treat the nirogen-containing wastewater [14]. Due to its wide treatment applications, ozone has been accepted as an effective disinfectant and chemical oxidant. However, those industrial applications have been handicapped by low ozone transfer efficiency and relatively high production cost. To overcome these deficiencies, an increase in ozone retention in aqueous solution or reuse of ozone in a multiple reactor system [12] has been attempted. Both methods will render the reactor system more complicated or lead to much larger footprint of the reactor system. In this aspect, gas-induced reactor could provide a good alternative [15–20]. In this gas-induced reactor, a vortex was created on the liquid surface by a high-speed impeller turbines and the gas in the headspace of reactor was drawn into the aqueous solution by such a strong action. This gas induction action was reported to considerably improve the ozone transfer [18,19].

The objective of this study was to further improve the design of gas-induced reactor by incorporating a fixed granular activated carbon (GAC) bed for enhanced treatment of industrial wastewater. The fixed GAC bed was situated between the draft tube and the reactor wall. In the present design, the advantages of gas induction were retained while the fixed GAC bed provided the benefits of solid-phase adsorption and catalytic reaction. Experiments were conducted to examine the operating characteristics of the new reactor design. Theoretical investigation was also made to verify a complex kinetic model proposed here using the observed data in an attempt to elucidate the reaction mechanism of industrial wastewater in the present reactor system. Due to the complexity of industrial wastewater obtained from the industrial park, chemical coagulation was adopted as a pretreatment prior to the gas-induced ozonation. Experimental tests were conducted to identify appropriate pretreatment operating conditions.

2. Materials and methods

The wastewater samples were obtained from an industrial park in northern Taiwan. The contents of these wastewaters were very difficult to ascertain due to different manufacturing plants in the industrial park. It contained to various amounts of dyestuff, organic

chemicals, inorganic salts, oil and grease and some heavy metals. The water quality of the wastewater samples, such as the COD (chemical oxygen demand) and suspended solids (SS) were measured by the standard methods [21]. The ADMI (American Dye Manufacturers Institute, a color indicator) was determined by the stand method [21] using a GBC 916 UV-Vis spectrophotometer (GBC Scientific Equipment, LTD, Vic., Australia). The wastewater ADMI was a measurement of UV light absorbance (or transmittance) of wastewater and hence it reflects quite well the color of the wastewater samples. The same methods were adopted for measuring the water quality of the wastewater effluents after chemical coagulation and ozonation treatments. During the experimental test period, the wastewater samples had a pH between 6.5 and 8, a COD between 400 and 850 mg/l, a SS between 50 and 300 mg/l and an ADMI between 650 and 1250. The wastewater samples were very frequently strongly colored (mostly in red, grey or black), implying a strong influence of the textile wastewater.

Chemical coagulation was conducted using a jar test apparatus. The apparatus consisted of six 1-l glass jars sitting in a constant temperature bath for temperature control. Each jar was equipped with a stirrer that was allowed to vary between 0 and 300 rpm. Generic polyaluminum chloride (PAC) and polymer were employed in the chemical coagulation tests. Both the PAC (a low bascity and non-sulfated type) and polymer (a polyelectrolyte coagulant aid), as obtained from Fu Chang Chemical Co. (Taoyuan, Taiwan), were the ones generally used in chemical coagulation of industrial wastewater. One liter of the industrial wastewater was put in a jar. The stirrer was turned on and set at 100 rpm. A desired amount of PAC chosen between 50 and 250 mg/l was added to the wastewater and the mixing continued for 15 min. The stirrer speed was then slowed to 30 rpm and a proper amount of polymer was added. According to our past experiences [12], a fixed PAC/polymer ratio of 100:1 yielded good performances for the chemical coagulation. After polymer addition, the mixing was continued for 30 min. The flocs formed in the treated wastewater were finally allowed to settle for 30 min. The water quality of supernatant was determined and the supernatant was employed for ozonation oxidation in the gas-induced reactor.

