



Combined fenton oxidation and biological activated carbon process for recycling of coking plant effluent

Wen-xin Jiang, Wei Zhang, Bing-jing Li, Jun Duan, Yan Lv, Wan-dong Liu, Wei-chi Ying*

School of Resources and Environmental Engineering, East China University of Science and Technology, No. 130, Mei Long Road Shanghai 200237, China

ARTICLE INFO

Article history:

Received 5 November 2010
Received in revised form 6 February 2011
Accepted 14 February 2011
Available online 5 March 2011

Keywords:

Fenton oxidation
Coagulation and flocculation
Adsorption
BAC
Total cyanide

ABSTRACT

Fenton oxidation and coagulation–flocculation–sedimentation (CFS) were both effective in removing many organic constituents of the biotreated coking plant effluent before the final treatment in an activated carbon adsorber. Fenton oxidation broke down most persistent organic pollutants and complex cyanides present in the feed stream and caused the eventual biodegradation of the organic residues in the adsorber. The results of Fenton oxidation followed by adsorption and biodegradation in two biological activated carbon (BAC) adsorbers show that the combined treatment consistently produced a high quality final effluent of <50 mg/L in COD_{Cr} and <0.5 mg/L in total cyanide during the 70-d study without replacing any activated carbon. The BAC function of the adsorber substantially reduced the need for replacing activated carbon making the combined Fenton oxidation–BAC treatment process a cost effective treatment process to recycle the final effluent for many beneficial reuses while meeting the much more stringent discharge limits of the future.

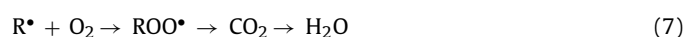
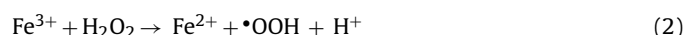
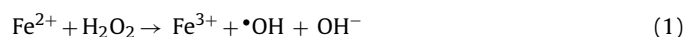
© 2011 Elsevier B.V. All rights reserved.

1. Introduction

A typical coking plant wastewater contains a wide variety of organic contaminants from coking, coal gasification, many other production and maintenance operations; some of the contaminants are present in high concentrations and/or are not removed by the conventional biological wastewater treatment processes. In China today, most existing chemical industry wastewater treatment plants are hard pressed to meet increasingly more stringent effluent discharge limits. There is also an urgent need to recycle well treated effluents for many beneficial reuse purposes. Relative to more highly developed countries, a much smaller fraction of industrial effluents is being recycled and/or reused [1]. Development of innovative cost effective processes for recycling chemical plant effluents is essential to ensure a sustainable development in China.

Granular activated carbon (GAC) is commonly employed for removing persistent organic pollutants (POPs) of biologically treated chemical plant effluents [2,3]. Fenton oxidation is highly effective for breaking up large organic molecules and has thus become a popular pretreatment step to improve biodegradability of organic constituents of biotreated effluent consisting of relatively small amounts of POPs, large amounts of metabolic intermediates and soluble microbial products (SMPs) [4–6]. The Fenton reactions

are dependent on the highly reactive •OH radicals according to the following mechanisms [7]:



The Fe³⁺ produced in the Fenton oxidation is a powerful coagulant for removing high molecular weight constituents of the feed by adsorption on the new Fe(OH)₃ flocs formed at a neutral pH [8]. Integrating Fenton oxidation with coagulation–flocculation–sedimentation (CFS) and/or carbon adsorption are attractive for advanced treatment for recycling coking plant effluents.

This research was conducted to: (1) evaluate the effectiveness of CFS, Fenton oxidation, and carbon adsorption for treating a biotreated coking plant effluent, (2) determine the effects of Fenton oxidation on biodegradability and adsorptive capacities of the residual contaminants, (3) identify the effluent recycling and cost saving potentials of Fenton oxidation of the coking plant effluent, and (4) demonstrate the long-term effective treatment of the

* Corresponding author. Tel.: +86 021 64252978; fax: +86 021 64252978.
E-mail addresses: wcying@ecust.edu.cn, wcying@yahoo.com (W.-c. Ying).

