

Extraction–Oxidation–Adsorption Process for Treatment of Effluents from Resin Industries

H. Jiang,* H. Q. Yu, and Q.-X. Guo

Renewable Energy Laboratory, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China

For phenol and formaldehyde wastewater (PFW) treatment, combined processes, such as extraction–oxidation–adsorption (EOA) and dilution–biological–disinfection (DBD), rather than a single technique (e.g., biological technique) are more efficient and effective. In this article, the EOA technique was introduced and experimental studies on PFW treatment were conducted. Two parallel experiments, adopting EOA and DBD processes, respectively, were carried out in a factory with a discharge capacity of 24 m³ PFW/d, containing 6000 mg/L phenol. Experimental results indicate that the DBD process is featured by long hydraulic retention time (HRT) (72.5 h) and high treatment cost and investment, whereas EOA is characterized by short HRT (0.73 h), low treatment cost, and low investment. Only when the concentration of phenol is lower than 2700 mg/L was the operational cost of DBD lower than that of EOA.

1. Introduction

Formaldehyde finds many varieties of usage due to its high reactivity, colorless nature stability, purity in commercial form, and low cost. It serves as a resinifier curing agent, synthetic agent, disinfectant, fungicide, and preservative. Formaldehyde and phenol are also key raw materials in the industrial manufacturing of resins. The effluents of resins industries without complete treatment are harmful to humans and, thereby, are prohibited from being discharged into the environment by the Environment Protection Law.^{1–3}

Some biotechnique based research results of PFW treatment were reported. Llana's laboratory reported that *Rhodococcus erythropolis* was effective when being used to degrade phenol wastewater up to the concentration of 800 mg/L.^{4,5} Biological transformation of phenol to a nontoxic entity is also possible through specialized microbes. Because transformation of phenol is inhibited by the presence of formaldehyde, Lotfy found that, by adding calculated amounts of sodium sulfite, phenol was able to react with formaldehyde and form sodium formaldehyde bisulfite, which is not only nontoxic to microorganisms but also a biodegradable substance.⁶ In recent years, researchers separated some special microbes to decompose the high concentrations of phenol. Arutchelvan reported an interesting discovery that *P. cepacia* and *B. brevis* were able to decompose 2500 and 1750 mg/L of phenol in 144 h, respectively, which had potential application in industry.⁷ However, the biodegradation rate of phenol decreased significantly when the concentration of formalin was higher than 300 mg/L according to the results of Lotfy and other researchers. No reports of PFW treatment ranging from 6000 to 10 000 mg/L of phenol with biological processes were published. Generally speaking, the formaldehyde and phenol concentrations of PFW discharged from most resin factories are above 1000 and 5000 mg/L, respectively, which are beyond the upper limit of biological treatment capacity.^{8–11}

Physical and chemical methods are alternative means for high concentrations of organic wastewater treatment. For instance, liquid–liquid extraction systems can reclaim more than 99%

of the phenolic compounds in high concentrations of PFW.^{12,13} Some interesting research indicated that adsorption and oxidation can also remove phenol and formaldehyde effectively.^{14–18} For example, under certain conditions, 99% phenol could be degraded by a Fenton reagent;¹⁹ 99% phenol removal and 87% COD removal was achieved for an initial phenol concentration of 2000 mg/L in less than 120 min;²⁰ about 70% formaldehyde could be degraded using TiO₂ and H₂O₂ in 100 min.²¹ However, whatever single method is chosen, extraction, oxidation, adsorption, or biological methods, to treat a concentration of PFW as high as 6000 mg/L up to the standard ([phenol] < 0.5 mg/L, [formaldehyde] < 0.1 mg/L, and COD_{Cr} < 100 mg/L) will be economically prohibitive. The present feasible process for PFW treatment is dilution–biological–disinfection (DBD); that is, diluting the PFW to reach the acceptable concentration, using biological reactors to degrade the organic compounds, and then disinfecting microbes. In this article, an alternative combined process called extraction–oxidation–adsorption (EOA) was proposed, and the efficiency of EOA process was studied.