The experimental apparatus of the gas-induced ozone reactor is shown in Fig. 1. The ozone reactor was a pyrex glass tube of 180 mm i.d. and 700 mm high. It was equipped with a water jacket for temperature control. The draft tube was a pyrex glass cylinder of 80 mm i.d. and 128 mm high (3 mm wall thickness) and was situated 75 mm above the reactor bottom. Two identical impeller turbines (top and bottom) of 76 mm in diameter were 40 mm apart from each other. The impeller turbine had six $45°$ downward facing impeller blades each to effect rapid downward movement of wastewater in the draft tube. A 1/4 HP high-speed AC motor was employed to drive the impeller turbines permitting a maximum speed of 4000 rpm. Between the draft tube and the reactor was a circular compartment that contained the GAC particles. The GAC was supported by a perforated bottom plate and a movable top perforated plate served as a cover. Both plates were drilled with many small holes (2 mm in diameter) that covered an area about 1/3 of the plate surface. In the experimental tests, up to 500 g of GAC were randomly packed in the circular compartment. The GAC was made from bituminous coal, as obtained from Chengtai Chemical Co., Taichung, Taiwan. According to the manufacturer, the GAC had an average diameter of 4.1 mm and a density of 0.39 g/cm^3. The BET surface area and the average pore size were measured by a porosimeter (Model ASAP 2000, Micrometric Instrument Corp., Norcros, Georgia) to be 1058 m^2/g and 23 Å,
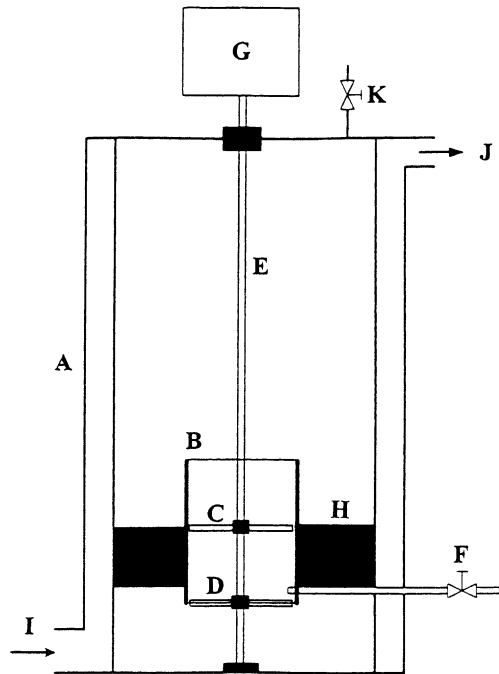
A. Reactor G. AC Motor
B. Draft Tube H. GAC Bed
C. Upper Impeller I. Cooling Water In
D. Lower Impeller J. Cooling Water Out
E. Motor Shaft K. To Vent
F. Ozone Input

Fig. 1. Schematic of the gas-induced ozonation reaction system.

respectively. The ozone generator was a Sumitomo SP-PSA-01A (Sumitomo Electric Co., Tokyo, Japan) that was equipped with a pressure swing (PSA) unit for air processing. The ozone gas inlet was located just above the bottom impeller turbine. The ozone generator had a maximum capacity of 30 g ozone/h. The actual ozone production rate was controlled by the current input and the air flow rate. The ozone mass flow rate and the ozone concentration in the gas mixture exiting the gas-induced reactor were measured by the standard KI (potassium iodide) absorption method [21].

At the beginning of a test run, 7 l of the effluent from chemical coagulation were placed in the ozone reactor. A constant reaction temperature of $30 \pm 1\,^{\circ}\text{C}$ was maintained and a GAC amount of 200 or 300 g was chosen for most test runs except for those conducted specifically to test the effect of the GAC amount on the ozonation oxidation. The impeller motor was turned on and kept at a desired constant speed of 1500 ± 10 rpm which was sufficient to maintain a steady vortex at the liquid surface. The ozone generator was warmed up for 30 min and the ozone gas generated at a 1 l/min air flow rate and a variable current input between

0.2 and 1 A was let in to start the ozone oxidation reaction. Small samples (20 ml each) were taken periodically from the reactor for water quality measurements by the standard methods [21]. A test run usually lasted not more than 2 h.

3. Results and discussion

3.1. Operating conditions of chemical coagulation

Chemical coagulation tests were conducted first to examine the effect of initial wastewater pH on the water quality improvement. Fig. 2 demonstrates the COD and ADMI removal as a function of the initial wastewater pH. Within the pH range between 5 and 10, the COD removal varied between 45 and 55%, with an average COD removal of about 50% and the ADMI removal exceeded 85% for wastewater pH $\leq$ 9. For such a high ADMI removal, the treated wastewater had only a faint color. For the wastewater pH $\geq$ 9, there was a sharp decrease in the ADMI removal to below 70%. The reason for such a sharp decrease in ADMI may be due to the fact that the wastewater ADMI was attributable to a large number of very fine colored particles suspended in the wastewater which were efficiently captured and removed for pH $\leq$ 9. On the other hand, the wastewater COD was represented by the dissolved organic pollutants that could not be as efficiently removed as the ADMI. Fortunately, a higher pH exceeding nine seldom occurred in the wastewater from the industrial park and hence adjustment of the wastewater pH appears to be unnecessary.