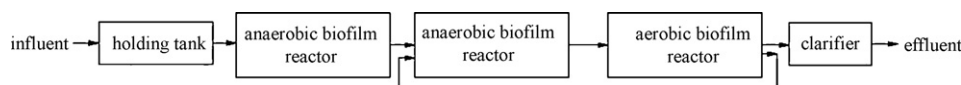


Fig. 1. Flow diagram of the coking wastewater treatment plant.

combined Fenton oxidation and adsorption/biodegradation in a biological activated carbon (BAC) adsorber.

2. Materials and methods

2.1. Source of the biotreated effluent samples

Shanghai coking plant (SCP) is one of the largest chemical plant in the city with capacities for producing 3.2 million m³/day of manufactured gas, 1.9 million ton/yr of coke, 350,000 ton/yr of methanol and more than 100 additional products. About 7000 m³/day of wastewater from chemical production, cleaning, washing and other operations is treated in the anaerobic and aerobic biofilm reactors as depicted in Fig. 1. Depending on influent composition and treatment effectiveness, characteristics of the many SCP effluent samples employed for the year long show a near constant pH of 6.8–7.0 and rather variable in NH₄⁺ (3.0–44 mg/L), NO₃⁻ (3.3–20 mg/L), COD_{Cr} (100–200 mg/L), and total cyanide (TCN, 2.0–7.0 mg/L). Advanced treatment of the biotreated effluent is desired to allow beneficial reuses of the final effluent and to meet the much more stringent discharge limits of the future.

2.2. Instrument, chemicals and activated carbons

The study employed the following instruments and equipments: UV–vis spectrophotometer (UV2000, Unico Shanghai Instrument), dissolved oxygen (DO) probe/meter (JPB-607 Shanghai Instruments), tubing metering pump (HL-2, Shanghai Huxi Analytical Instrument), piston metering pump (S-B10 Shanghai IWAKI Pumps), and auto sampler (modified BSZ-160, Shanghai Huxi Analytical Instruments).

Commercial polymeric ferric sulfate (PFS, Fe³⁺: 19% by weight) was dissolved, and the solution (20 g/L) was employed as the coagulant. FeSO₄ solution (6 g/L, FeSO₄·7H₂O) and hydrogen peroxide (30% H₂O₂) were employed as the Fenton reagents. All other chemicals employed for pH adjustment and analytical measurements were reagent grades. Three GACs made from coal, apricot nut and walnut (fruit) shell, and coconut shell, and a spent coconut carbon after 1 yr of dechlorination service were employed in this study.

2.3. Analytical methods

UV₂₅₄ and vis₃₈₀: light absorbance of 3 mL sample was measured with 1 cm quartz cell at 254 nm and 380 nm, respectively. DO: the DO probe/meter was calibrated each time before the DO measurements. The Standard Methods [9] procedures were employed for measurements of COD (the modified Hach COD_{Cr} Method [10]), TOC (TOC analyzer), TCN (the isonicotinic acid-pyrazolone colorimetric methods) and H₂O₂ (the KMnO₄ method).

2.4. CFS experiments

The use of PFS as the coagulant and the CFS treatment procedure were established in a side-by-side study [11]. 200 mL of the biotreated coking plant effluent was poured to series of 500 mL glass beakers; a fixed volume of the PFS stock solution (10% of the commercial grade) was added to each beaker. The beaker content was mixed rapidly (200 rpm) for 1 min and then slowly (20 rpm)

for 30 min; pH was kept at 7.0 using 1 M NaOH. The supernatant after 3 h of settling was the CFS treated effluent sample.

2.5. Fenton oxidation experiments: effects of pH and chemical doses

200 mL of the biotreated coking plant effluent was poured to series of 500 mL glass beakers; a fixed volume of each reagent solution (FeSO₄ and H₂O₂) was added to every beaker under moderate mixing (50 rpm); pH was adjusted to the test level using 1 M NaOH. After 20 min of reaction, the pH was adjusted back to 7, and the mixing was continued at a reduced speed (20 rpm) for another 10 min to achieve good flocculation of the newly formed Fe(OH)₃ precipitates before stopping. The supernatant after 3 h of settling was taken as the Fenton oxidized effluent sample. The Fenton oxidation pretreatment runs were performed using a 4 L or larger glass beaker to produce more samples for the adsorption capacity and column breakthrough experiments.

