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The Effectiveness of a New Gas-Induced Reactor in Treating Phenolic Wastewater by Ozonation and Hydrogen Peroxide

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ABSTRACT

A new Gas-Induced Reactor (GIR) has been developed to improve the efficiency of ozone utilization in water treatment. In this study, the GIR was used to investigate the behavior of ozonation of aqueous phenol solution by means of O_3 and O_3/H_2O_2 processes in order to explore the feasibility and efficiency of treating such wastewater using the new GIR. The study observed the decomposition of phenol, utilization of ozone, and variation of TOC during ozonation, varying pH values, phenol initial concentrations, ozone input concentrations, and hydrogen peroxide dosages. The study concluded that the new GIR was capable of performing effective and efficient ozonation of phenolic wastewater, maintaining high ozone utilization ratios at all experimental pH values and initial phenol and ozone concentrations. The optimal pH condition for phenol removal was around 11. The best molar ratios of initial hydrogen peroxide over input ozone among the performed experiments were about 20 at pH 7 and 10

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at pH 9 and 11. The primary operational energy used for treating a tonne of wastewater was 66 MJ, giving treatment costs of about US\$1.0 per tonne.

Key Words: Gas-induced reactor; Advanced oxidation process; Ozone; Hydrogen peroxide; TOC.

INTRODUCTION

Phenolic compounds are of concern because of their toxicity and biorefractory characteristics.^[1,2] For example, the U.S.EPA has ranked phenol, dichlorophenol, trichlorophenol, pentachlorophenol, chloromethyl phenol, 2,4-dimethyl phenol, and nitrosophenol among 129 priority toxic pollutants. Phenolic compounds exist widely in the wastewater released from oil-refining, coking, petrochemical, painting, steel, and textile industries;^[3,4] these residuals will lead to serious environmental problems if not subject to appropriate treatment.

Based on phenol concentration, composition of wastewater, and cost, the techniques used for treating phenol-containing wastewater are usually selected from recycling, incineration,^[5] adsorption,^[6] bio-treatment,^[7] or chemical oxidization.^[8,9] With advancing pollutant-controlling technologies and more stringent regulatory environmental standards, the combination of the advanced oxidation process (AOP) with biological treatment in treating wastewater has been widely discussed. Ozone can break down many refractory organics effectively because as a strong oxidant it is decomposed in aqueous solutions to produce stronger hydroxyl radicals.^[10,11] However, in spite of the merits of ozone, its use is limited by high generation cost and low ozone utilization ratio. The utilization of ozone is hampered by the mass transfer resistance between gas and liquid phases.^[12,13] To address this vital issue, a new gas-induced reactor (GIR) has been developed to promote the utilization efficiency of ozone by enhancing the transfer between gas and liquid phases. The characteristics of the GIR and the associated optimal geometric configuration have been provided in early studies.^[14,15] This research was aimed at investigating the feasibility of treating phenolic wastewater with the new developed GIR. By changing pH value, initial concentration of phenol, input ozone concentration, and $[H_2O_2]/[O_3]$ ratio, the ozone utilization ratios as well as the rates of phenol removal and TOC degradation during the treatment process were explored to assess the GIR's potential in phenol-containing wastewater treatment.

EXPERIMENTAL

Instrumentation

Figure 1 shows the experimental apparatus, primarily consisting of the GIR, an ozone generator, and an ozone analyzer. The reactor was an acrylic resin cylinder, with 17 cm inside diameter, 0.5 cm thickness and 80 cm height, which was surrounded by a thermostatic jacket to maintain a constant temperature of 25° C



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Figure 1. Experimental apparatus.

in all experiments. A pH meter connected with a pH controller was used to maintain the pH at a preset value. The Seki-Electronics (Japan) model SOZ-302C UV photometric analyzer calibrated by KI titration method was used to measure the ozone concentration in the gas phase. The Spectra-Physics (USA) model SP8800 HPLC was used to measure phenol aqueous concentrations while ASTRO (USA) model 2001 TOC analyzer was used to gauge TOC. Detailed description of the apparatus refers to Hsu and Huang.^[14,15]

Experimental Procedures

Seven liters of phenol solution with desired initial concentrations ($C_0 = 50, 100, 300, \text{ and } 600 \text{ mg/L}$) were put into the reactor and the pH was adjusted to specific

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levels (pH = 3, 7, 9, 11, and 13) by using NaOH and H₂SO₄. When the effects of adding H₂O₂ were studied, proper dosage ratios of [H₂O₂]/[phenol] were used to prepare the 7 L solution in order to obtain desired [H₂O₂]/[O₃] molar ratios (9, 20, 38, and 57). The stirring speed was kept at 1500 rpm. The ozone generator's gas flow was set at 300 NL/h with experimental ozone inlet concentrations ($C_{O_3,in} = 13$, 20, 30, 40, and 50 mg/NL). When the ozone generation achieved steady state, ozone was introduced into the reactor and the ozone concentrations in the exit gas were recorded every 20 s to calculate the ozone utilization ratio, which was defined as the difference between total amount of ozone input and total amount of ozone exit divided by the total ozone input.^[14] Samples from the ozonated solution were withdrawn at appropriate intervals. Na₂S₂O₃ · 5H₂O was added into the samples to prevent further reaction and then analyzed TOC and phenol concentrations.