The COD and ADMI removal as a function of the PAC amount is demonstrated in Fig. 3, noting that the PAC/polymer ratio was kept at 100:1. The effect of the PAC amount on
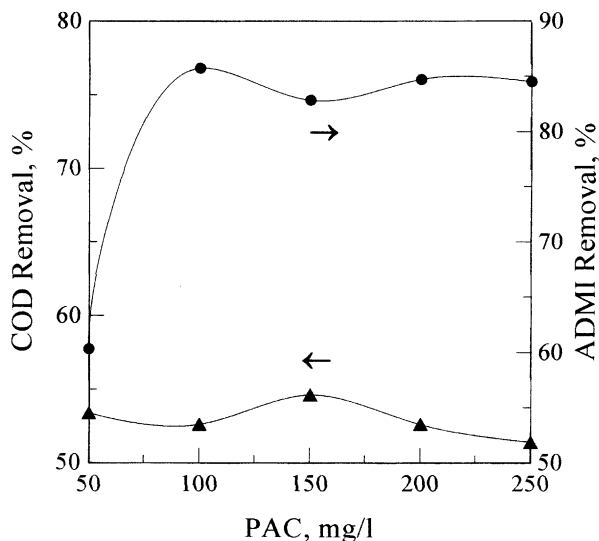

Fig. 2. The pH effect on the wastewater COD and ADMI removal with 806 initial ADMI, 878 mg/l initial COD, 100 mg/l PAC and 1 mg/l polymer.
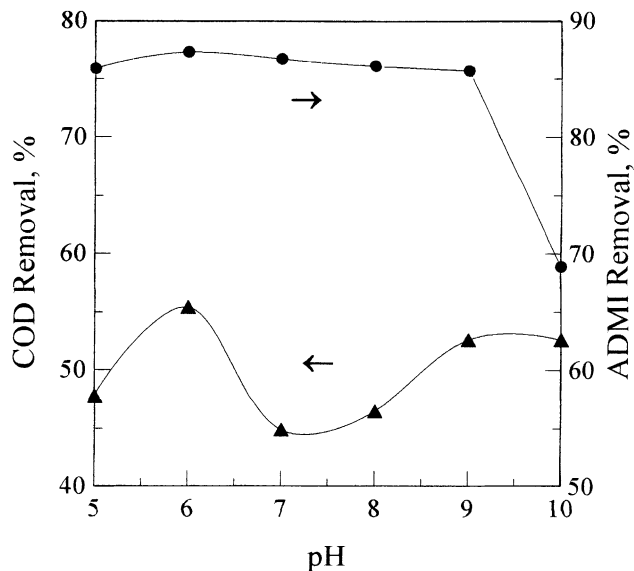
Fig. 3. The effect of PAC concentration on the wastewater COD and ADMI removal with initial ADMI 806, initial COD 878 mg/l, PAC/polymer of 100:1 and pH 9.

the COD removal is relatively small. However, the improvement in the ADMI removal from 60% at 50 mg/l PAC to 85% at 100 mg/l PAC is much pronounced. Above 100 mg/l, the PAC effect becomes marginal. Hence, 100 mg/l PAC and 1 mg/l polymer are deemed as the optimum dosage for the present chemical coagulation. For chemical coagulation of other wastewater samples (over 20 samples) using this fixed PAC/polymer dosage, the removal efficiencies varied between 48 and 56% with an average of 51% for COD and 78 and 87% with an average of 83% for ADMI. The pH of the wastewater samples varied between 6.3 and 8.6 that was a good pH range for efficient chemical coagulation according to Fig. 2. It is noted that the more pronounced PAC effect on the wastewater ADMI than on the COD may be due to the same reason as that of the pH effect as noted in the previous section.

3.2. Performance characteristics of gas-induced ozone reactor

Ozone has been known as an excellent decoloration agent for textile wastewater [9,10–12]. Fig. 4 shows the change in ADMI during the ozonation period for wastewater effluent from chemical coagulation with different inlet ADMIs to the ozone reactor. In spite of its inlet variation, the wastewater ADMI was reduced efficiently to be much less than 50 in 10 min of ozonation. The different initial ADMIs were achieved by properly diluting the wastewater with tap water. At this final ADMI level, the wastewater had no visible color. In fact, the same results of very low final ADMI were consistently obtained for ozonation runs using different wastewater samples. Hence, the wastewater color in comparison is a much lesser concern than the wastewater COD in all ozonation tests.
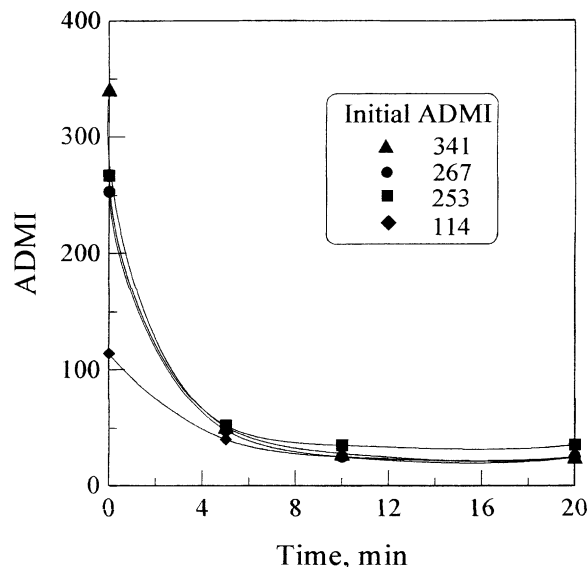
Fig. 4. The final ADMI of wastewater as a function of different initial ADMIs of gas-induced ozonation after chemical coagulation with 200 g GAC, 1500 rpm impeller speed, 1 l/min air flow rate, 141.6 mg/min ozone mass flow rate and 30 °C.