2.6. DO decay experiments: effect of Fenton oxidation on biodegradability of the residual organics

A mixed liquor sample of the coking plant's aerobic biofilm reactor was washed and then aerated in dechlorinated tap water for 24 h; the settled sludge was transferred to 1 L of Fenton oxidized effluent for 48 h of acclimation. The DO decay experiments were conducted using water/effluent samples after they were aerated for 10 min to raise their DOs to near saturation levels and supplemented with a fixed amount of the acclimated sludge (250 mL with 50 mg/L of sludge); the DO of each sample was monitored for biodegradability assessment.

2.7. Carbon adsorptive capacity experiments: capacity indicators and Freundlich isotherms

The batch adsorption capacity experiments were performed to determine the four adsorptive capacity indicators of the activated carbon samples and their effectiveness in removing the organic constituents, measured as COD, UV₂₅₄ (for aromatic organic compounds) and vis₃₈₀ (for color ingredients), and total cyanide of the effluent samples. The detailed procedures are described in a related paper [12].

2.8. BAC treatability study: GAC presaturation and inoculation of the carbon columns

About 15 g of the GAC sample was placed in a 4 L beaker containing 3 L of Fenton oxidized effluent sample under moderate mixing. After several hours of contact to allow adsorption of the residual organic and cyanide constituents, the mixing was stopped for replacement of the liquid with another volume of Fenton treated effluent; the liquid exchange continued many times until no significant changes in concentrations of the organics and cyanide. The presaturated carbon was filled to a small glass column which was then inoculated with the supernatant of the acclimated sludge employed in the DO decay experiments after further acclimation with more of the Fenton oxidized effluent in a 4 L beaker. The inoculation was conducted for 24 h to allow retention of the acclimated bacteria on the four columns (Col. A–D of Table 5), while the fifth

Table 1
Results of CFS, Fenton oxidation and CFS + Fenton oxidation for pretreating a coking plant effluent sample^a.

	Raw sample	CFS	Fenton oxidation	CFS + Fenton
UV ₂₅₄ (abs)	1.789	0.983	0.888	0.503
vis ₃₈₀ (abs)	0.411	0.152	0.174	0.098
COD (mg/L)	88.9	49.0	48.8	35.7
Total cyanide (mg/L)	5.07	1.131	0.236	0.13

^a Average chemical doses of multiple test runs. CFS: PFS ($\text{Fe}^{3+} = 57 \text{ mg/L}$), Fenton. Oxidation: ($\text{Fe}^{2+} = 56 \text{ mg/L}$ and $\text{H}_2\text{O}_2 = 27.2 \text{ mg/L}$), and CFS + Fenton: PFS ($\text{Fe}^{3+} = 57 \text{ mg/L}$) followed by $\text{Fe}^{2+} = 28 \text{ mg/L}$ and $\text{H}_2\text{O}_2 = 13.6 \text{ mg/L}$.

column was filled with new coal carbon and operated without inoculation. To simulate the full scale adsorption treatment, the five columns were in an upflow manner at an empty bed contact time (EBCT) of 40 min. The BAC treatability study was conducted to verify the BAC functions in the adsorbers and to compare the BAC treatment effectiveness of different GACs.

3. Results and discussions

3.1. Feasibility study employing coagulation and flocculation

Results of previous experiments showed that the coagulation and flocculation treatment employing 2 min of high speed mixing (200 rpm) flowed by 30 min of low speed mixing (20 rpm) was most effective for removing organic constituents of the effluent. Although the coagulation and flocculation treatment was capable of producing an effluent with a COD of $<50 \text{ mg/L}$ (Table 1) required for recycling as a cooling water make-up, the treatment, even at much higher dose of Fe^{3+} , was unable to lower the total cyanide concentration below the present discharge limit of 0.5 mg/L as shown in Fig. 2.