2. Materials and Methods

The main agents used in experiments, extractant (QY, a commercial reagent, made by the University of Science and Technology), oxidant (Fenton reagent), and absorbent (granular activated carbon, diameter of Φ 0.28–0.84 mm), are commercially available. PFW was sampled from a resin factory, which discharged 24 m³/h PFW containing 6200 mg/L phenol and 1200 mg/L formaldehyde.

The 4-aminoantopyrine spectrometric method was used to determine the concentration of phenol. In alkali solution, phenol interacted with 4-aminoantopyrine and ferricyanide to produce red 4-aminoantopyrine dye. The absorption spectra at wavelength of 460 nm was measured by the UV–vis spectrophotometer (Lambda 45, Perkin-Elmer Co. Ltd). And, the COD_{Cr} was determined by means of the potassium dichromate oxidation method (EPA410.4). Formaldehyde was determined quantitatively by using the iodometric method. A transmission electron microscope (H-800, Hitachi Co. Ltd) and an electron spectrometer (ESCALAB MK II, VG Co. Ltd) were the two main instruments used for analysis of the characteristics of GAC.

The main experiments were based on EOA and DBD systems. The former was designed and set up by our laboratory, and the

* To whom correspondence should be addressed. No.96, Jinzhai Road, Hefei 230026, China, Department of Chemistry, University of Science & Technology of China. E-mail: jhong@ustc.edu.cn. Tel.: +86-551-3607482. Fax: +86-551-3606689.

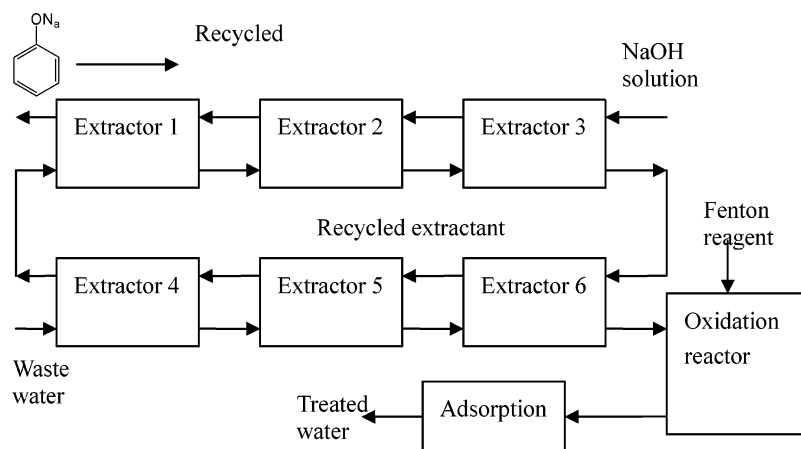


Figure 1. Schematic flow chart of EOA.

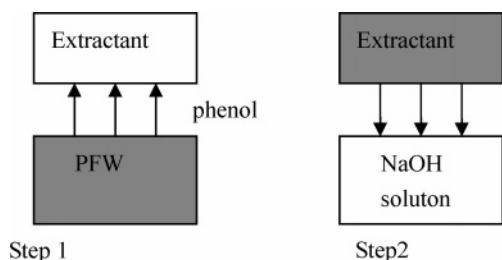
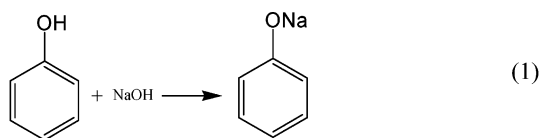


Figure 2. Main principle of extraction and reverse extraction.

latter has been used in the resin factory since the mid-1990s. Figure 1 was the schematic flow chart of the EOA system. Centrifugal extractors 1–6 rotated at about 3000 rev/min. The capacity of the system increased (from 1 to 2 m³/h) with the increasing rotating speed of the extractors. The detailed construction of the extractors and the extraction process equilibrium conditions were illustrated in our previous work.^{12,13} The main principle of EOA is illustrated in Figure 2. Step 1 was an extraction process, and step 2 was a reverse extraction with chemical reaction (reaction 1), by which extractant was recycled in the system.