The impeller speed is the key parameter in forming a gas induction on the wastewater surface in the ozone reactor. It was observed in the experimental tests that vortex began to form for an impeller speed above 900 rpm and the vortex formation became well established and stable at 1500 rpm. Fig. 5 demonstrates the impeller speed on the wastewater COD removal. The influence of the impeller speed becomes increasingly small for an impeller speed above 1200 rpm. Hence, an impeller speed of 1500 rpm was deemed as sufficient for practical purposes.

The effect of input ozone mass flow rate on the wastewater COD removal was demonstrated in Fig. 6. The input ozone mass flow rates of 47.1, 79.6, 141.6 and 238.8 mg/min correspond, respectively, to current inputs of 0.2, 0.4, 0.6 and 0.9 A, the latter being the real control variable in the ozone generation. Note that the COD removal at zero ozone mass flow rate denotes the case by GAC adsorption alone. Fig. 6 reveals that the COD removal increases rapidly with an increase in the ozone mass flow rate up to 141.6 mg/l and beyond that improvement in the COD removal becomes much less significant. In the ozone oxidation of organic compounds, the rate of oxidation reaction has been reported to be dependent of the amount of dissolved ozone in the aqueous solution [6,10]. As the amount of dissolved ozone becomes excessive at sufficiently high ozone mass flow rate, such an ozone dependence of oxidation reaction vanishes. This may be the case in Fig. 6 when the ozone mass flow rate exceeds 141.6 mg/min. Hence, 141.6 mg/min ozone mass flow rate (or 0.6 A current input) is considered as an appropriate operating condition. It is noted that the wastewater effluent after chemical coagulation and combined GAC adsorption/ozonation treatments was excellent and could be considered for non-potable use.
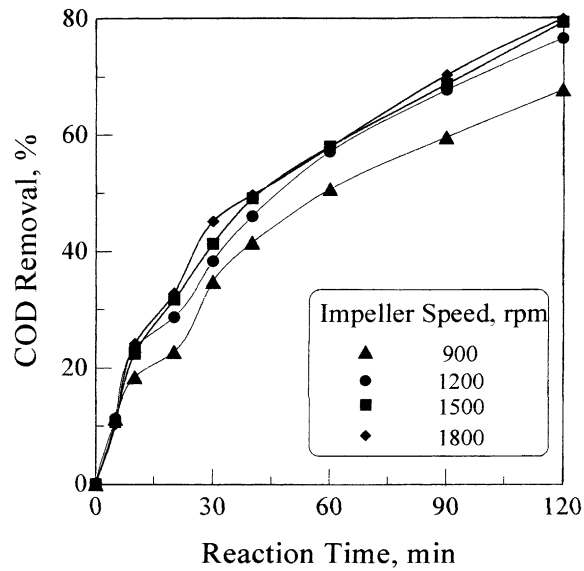
Fig. 5. The wastewater COD removal as a function of impeller speed of gas-induced ozonation after chemical coagulation with 200 g GAC, 287 mg/l initial COD, 1 l/min air flow rate, 141.6 mg/min ozone mass flow rate and 30 °C.
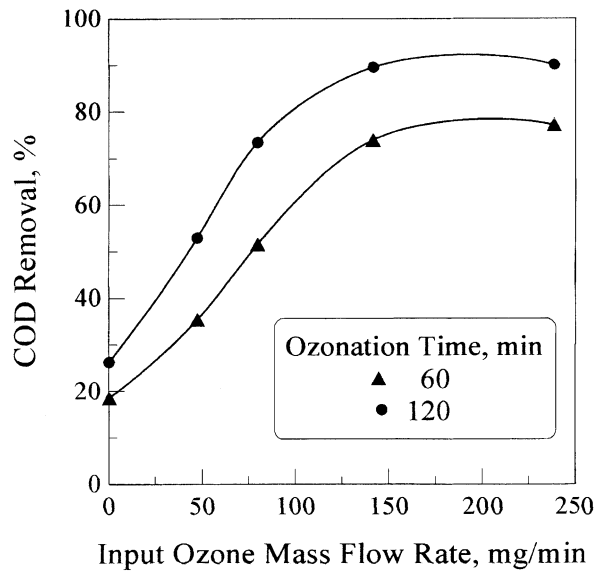

Fig. 6. The wastewater COD removal as a function of ozone mass flow rate of gas-induced ozonation after chemical coagulation with 200 g GAC, 391 mg/l initial COD, 1 l/min air flow rate, 1500 rpm impeller speed and 30 °C.