3.2. Feasibility study employing Fenton oxidation

The effectiveness of Fenton oxidation is pH dependent as illustrated in Eqs. (1) and (2). The production of active radicals would be inhibited at a pH lower [13] or higher [14] than the optimum. The basic pH also would reduce the effectiveness of Fe^{2+} as a catalyst [15]. Fig. 3 presents the effect of pH adjustment on removal of organic constituents, as measured by COD, UV₂₅₄ and vis₃₈₀, by Fenton oxidation of the raw coking plant effluent. Therefore, in the subsequent study, Fenton oxidation was performed directly on the raw effluent without pH adjustment as its pH (6.8–7.0) was very close to the best initial pH. The actual oxidation was taken place at an acidic pH of about 3.0–5.0 after the desired amount of FeSO_4

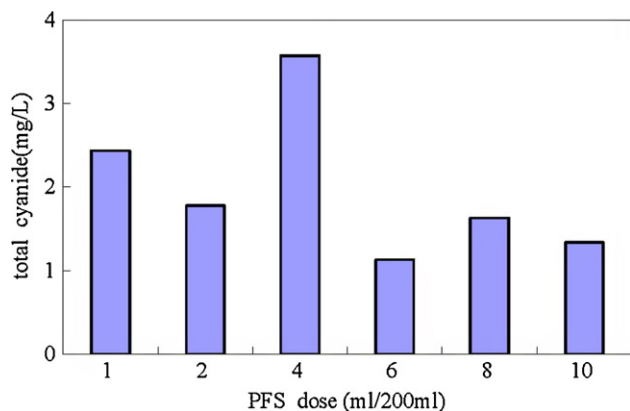


Fig. 2. Effect of PFS dose on the residual total cyanide after coagulation and flocculation.

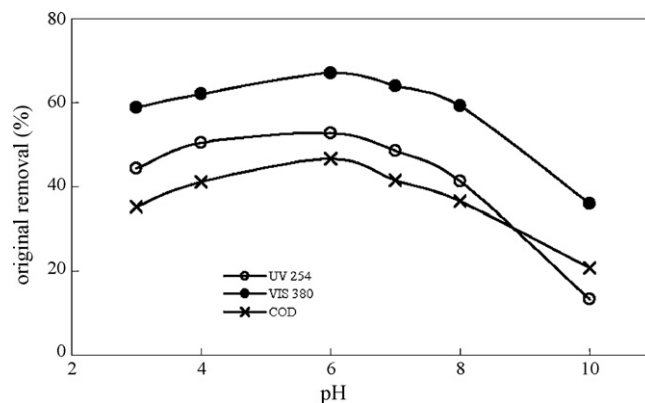


Fig. 3. Effect of pH adjustment on organic removal by Fenton oxidation.

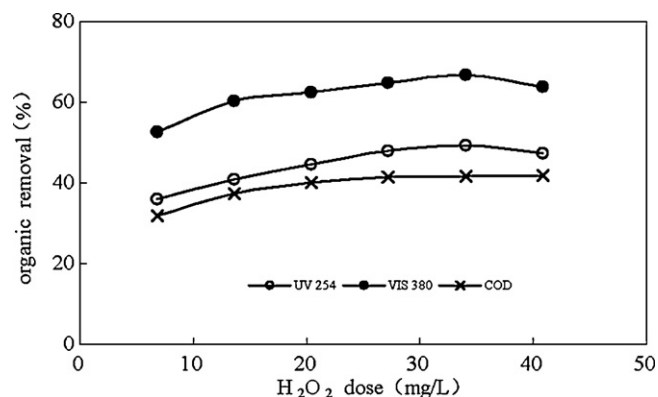


Fig. 4. Effect of H_2O_2 dose on organic removal by Fenton oxidation.

solution was added. The results were consistent with the literature report and an acidic pH 2–4 was preferred for Fenton oxidation [16].