The DBD system for PFW shown in Figure 3 was set up in the mid-1990s, including an anaerobic reactor with a volume of 64 m³, an aerobic reactor of 22 m³, and a disinfection reactor of 2.2 m³. Although the system was running stably, long hydraulic retention time (HRT) and additional diluted water

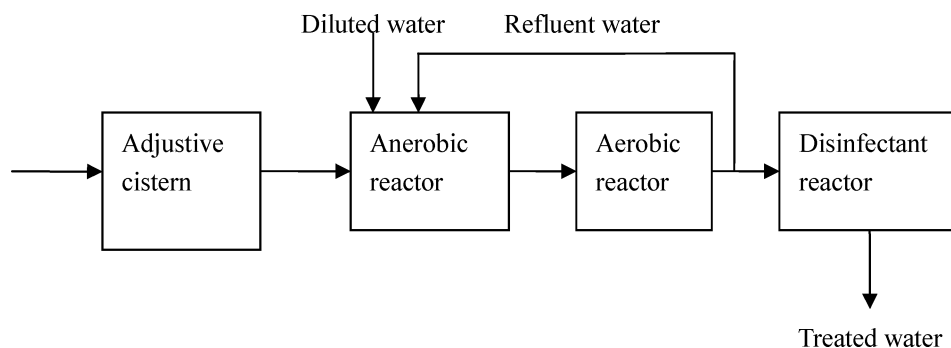


Figure 3. Schematic flow chart of DBD.

Table 1. Concentration of Main Pollutants in PFW (mg/L), pH, and Extraction Efficiencies Using Different Stages of Extractor

	phenol (mg/L)	formaldehyde (mg/L)	COD _{Cr} (mg/L)	pH
original PFW	6200	1200	22000	
one-stage extraction	820	965	6650	
two-stage extraction	158	860	4250	3
three-stage extraction	32	620	3540	
extraction efficiencies (%)	99.5	48.3	83.9	

supply to keep a stable, low concentration of phenol and formaldehyde resulted in low efficiency and waste of resources.

3. Results and Discussions

3.1. Extraction Experiments. Due to the different solubility of phenol in extractant and water, some compounds can be selected to separate phenol from wastewater, especially for a high concentration of phenol wastewater. Herein, extractant QY was used in a three-stage extractive process to recycle most of the phenol from PFW. All experiments were performed on the pilot scale, during which the flow rate of the PFW was 1.0 m³/h and that of the extractant was 0.3 m³/h. The extractors were regulated to reach the optimum conditions (at ambient temperature, the separated factor defined as the ratio of centrifugal force to gravity of liquid $S_f = 750$ and pH = 1–3), which had been reported before.¹² The experimental results were shown in Table 1.

Table 1 indicates that the extraction efficiency of phenol is significantly higher than that of formaldehyde. Most phenol and COD_{Cr} in PFW can be removed by a three-stage extraction process. Theoretically, though the remnant phenol decreases with the increase of the number of stages, further experiments showed that four or more stages of extraction would not promote the extractive efficacies (Figure 4). The main reason was that the emulsification of the extractant intensified with the addition of

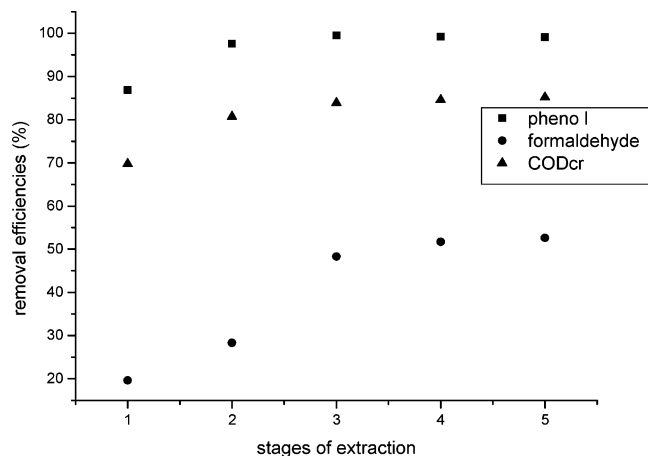


Figure 4. Removal efficiencies of pollutants at different stages.