3.3. Regeneration of exhausted GAC

In a GAC adsorption process, the GAC will become saturated after all active adsorption sites are taken up by the pollutant molecules. High temperature steam is generally employed in industrial practice for regenerating the exhausted GAC. Although reasonably effective, this process can lead to a significant loss of GAC (up to 20 wt.%) and is costly. This partially negates the advantages of the GAC adsorption process. Hence, search for an effective and inexpensive GAC regeneration method is an important issue confronting the applications of GAC adsorption process.

In the present study, it was observed that the GAC regeneration occurred in situ during the ozonation period. To ascertain the GAC regeneration efficiency by ozonation, experimental tests were conducted by starting with a fresh batch of GAC to treat the wastewater. The COD concentrations were determined for ozonation times at 60, 90, 120, 180 and 240 min. The treated water was drained and the GAC bed was washed twice with deionized water to rid of the residual pollutants. The test was repeated with a new batch of wastewater. The same test process was repeated for three times and the test results were shown in Fig. 7. Note that the first set of data points were the COD removal of fresh GAC at various ozonation times. This figure reveals that the COD removal decreases slightly with the number of repeated use of GAC. The COD removal at 60 min of ozonation decreases from 47.8% for fresh GAC to 44.9% for the third repeated use while at 240 min of ozonation, the corresponding COD removal decreases from 85.1 to 83.2%. The decrease in the COD removal with the number of repeated use of GAC can be represented by the regeneration efficiency degradation
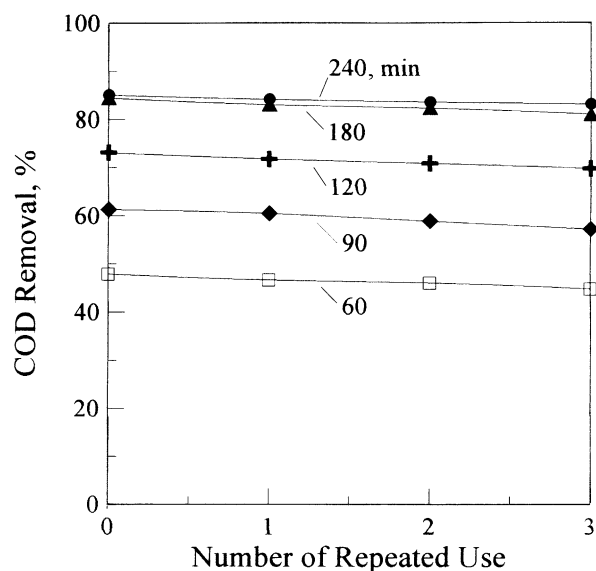

Fig. 7. The wastewater COD removal as a function of ozonation time and number of repeated use of GAC of gas-induced ozonation after chemical coagulation with 300 g GAC, 416 mg/l initial COD, 1 l/min air flow rate, 141.6 mg/min ozone mass flow rate, 1500 rpm impeller speed and 30 °C.

defined below:

$$\text{regeneration efficiency degradation} = \frac{(CR)_f - (CR)_r}{(CR)_f} \times 100\%$$

where $(CR)_f = COD$ is the removal by fresh GAC and $(CD)_r = COD$ is the removal by regenerated GAC and this quantity can be readily calculated from Fig. 7. According to this definition, the lower the regeneration efficiency degradation, the better. Fig. 7 shows that the regeneration efficiency degradation is reduced steadily from 6.25% at 60 min of ozonation to 2.23% at 240 min. Such a good regeneration efficiency was consistently observed in all ozonation test runs. Hence, it can be concluded that 240 min of ozonation is sufficient to exert a very good GAC regeneration for practical purposes while it also achieves an excellent COD removal.