The organic removal increased with the amounts of Fenton reagents (H_2O_2 and FeSO_4 , Figs. 4 and 5). A much larger than desired dose of H_2O_2 would consume $\cdot\text{OH}$ (Eq. (3)) reducing the oxidation potential [17], while too much Fe^{2+} also consume $\cdot\text{OH}$ (Eq. (4)) to form Fe^{3+} which would result in excessive amount of sludge after neutralization. Based on the results of many test runs and considering the cost of chemicals and sludge disposal [18], 27.2 mg/L of H_2O_2 and $56 \text{ mg Fe}^{2+}/\text{L}$ were selected for treating the biotreated coking plant effluent samples.

H_2O_2 may oxidize both free and complex cyanide stepwise to CNO^- [19] and finally to N_2 [20]. Most of the total cyanide present

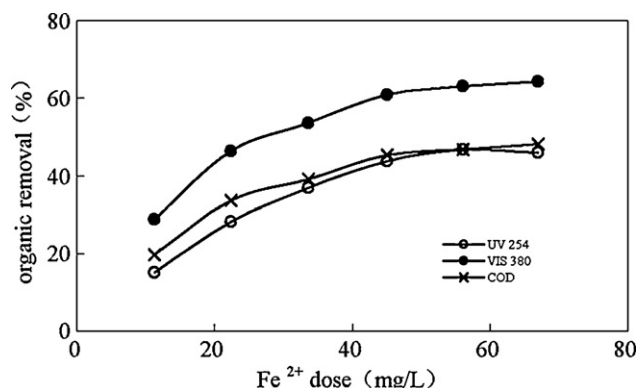


Fig. 5. Effect of Fe^{2+} dose on organic removal by Fenton oxidation.

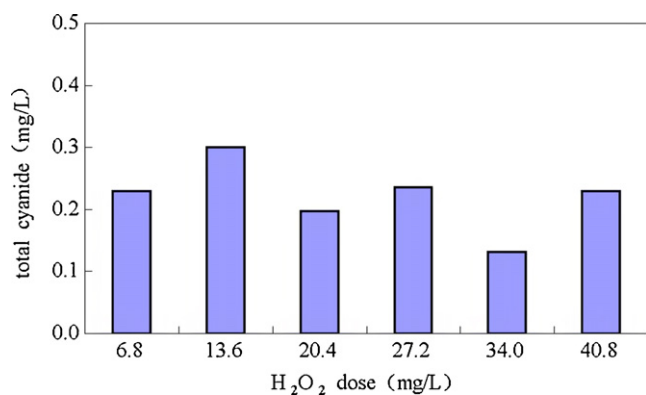


Fig. 6. Effect of H_2O_2 dose on the residual total cyanide after Fenton oxidation.

in the coking plant effluent was removed in 20 min by the Fenton oxidation; the total cyanide concentration was easily reduced <0.5 mg/L using a range of H_2O_2 doses as shown in Fig. 6.

Results of multiple treatment runs, employing CFS, Fenton oxidation, and CFS followed by a polishing Fenton oxidation step, performed on a biotreated coking plant sample are summarized in Table 1. Both the optimized Fenton oxidation and the CFS + the polishing Fenton oxidation at a much reduced chemical doses achieved the objectives of <50 mg/L of COD and <0.5 mg/L required for reusing the final effluent as cooling water make-up; at about the same treatment cost, the latter alternative (CFS + Fenton) is a preferred simple solution to produce a directly dischargeable effluent since the simple Fenton was unable to do so, when the raw effluent sample quality was much worse as illustrated in the example of the treatability study.

3.3. Effect of Fenton oxidation on biodegradability of residual organic constituents

Fig. 7 depicts the DO decay curves for the raw and Fenton oxidized coking plant effluents and the dechlorinated tap water after they were first aerated to raise the DOs. The data have demonstrated that some organic ingredients of the raw coking plant effluent were slowly biodegraded [21] and that Fenton treatment made the residual organics more biodegradable. Continued acclimation of the bacteria in the seeding solution was demonstrated by the higher oxygen utilization rates of the Fenton oxidized samples of more aerations.