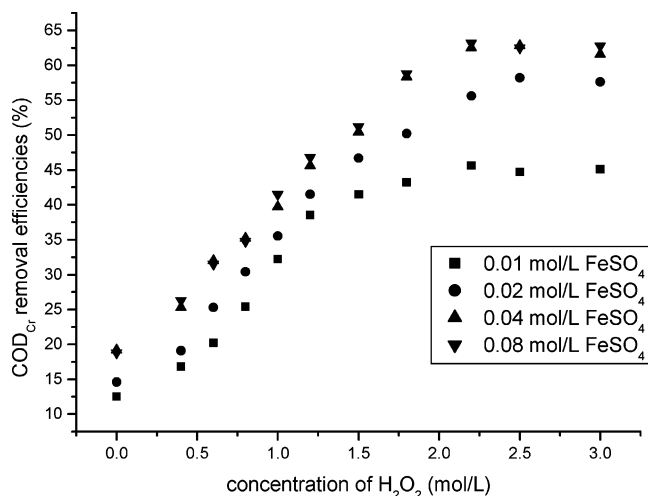


Figure 5. COD_{Cr} removal efficiencies at different concentrations of H₂O₂ and FeSO₄.

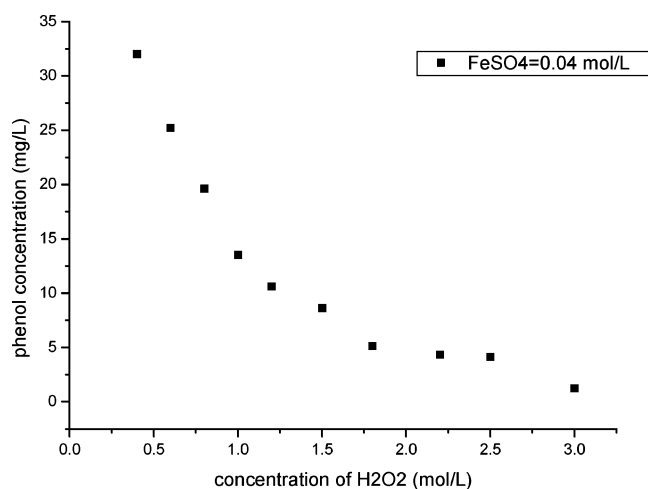


Figure 6. Remnant phenol in oxidized wastewater at different concentrations of H₂O₂.

extraction stages. Therefore, a three-stage system was optimum for PFW extraction.

For the reason that phenol was the major organic compound in PFW contributing to COD_{Cr} (Table 1), the removal efficiencies of COD_{Cr} were largely influenced by that of phenol. Figure 4 shows the consistency between removal efficiencies of phenol and COD_{Cr}. Due to formaldehyde's minor contribution to COD_{Cr}, the removal efficiencies of formaldehyde were inconsistent with those of COD_{Cr}.

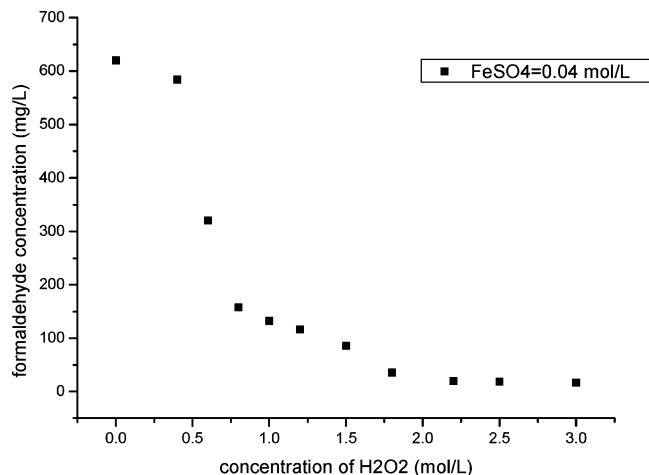


Figure 7. Remnant formaldehyde in oxidized wastewater at different concentrations of H₂O₂.