In a previous study, Cooney and Xi [22] reported that GAC is capable of simultaneous adsorption and catalytic oxidation of phenolic compounds in aqueous solution. These two GAC functions could occur in the present treatment system also. To ascertain this point, experimental tests were conducted separately for GAC adsorption, ozonation and combined GAC adsorption/ozonation of wastewater. The results of the three separate tests are compared in Fig. 8. The COD removal with GAC adsorption alone was fairly rapid for the first few minutes and it started to level off after 60 min, reaching a maximum COD removal of 27.9%. This is presumably due to GAC saturation by the organic pollutants in the aqueous solution. By ozonation alone without GAC, the wastewater COD removal increased steadily in Fig. 8 and reached 43.2% at 120 min. With combined GAC adsorption and
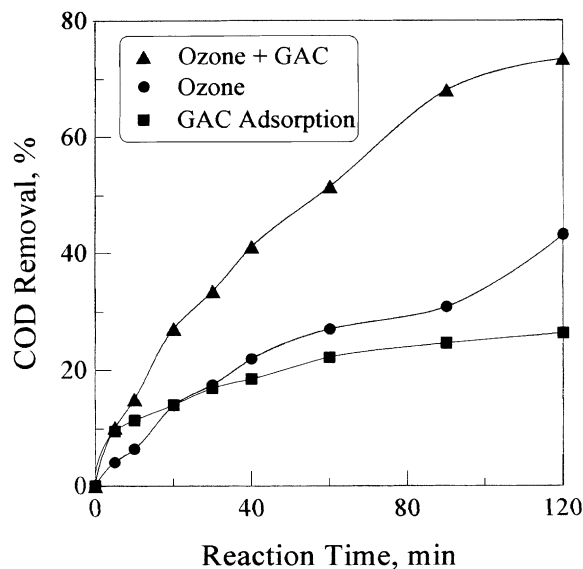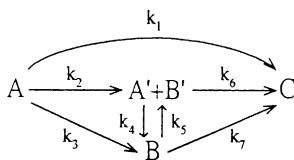

Fig. 8. The wastewater COD removal as a function of reaction time for GAC adsorption alone, ozonation alone and combined GAC adsorption/ozonation after chemical coagulation with 200 g GAC, 389 mg/l initial COD, 1 l/min air flow rate, 141.6 mg/min ozone mass flow rate, 1500 rpm impeller speed and 30 °C.
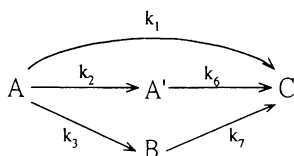
ozonation, the wastewater COD removal was essentially the same as that of GAC adsorption within a short time period. This implied that GAC adsorption plays a predominating role in the wastewater COD removal within that period. Beyond that, ozonation started to exert strong influence on the liquid-phase (homogeneous) and solid-phase (heterogeneous) wastewater oxidation. The homogeneous and heterogeneous oxidation by ozonation, coupled with GAC adsorption and catalytic oxidation attributed to the rapid COD removal that reached 73.4% at 120 min. This clearly shows the advantages of combined ozonation and GAC adsorption, justifying incorporation of the fixed GAC bed in the gas-induced ozone reactor.

3.4. Oxidation kinetics of wastewater by combined GAC and ozonation

Oxidation of organic pollutants involves complex reaction pathways and generation of many small intermediate organic compounds [5,23,24]. Different mathematical models have been suggested for representing the oxidation kinetics [5,23–25]. In comparison with conventional oxidation with or without ozone, modeling the present gas-induced ozonation system was further complicated by the presence of fixed GAC bed. Thus, a complex kinetic model for representing the present ozonation reaction system was proposed below:

$$
\begin{array}{c}
\xrightarrow{\quad k_1 \quad} \\
A \xrightarrow{\ k_2\ } A'+B' \xrightarrow{\ k_6\ } C \\
\underset{k_3}{\searrow} \quad k_4 {\downarrow}{\uparrow} k_5 \quad \underset{k_7}{\nearrow} \\
B
\end{array}
$$

According to the above mechanism, organic pollutants (A) can be oxidized by ozone in the aqueous phase directly to final products (C) via k_1 reaction or to small intermediate organic compounds (B) via k_3 reaction. They can be adsorbed onto to GAC via k_2 path. The intermediate organic compounds can also be adsorbed onto GAC via k_5 path or can be converted to final products via k_7 reaction. On the GAC surface, the adsorbed species $(A' + B')$ can be oxidized to intermediate B via k_4 reaction or be converted to final product via k_6 reaction. The above mechanism, though comprehensive, involves seven reaction and adsorption steps and is rather difficult to use. Attempts were made to adopt the comprehensive reaction mechanism to model the experimental data. The nonlinear least square curve fitting process was found rather difficult to converge. Furthermore, the values for k_4 and k_5 obtained in these attempts were in the order of magnitude of 10^{-8} that was much smaller than the others. Hence, the k_4 and k_5 reaction steps were excluded and the following simplified version was adopted:

$$
\begin{array}{c}
\xrightarrow{\quad k_1 \quad} \\
A \xrightarrow{\ k_2\ } A' \xrightarrow{\ k_6\ } C \\
\underset{k_3}{\searrow} \qquad \underset{k_7}{\nearrow} \\
B
\end{array}
$$