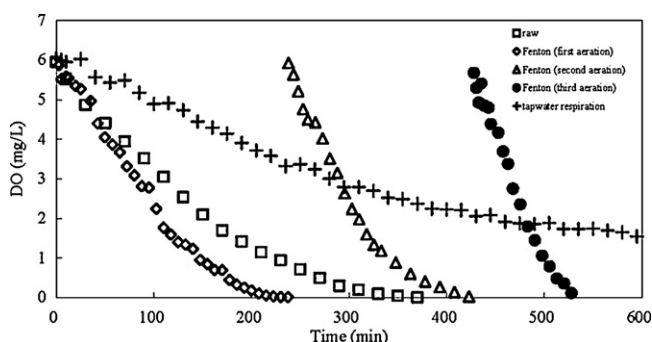


Fig. 7. DO decay curves for the raw and Fenton oxidized coking plant effluents and tapwater.

Table 2
Adsorptive properties of the activated carbon samples.

Activated carbon	Phenol no.	Iodine no.	Methylene blue no.	Tannic acid no.
Coal	81	1114	313	42.3
Coconut	126	1154	303	16.7
Fruit	111	1033	307	105.0
Spent Coconut	67.0	837	<150	8.2

Mg of phenol adsorbed by 1 g of carbon at an equilibrium phenol conc. of 20 mg/L. Mg of iodine adsorbed by 1 g of carbon in at an equilibrium iodine conc. of 0.02 N. Mg of methylene blue adsorbed by 1 g of carbon at an equilibrium methylene blue conc. of 1 mg/L. Mg of tannic acid adsorbed by 1 g of carbon in at an equilibrium tannic acid conc. of 2 mg/L.

Table 3
Freundlich isotherm parameters for the coal carbon.

Effluent sample	Organic	K^a	$1/n^a$	R^{2b}
Raw effluent	UV ₂₅₄	2.563	1.194	0.9905
	vis ₃₈₀	1.727	0.976	0.9738
	COD	0.065	1.873	0.9950
CFS treated effluent	UV ₂₅₄	7.422	0.979	0.9776
	vis ₃₈₀	7.292	1.058	0.9685
	COD	0.309	1.792	0.9868
Fenton oxidized	UV ₂₅₄	6.420	0.938	0.9996
	vis ₃₈₀	8.734	0.994	0.9739
	COD	0.002	3.252	0.9862

^a X/M (mg/g) = $KC_f^{1/n}$.

^b R^2 : Correlation coefficient.

3.4. Feasibility study employing carbon adsorption (GAC, CFS + GAC and Fenton + GAC)

Activated carbon's BET surface area and pore volume for pore diameters of <10, 10–15, 15–28, and >28 Å are properly disclosed by its phenol, iodine, methylene blue and tannic acid numbers [22]. Table 2 data shows that the four carbons had highly different adsorptive properties; coconut carbon was effective for removing small size pollutants but ineffective for removing large adsorbates that coal and fruit carbons were effective for removing water pollutants of all sizes and that the spent coconut carbon had the lowest capacities of all. The adsorptive capacities of the lower cost coal carbon for the organic constituents of the raw, CFS treated and the Fenton oxidized effluent samples were represented by the Freundlich isotherms as summarized in Table 3. To allow a fair estimate of the coal carbon's capacity for total cyanide, the removal capacities vs. residual cyanide data for four series of experiments (1- and 2 hr of contact with 10 m/L solutions of free cyanide and Fe complexed cyanide) were plotted as the Freundlich isotherms (Fig. 8).