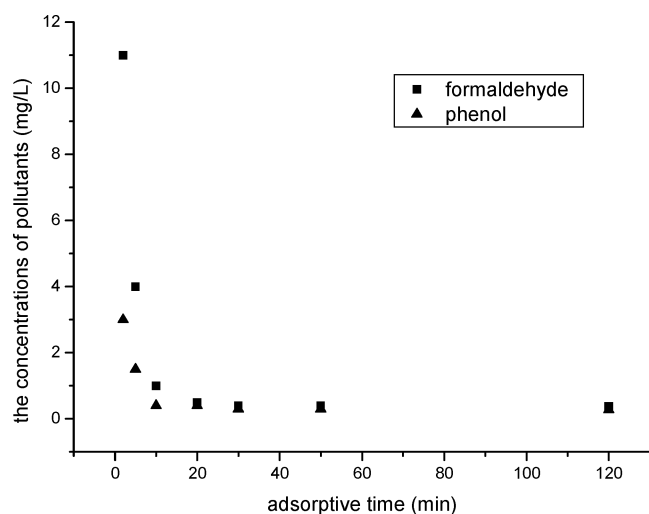


Figure 8. Adsorption of phenol and formaldehyde with 0.3% (w/w) GAC.

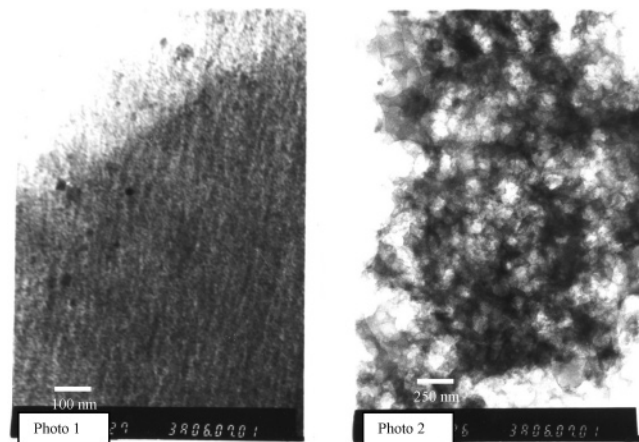


Figure 9. TEM photos of GAC.

3.2. Oxidation with Fenton Reagent. Although formaldehyde was difficult to extract because of its high solubility in both organic solvents and water, it can be easily oxidized by some reagents with high electronegativities, such as F⁻, H₂O₂, etc. In this study, the extracted wastewater was oxidized by a Fenton reagent in an oxidation reactor with a diameter of 0.8 m and an efficient volume of 1.0 m³. Different concentrations of H₂O₂ and FeSO₄ were added in the wastewater to test the oxidized effects. Mixed liquid was stirred with a beater rotating at 400 rev/min for 0.5 h. The COD_{Cr} removal efficiencies with

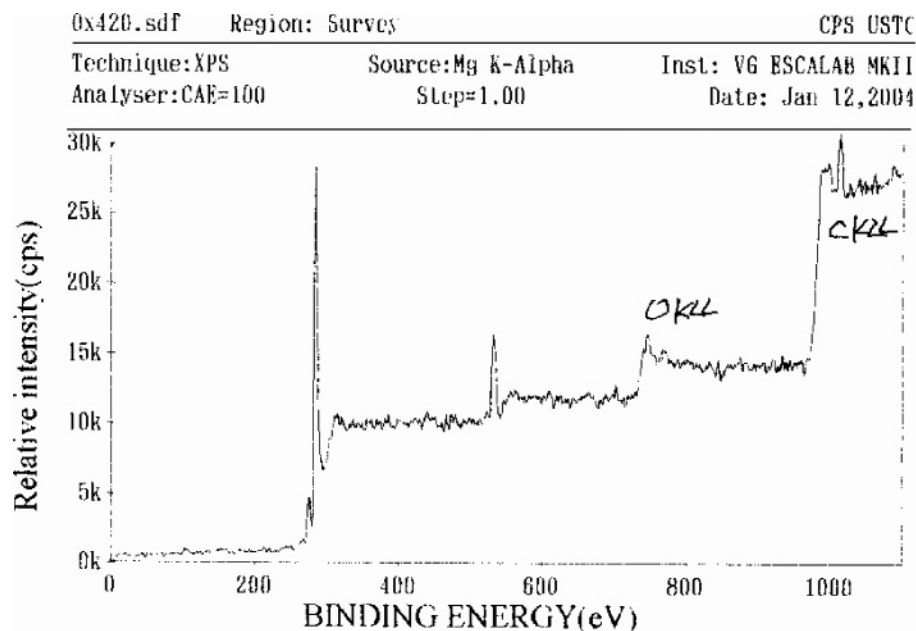
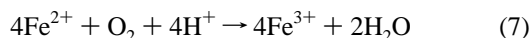
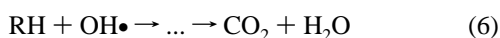
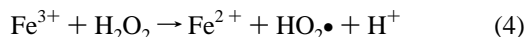
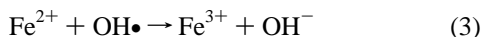
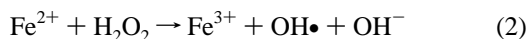