Assuming a first order reaction and adsorption for all paths, the following equations can be established:

$$\frac{d[A]}{dt} = -(k_1 + k_2 + k_3)[A] \tag{1}$$

$$\frac{d[A']}{dt} = k_2[A] - k_6[A'] \tag{2}$$

$$\frac{d[B]}{dt} = k_3[A] - k_7[B] \tag{3}$$

It was assumed that ozone was in ample supply and its concentration remained constant during the ozonation oxidation and hence the ozone concentration was incorporated into the rate coefficients (k_i) in the above equations. Integration of the above equations with the initial conditions: $[A] = [A_0]$, $[A'] = 0$ and $[B] = 0$ at $t = 0$ yields:

$$[A] = [A_0]\, e^{-(k_1+k_2+k_3)t} \tag{4}$$

$$[A'] = \frac{k_2[A_0]}{k_1 + k_2 + k_3 - k_6}[e^{-k_6 t} - e^{-(k_1+k_2+k_3)t}] \tag{5}$$

$$[B] = \frac{k_3[A_0]}{k_7 - (k_1 + k_2 + k_3)}[e^{-(k_1+k_2+k_3)t} - e^{-k_7 t}] \tag{6}$$

Addition of Eqs. (4) and (6) finally yields

$$\frac{[A+B]}{[A_0]} = e^{-(k_1+k_2+k_3)t}\left[1 - \frac{k_3}{k_1 + k_2 + k_3 - k_7}\right] + \frac{k_3}{k_1 + k_2 + k_3 - k_7}e^{-k_7 t} \tag{7}$$

The left-hand quantity $[A + B]/[A_0]$ is equal to $[COD]/[COD_0]$, a parameter measured in the experiments. It should be noted that $[A']$ in Eq. (5) represents those organic pollutants that get adsorbed onto the GAC and hence it is not the part of COD measured from the aqueous phase sample. That was the reason $[A']$ was excluded from Eq. (7). It is further noted that when there is no fixed GAC bed in the gas-induced reactor, then $k_2 = 0$ according to the reaction scheme and Eq. (7) is reduced to:

$$\frac{[A+B]}{[A_0]} = e^{-(k_1+k_3)t}\left[1 - \frac{k_3}{k_1 + k_3 - k_7}\right] + \frac{k_3}{k_1 + k_3 - k_7}e^{-k_7 t} \tag{8}$$

which is identical to that developed by Foussard et al. [24] and Li et al. [25]. Using the observed data, the kinetic rate coefficients (k_1, k_2, k_3 and k_7) were estimated by nonlinear regression analysis method and are listed in Table 1. This table reveals that the rate coefficient for oxidation of the small intermediate organic compounds (B) to the final products (C) is relatively small compared to others and hence this oxidation is negligible. The predictions based on the above kinetic model and the estimated coefficients in Table 1 are compared with the observed COD data in Figs. 9 and 10 for different GAC amounts and input ozone mass flow rates, respectively. Both figures show that the kinetic model describes well the observed COD behaviors, validating the various assumptions made in the model developments. According to the kinetic model proposed here, the first three kinetic parameters (k_1–k_3) represent the relative speed of the corresponding liquid-phase ozonation reactions

Table 1
Model fit of the reaction rate coefficients

	k_1	k_2	k_3	k_7
GAC amount (g)				
100	0.0036	0.0056	0.0043	3.31E−5
200	0.0091	0.0621	0.0099	3.12E−5
300	0.0212	0.0794	0.0119	3.82E−5
400	0.0493	0.1115	0.0146	5.44E−5
500	0.0859	0.1202	0.0166	6.13E−5
Ozone mass rate (mg/min)				
0	0.0124	0.0981	0.0002	2.21E−5
47.1	0.0171	0.1607	0.0011	3.13E−5
79.6	0.0256	0.1892	0.0022	9.71E−5
141.6	0.0406	0.2318	0.0025	4.79E−5
238.8	0.0463	0.2637	0.0029	2.48E−5

and GAC adsorption. These kinetic parameters in general follow the order $k_2 > k_1 > k_3$. This implies that in the present ozonation reaction with fixed GAC bed, pollutant adsorption onto GAC proceeded more rapidly then direct liquid-phase oxidation of organic pollutants to final products which in turn was faster than the liquid-phase decomposition of organic pollutants to intermediate organic compounds. This explains the synergistic effect of the presence of fixed GAC bed.
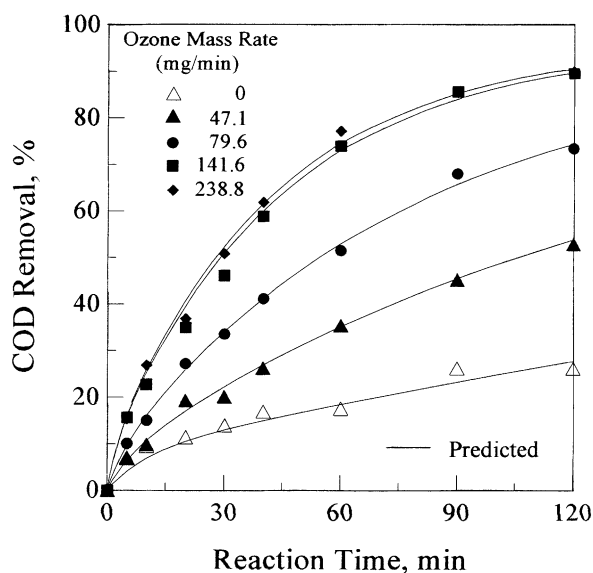