RESULTS AND DISCUSSION

The effects of operational conditions (pH, initial phenol concentration, and inlet ozone concentration) on the treatment of phenolic aqueous solution and the results of the optimum $[H_2O_2]/[O_2]$ ratio investigation are presented and discussed below.

The Effect of pH

The Rate of Phenol Removal

Figure 2 shows the variation of phenol concentration at different pH values during the ozonation process. It was found that the time needed to remove phenol decreased with increase of pH values, with exception of pH 13. The trend resulted from the fact that phenol existed mostly in molecular form under acid conditions and existed mostly in phenolate ionic form, which was more reactive than the molecular form, in alkaline environment.^[16] Also, under alkaline conditions ozone reacted with OH⁻ to form OH[•], a stronger oxidant. However, when pH was even higher (pH = 13), OH[•] decomposed to produce $^{\circ}O^{-}$, a weaker oxidant, and thus lowered the rate of phenol removal.^[17]

TOC Degradation

Figure 3 shows the change of TOC with time at different pH values. The rate of TOC degradation increased with ascending pH values, with exception of pH 13, because at higher pH ozone decomposed to produce a stronger oxidant, OH^{\bullet} , which was less selective in organics oxidation and thus mineralized intermediates more completely.^[16,17] However, at even higher pH (pH = 13), the CO_3^{2-} and HCO_3^{-} produced when intermediates were mineralized captured OH^{\bullet} and subsequently lowered the TOC degradation rate.



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Figure 2. The decomposition of phenol at different pH values (symbol: *C*: phenol concentration at time *t*; C_0 : initial phenol concentration; $C_{O_3,in}$: input ozone concentration).



Figure 3. Effect of pH on TOC decay of phenol solution (symbol: C_0 : initial phenol concentration; $C_{O_3,in}$: input ozone concentration; TOC: TOC at time *t*; TOC₀: initial TOC).

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Table 1.	Phenol removal	time and	ozone consum	ption rates	during ozonation
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	pН	<i>t</i> at 90% removal (s)	O ₃ consumption/phenol removal (mg/mg)
Phenol initial concentration $= 600 \text{ mg/L}$	3	7560	1.48
$C_{\rm O_2,in} = 13 \pm 0.3 {\rm g/m^3}$	7	5262	1.326
- 3/	9	3620	0.927
	11	2978	0.765
	13	4186	1.08
Phenol initial concentration $= 300 \text{ mg/L}$	3	3600	1.496
$C_{\rm O_2,in} = 13 \pm 0.3 {\rm g/m^3}$	7	3086	1.332
- 3/	9	1840	0.934
	11	1498	0.767
	13	1994	1.024
Phenol initial concentration $= 100 \text{ mg/L}$	3	1646	1.647
$C_{\rm O_2,in} = 13 \pm 0.3 {\rm g/m^3}$	7	1118	1.547
- 3,	9	842	1.218
	11	801	1.206
	13	1057	1.615

Note: t: reaction time; ozone flow rate = 5 NL/min.

Ozone Utilization Ratio

The ozone utilization increased with increasing pH values. This was because at higher pH values the generated OH[•] reacted with organics rapidly and subsequently increased the driving force of ozone mass transfer from gas phase to liquid phase. As a result, the dissolution and utilization of ozone were increased. However, the amount of ozone consumed for a unit of phenol removal under pH 13 was not the lowest among the five experimental pH conditions, since there was retardation of the removal rates of phenol and TOC at pH 13 as described previously. Table 1 shows the O₃ consumption (mg) per mg of phenol removal as well as the time needed for 90% removal for different initial phenol concentrations and pH values.

The previous results indicated that increasing pH values promoted the rates of oxidation of phenol and intermediates as well as the efficiency of ozone utilization. However, at pH 13, the benefits are reduced.

The Effect of Phenol and Ozone Concentration

Rates of Phenol Removal and TOC Degradation

Figure 4 shows the variation of phenol concentration with time for different initial phenol concentrations. When input ozone concentration was fixed and the ozone utilization ratio was kept high, the amount of phenol removed was also fixed. Therefore as shown in Fig. 4 the rate of phenol removal decreased with increasing initial phenol concentration. TOC degradation had the same trend. In contrast,



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Figure 4. Plot of C/C_0 vs. time for different initial phenol concentrations (symbol: *C*: phenol concentration at time *t*; C_0 : initial phenol concentration; $C_{O_v,in}$: input ozone concentration).

as increasing input ozone concentration increased the amount of oxidants that reacted with phenol, the removal rates of phenol and TOC increased with increasing input ozone concentration, as shown in Fig. 5 for phenol removal.