Figure 10. Full scan of the GAC surface with the electron spectrometer.

different concentrations of H_2O_2 and FeSO_4 were determined and plotted in Figure 5.

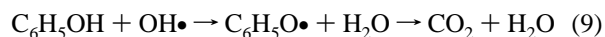
At the concentration of 2.2 mol/L (H_2O_2), the maximum COD_{Cr} removal efficiency reached 68%. Before the transition point, the COD_{Cr} removal efficiencies increased dramatically with the increase of H_2O_2 concentration. Beyond the transition point, the COD_{Cr} removal efficiencies were almost stable with the increase of the H_2O_2 concentration. The concentration of FeSO_4 was another key factor that influenced the COD_{Cr} removal efficiency during the oxidation process. FeSO_4 was effective in catalyzing the oxidation reaction of organic compounds at low concentrations. A 0.04 mol/L FeSO_4 concentration was the appropriate catalytic value (Figure 5).

The phenol and formaldehyde concentrations in oxidized wastewater were shown in Figures 6 and 7. The phenol and formaldehyde removal efficiencies increased with the increase of the H_2O_2 concentration, which were in accordance with that of COD_{Cr} . When the H_2O_2 concentration reached 1.8 mol/L, the oxidized PFW was economically acceptable to adsorptive technique. The oxidation principle of the Fenton reagent is as follows:



Reactions 2–5 produce a series of functional groups which can oxidize the organic compounds, such as phenol and formaldehyde.

The $\text{OH}\cdot$ produced from reaction 2–8 was a main oxidant, by which the phenol was able to be oxidized to CO_2 and H_2O as eq 9 shows.



The oxidation of formaldehyde can be divided into two steps. First, oxidation of formaldehyde yields HCOOH , and then, the HCOOH is decomposed into CO_2 and H_2O .



Formic acid can be detected in the oxidation process owing to the fast reaction rate of reaction 10 compared to reaction 11.

3.2. Adsorption with GAC. Despite the fact that the pollutants in PFW were dramatically reduced through extraction and oxidation process, the concentrations of phenol and formaldehyde could not meet emission standards. And the remnant complex organic compounds in PFW were difficult to extract and oxidize. To meet the emission standards, an adsorption column, 0.3 m in diameter and 1.5 m in length, was adopted in this experiment. An analysis of the breakthrough curves for both pollutants indicates that 0.3% (w/w) granular activated carbon was able to keep the concentrations of pollutants below the national standards. The scatter diagram of the adsorption results and adsorptive duration time was shown in Figure 8.