Fig. 9. Kinetic model fit of the wastewater COD removal as a function of ozone mass flow rate of gas-induced ozonation after chemical coagulation with 200 g GAC, 391 mg/l initial COD, 1 l/min air flow rate, 1500 impeller speed and 30 °C.
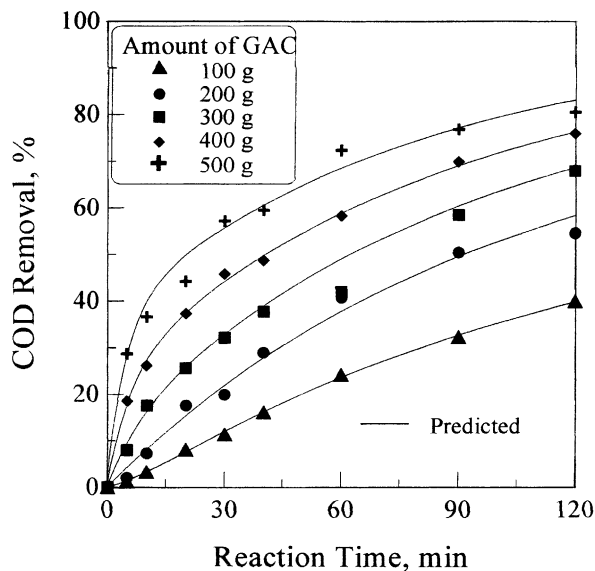
Fig. 10. Kinetic model fit of the wastewater COD removal as a function of GAC amount of gas-induced ozonation after chemical coagulation with 391 mg/l initial COD, 1 l/min air flow rate, 141.6 ozone mass flow rate, 1500 impeller speed and 30 °C.

4. Conclusions

Industrial wastewater treatment in a new gas-induced ozone reactor was investigated. A fixed GAC (granular activated carbon) bed was incorporated into the present reaction system. The incorporation of fixed GAC bed represented an advantageous addition to the previous gas-induced reactor employed by many investigators. Chemical coagulation was adopted for pretreatment of the wastewater. Experimental tests were conducted to identify the optimum operating conditions and to ascertain the important role played by the fixed GAC bed. Based on the results of experimental and theoretical investigations, the following conclusions can be drawn.

1. Chemical coagulation using 100 mg/l PAC and 1 mg/l polymer was able to efficiently removing over 85% ADMI and about 50% wastewater COD. Thus, the strong color of the original wastewater was considerably reduced, conducive to the ensuing ozonation treatment.
2. The fixed GAC bed was found to significantly enhanced ozonation oxidation of the wastewater effluent from chemical coagulation. The test results reveal that the gas-induced ozone oxidation achieves an excellent ADMI removal by reducing the final wastewater ADMI to less than 50. Under these conditions, the wastewater effluent was very clear with no visible color.
3. The in situ regeneration of exhausted GAC was observed in the experimental tests that was considered crucial to the present GAC/ozonation system. Repeated experimental

runs were performed to test the exhausted GAC regeneration efficiency. In terms of wastewater COD removal, over 95% regeneration of exhausted GAC was achieved in about 240 min of ozonation which was deemed quite good. For 99% regeneration of exhausted GAC, longer ozonation would be necessary.

4. A complex kinetic model was proposed for describing the gas-induced ozonation reaction. The kinetic model consists mainly of liquid-phase oxidation of organic pollutants to final products, GAC adsorption of these pollutants followed by solid-phase decomposition, and liquid-phase oxidation to small intermediate organic compounds which are further oxidized to final products. The complex kinetic model with kinetic parameters properly estimated was able to faithfully describe the behaviors of COD change during the ozonation period. Kinetic modeling reveals that adsorption of organic pollutants onto GAC is a faster and more important step than liquid-phase oxidation of these pollutants. The latter is in turn faster than oxidation of organic pollutants to intermediate organic compounds. Further decomposition of the intermediate organic compounds to final products was found to be negligible.

5. The final wastewater effluent after chemical coagulation and combined GAC adsorption/ozonation treatments was free from any color and had a COD concentration much lower than 100 mg/l. It could be considered for non-potable use.

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