Ozone Utilization Ratio

Figures 6(a) and 6(b) shows the ozone utilization at different initial phenol concentrations and input ozone concentrations, respectively, at pH 9. It was found that the ozone utilization ratio was greater than 90% at all phenol and ozone concentrations. In addition to increased dissolution of ozone due to self-decomposition under the alkaline condition, effectively extending the retention time of ozone in liquid phase in the apparatus, the newly developed GIR enhanced the solubility of ozone and thus promoted the rate of utilization.^[15] As also shown in Table 1, the consumptions of ozone per unit of phenol removal were low (ranging from 0.765 to 1.647) at all experimental pH and initial phenol concentrations. In conventional reactors, a sizable amount of ozone may be released without participating in reactions due to the resistance to mass transfer between gas and liquid phases, and the ozone consumption per unit of phenol removal was usually around 5.2–8.8.^[18] The fact that the new GIR provided a better mass transfer and promoted the ozone utilization demonstrated the importance of the reactor in treating phenolic wastewater.



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Figure 5. Plot of C/C_0 vs. time for different ozone inlet concentrations (symbol: C: phenol concentration at time t; C_0 : initial phenol concentration; $C_{O_3,in}$: input ozone concentration).



Figure 6. Ozone utilization ratios at pH 9 and (a) at different initial phenol concentrations, C_0 ; (b) at different input ozone concentrations, $C_{O_3,in}$.



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Figure 7. Decomposition kinetics of phenol at different pH values (symbol: C: phenol concentration at time t; C_0 : initial phenol concentration; $C_{O_3,in}$: input ozone concentration).

Optimal pH Conditions

Pseudo 0.5 order kinetics can describe the ozonation of phenol solution in this study.^[19] Figure 7 shows that the data fitting conformed to the proposed kinetics. Figure 8 shows the change of the overall removal rate constant, k_{obs} , with pH for three initial phenol concentrations. The best pH value was found to be 11. The result was compatible with that found by Beltran et al.^[20]

Optimal [H₂O₂]/[O₃] Ratio for Phenol Removal

In order to explore the effect of adding hydrogen peroxide into the ozone reaction system, the change of phenol concentrations with time at different $[H_2O_2]/[O_3]$ ratios for pH 7, 9, 11 were investigated. It was found that, although phenol was degraded faster when hydrogen peroxide was added, in the beginning the removal rates were slower than when hydrogen peroxide was not added. This was because competition between HO_2^- , O_3 , OH^- and phenol for OH radical at the beginning of the reaction decreased the degradation rate of phenol. The effect of adding hydrogen peroxide under acidic conditions can be ignored because H_2O_2 , with pKa 11.8, not only reacted very slowly with phenol and ozone but also generated little HO_2^- . Figure 9 shows how k_{obs} varied with $[H_2O_2]/[O_3]$ at different pH values. The result indicates that there exists optimal $[H_2O_2]/[O_3]$ molar ratios; the best ratios were 20 at pH 7



Figure 8. k_{obs} vs. pH value for different initial phenol concentrations (symbol: C_0 : initial phenol concentration; $C_{O_3,in}$: input ozone concentration; k_{obs} : the overall removal rate constant).



Figure 9. k_{obs} vs. hydrogen peroxide dosage at different pH values (symbol: C_0 : initial phenol concentration; $C_{O_3,in}$: input ozone concentration; k_{obs} : the overall removal rate constant).

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and 9 at pH 9 and 11 among the performed experiments. The addition of more hydrogen peroxide beyond the optimal dosage levels would decrease the reaction rates as a result of competition between phenol, phenol's oxidation intermediates, H_2O_2 , HO_2^- for hydroxyl radicals.^[21,22]

Primary Operational Cost Estimation

The electricity needed for generation of ozone and stirring in the GIR was the primary operational cost. The reaction that took 2857 s to treat 7 L phenol solution of 600 mg/L with ozone of 20 mg/NL at pH 9 is taken as an example. The amperage needed to generate the ozone for 300 NL/h was 0.65 A, so the energy needed was $0.65 \text{ A} \times 220 \text{ V} \times 2857 \text{ s}$, i.e., 0.408 MJ. The power need for stirring the 7 L solution after deducting the power needed for starting up was 0.019 kW, so the energy required was 0.054 MJ. Therefore by ignoring other expenses, the primary operational energy used for treating a ton of wastewater was 66 MJ, costing about US\$1.0 per tonne.

CONCLUSION

This research used a new developed GIR to treat phenol-containing wastewater and found that the reactor was capable of performing effective ozonation of phenolic wastewater. In particular, high rates of ozone utilization were sustained at all experimental pH values and initial phenol and ozone concentrations. This was a critical improvement to the key issue that the resistance of mass transfer of ozone between gas and liquid phases boosted the operational cost and thus impeded the wide use of ozonation. In addition, the investigation of optimal operational conditions showed that while the removal of phenol and TOC as well as ozonation utilization increased with increasing pH values and hydrogen peroxide dosages, too high a pH or excessive hydrogen peroxide dosages reduced treatment efficiency instead of improving it. The optimal molar ratios of initial hydrogen peroxide concentration over input ozone concentration among the performed experiments were found to be 20 at pH 7 and 9 at pH 9 and 11. Finally the calculated primary operational cost indicated that the GIR could reduce the expenses of treatment by enhancing the ozone utilization.

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