Figure 8 shows that after a certain adsorption time the concentration of organic matter will remain constant, which can be explained by the adsorptive mechanism. The adsorption of GAC includes surface adsorption and chemical adsorption caused by interaction of a chemical bond between organic compounds and function groups of GAC. The surface adsorption rate is positively correlated to the active surface area of GAC, and the concentrations of organic compounds. Figure 9 shows the changes of the GAC surface before (photo 1) and after (photo 2) adsorption. These photos were taken by transmission electron

Table 2. Composition of Functional Groups on the GAC Surface (mol %)

function group composition	C—H, C—C	C—O	C=O	O=C—O
	63.85	13.33	6.95	11.30

Table 3. Comparison of Cost and Efficiency between EOA and DBD

	HRT (min)	treatment cost (\$/ton PFW)	total investment (\$)
extraction	1.0	3.5	20 000
oxidation	30.0	0.5	10 000
adsorption	20.0	0.8	5 000
dilution	0	1.2	2 000
bioprocess	4320.0	0.3	150 000
disinfection	25.0	0.6	12 000
EOA	51.0	−1.4 (including recycled phenol)	35 000
DBD	4345.0	2.1	164 000

microscopy (TEM). With the decrease of the active surface area and the concentrations of pollutants, the adsorption rate continued to decline in the process of adsorption. Chemical adsorption, on the other hand, is determined by the chemical characteristics of GAC and dissolved compounds. A full scan of the GAC surface was taken by the electron spectrometer (Figure 10). It shows that there existed functional groups of different types and contents on the surface of GAC. The calculated results were listed in Table 2 based on Figure 10.

Strong hydrogen bonds existed between function groups (C=O and O=C—O) on the GAC surface and some organic compounds, which increased the efficiencies of adsorption. However, with the aggregation of pollutants on the GAC surface, the interaction between function groups and pollutants diminished gradually, and the adsorption rate decreased correspondently.

3.4. Comparison of Two Systems. Although the EOA and DBD are available for wastewater treatment, the operational cost and treatment efficiency of the two systems are significantly different. Table 3 showed the main differences in cost and efficiency.

Table 3 shows that the EOA process took much less time (51.0 min) for PFW treatment than the DBD process did (4345.0 min). The total investment of EOA was just about 1/5 that of DBD. The operational cost of EOA decreased with the increase of concentrations of phenol considering the value of reclaimed phenol. The PFW containing 6200 mg/L phenol was treated with EOA, and about 6.2 kg phenol was reclaimed from 1 ton of PFW, which was worth \$6.2 according to the phenol price (\$1000/ton) as of June, 2006. So, an additional \$1.4 was gained from 1 ton PFW treatment after deducting the cost of operation (\$4.8). According to calculations, if the PFW contained 2700 mg/L phenol, the treatment costs of EOA and DBD were the same.

4. Conclusions

For phenol and formaldehyde wastewater (PFW) treatment, combined processes, such as extraction—oxidation—adsorption (EOA) and dilution—biological—disinfection (DBD), rather than a single technique (e.g., biological technique) are more efficient and effective. In this article, the EOA technique was introduced and experimental studies on PFW treatment were conducted. Two parallel experiments, adopting EOA and DBD processes respectively, were carried out in a factory with a discharge capacity of 24 m³ PFW/d, containing 6000 mg/L phenol. Experimental results indicated that the DBD process is featured

by long hydraulic retention time (HRT) (72.5 h) and high treatment cost and investment, whereas EOA was characterized by short HRT (0.73 h), low treatment cost, and low investment. Only when the concentration of phenol was lower than 2700 mg/L was the operational cost of DBD lower than that of EOA.

Literature Cited

- (1) Hosseini, S. H.; Borghei, S. M. The treatment of phenolic wastewater using a moving bed bio-reactor. *Process Biochem.* **2005**, *40*, 1027.
- (2) Rajkumar, D.; Palanivelu, K. Electrochemical treatment of industrial wastewater. *J. Hazard. Mater.* **2004**, *B113*, 123.
- (3) Maloney, S. W.; Adrian, N. R.; Hickey, R. F.; Heine, R. L. Anaerobic treatment of pinkwater in a fluidized bed reactor containing GAC. *J. Hazard. Mater.* **2002**, *9*, 77.
- (4) Prieto, M. B.; Hidalgo, A.; Serra, J. L.; Llama, M. J. Degradation of phenol by *Rhodococcus erythropolis* UPV-1 immobilized on Biolite in a packed-bed reactor. *J. Biotechnol.* **2002**, *97*, 1.
- (5) Hidalgo, A.; Jaureguibeitia, A.; Prieto, M. B.; Concepción, R. F.; Serra, J. L.; Llama, M. J. Biological treatment of phenolic industrial wastewaters by *Rhodococcus erythropolis* UPV-1. *Enzyme Microb. Technol.* **2002**, *31*, 221.
- (6) Lotfy, H. R.; Rashed, I. G. A method for treating wastewater containing formaldehyde. *Water Res.* **2002**, *36*, 633.
- (7) Arutchelvan, V.; Kanakasabai, V.; Nagarajan, S.; Muralikrishnan, V. Isolation and identification of novel high strength phenol degrading bacterial strains from phenol-formaldehyde resin manufacturing industrial wastewater. *J. Hazard. Mater.* **2005**, *B127*, 238.
- (8) Uygur, A.; Kargi, F. Phenol inhibition of biological nutrient removal in a four-step sequencing batch reactor. *Process Biochem.* **2004**, *39*, 2123.
- (9) Campos, J. L.; Sánchez, M.; Mosquera-Corral, A.; Méndez, R.; Lema, J. M. Coupled BAS and anoxic USB system to remove urea and formaldehyde from wastewater. *Water Res.* **2003**, *37*, 3445.
- (10) Vidal, G.; Jiang, Z. P.; Omil, F.; Thalasso, F.; Méndez, R.; Lema, J. M. Continuous anaerobic treatment of wastewaters containing formaldehyde and urea. *Bioresour. Technol.* **1999**, *70*, 283.
- (11) Oliveira, S. V. W. B.; Moraes, E. M.; Adorno, M. A. T.; Varesche, M. B. A.; Foresti, E.; Zaiat, M. Formaldehyde degradation in an anaerobic packed-bed bioreactor. *Water Res.* **2004**, *38*, 1685.
- (12) Jiang, H.; Fang, Y.; Fu, Y.; Guo, Q.-X. Studies on the extraction of phenol in wastewater. *J. Hazard. Mater.* **2003**, *B101*, 179.
- (13) Jiang, H.; Tang, Y.; Guo, Q.-X. Separation and recycle of phenol from wastewater by liquid-liquid extraction. *Sep. Sci. Technol.* **2003**, *38*, 2579.
- (14) Guo, J.; Al-Dahhan, M. Catalytic Wet Oxidation of Phenol by Hydrogen Peroxide over Pillared Clay Catalyst. *Ind. Eng. Chem. Res.* **2003**, *42*, 2450.
- (15) Fongsatitkul, P.; Elefsiniotis, P.; Yamasmith, A.; Yamasmith, N. Use of sequencing batch reactors and Fenton's reagent to treat a wastewater from a textile industry. *Biochem. Eng. J.* **2004**, *21*, 213.
- (16) Pérez, I. V.; Rogak, S.; Branon, R. Supercritical water oxidation of phenol and 2,4-dinitrophenol. *J. Supercrit. Fluids* **2004**, *30*, 71.
- (17) Araña, J.; Martínez, N. J. L.; Herrera, M. J. A.; Doña, R. J. M.; González, D. O.; Pérez, P. J.; Bergasa, O.; Alvarez, C.; Méndez, J. Photocatalytic degradation of formaldehyde containing wastewater from veterinarian laboratories. *Chemosphere* **2004**, *55*, 893.
- (18) Meriç, S.; Kaptan, D.; Ölmez, T. Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process. *Chemosphere* **2004**, *54*, 435.
- (19) Kavitha, V.; Palanivelu, K. The role of ferrous ion in Fenton and photo-Fenton processes for the degradation of phenol. *Chemosphere* **2004**, *55*, 1235.
- (20) Lin, S. H.; Wang, C. H. Ozonation of phenolic wastewater in a gas-induced reactor with a fixed granular activated carbon bed. *Ind. Eng. Chem. Res.* **2003**, *42*, 1648.
- (21) Yamada, K.; Akiba, Y.; Shibuya, T.; Kashiwada, A.; Matsuda, K.; Hirata, M. Water purification through bioconversion of phenol compounds by tyrosinase and chemical adsorption by chitosan beads. *Biotechnol. Prog.* **2005**, *21*, 823.

Received for review August 6, 2006

Revised manuscript received January 14, 2007

Accepted January 22, 2007