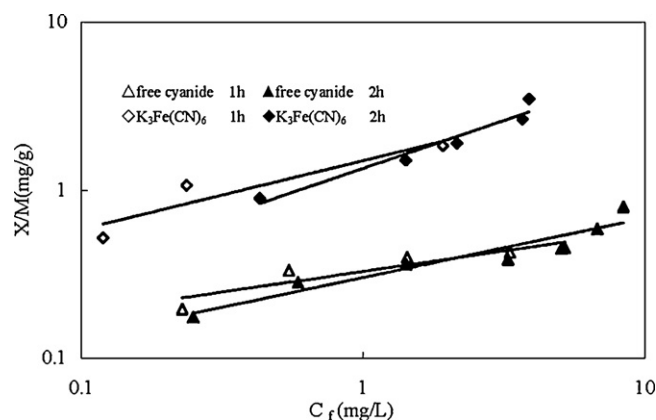


Fig. 8. Adsorption isotherms of free and complex cyanide for the coal carbon.

Table 4
Isotherm based requirements for the coal carbon.

Contaminants	Effluent	C_{in}^a	GAC ^b
UV ₂₅₄ (abs)	Raw	1.723	0.35
	CFS	0.983	0.20
	Fenton	0.888	0.15
VIS ₃₈₀ (abs)	Raw	0.411	0.57
	CFS	0.152	0.15
	Fenton	0.174	0.11
COD (mg/L)	Raw	88.9	0.29
	CFS	49.0	0.15
	Fenton	48.8	0.07
Total cyanide (mg/L)	Raw	5.03	1.30
	CFS	1.13	0.78
	Fenton	0.236	0.398

^a C_{in} : feed concentration.

^b $GAC (g/L) = C_{in}/(X/M)_{C_{in}}, (X/M)_{C_{in}}$: the capacity at C_{in} ; for organics, use Table 2 isotherms; for CN, use CN in $K_3Fe(CN)_6$, $X/M (mg/g) = 1.346C_{in}^{0.569}$ ($R^2 = 0.949$).

The isotherm based requirements for the coal carbon are listed in Table 4 in which the coal carbon's capacity for total cyanide was its 2 h isotherm of CN in the $K_3Fe(CN)_6$ solution. In addition to having accomplished the removals of organics and total cyanide, the Fenton oxidization made the residual organics more adsorbable on activated carbon as evidenced by the greater reduction in carbon requirements than the corresponding concentration reductions.

3.5. BAC treatability study

Five small carbon columns were operated at the same time for 70 days treating H_2O_2 supplemented (40 mg/L) Fenton oxidized effluent; four columns filled with presaturated carbons were inoculated with the acclimated bacteria originated from the coking plant's aerobic biofilm reactor, while the fifth column filled with new coal carbon was not inoculated. The operating conditions and the treatment performance are summarized in Table 5. The column performance data for removing organic constituents and total cyanide of the feed are depicted in Figs. 9–12. Immediate breakthrough of organic constituents, measured as, UV₂₅₄ (Fig. 9), vis₃₈₀ (Fig. 10) and COD (Fig. 11), and total cyanide (Fig. 12) were observed in the effluents of Col. A–D since the presaturated carbons had virtually no adsorptive capacities available at the start up; the effluent concentrations began to decline, as the inoculated acclimated bacteria started to grow actively, until they reached near steady low values in about 30 days. The data for the new carbon column without inoculation (Col. E) shows almost total removal of the organics and total cyanide initially and their increasing presence in the effluent as breakthrough occurred; bacteria present in the feed were

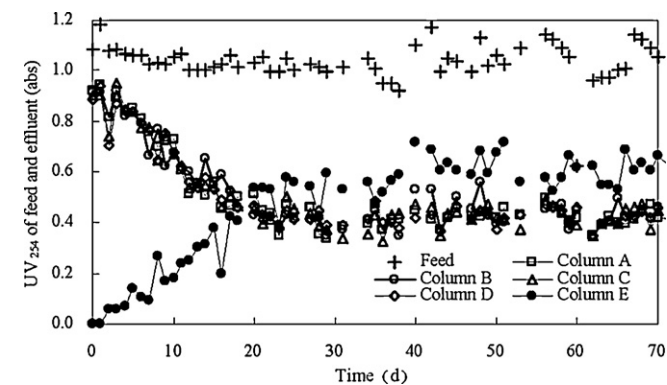


Fig. 9. Performance of the BAC treatment of the Fenton oxidized effluent sample UV₂₅₄.

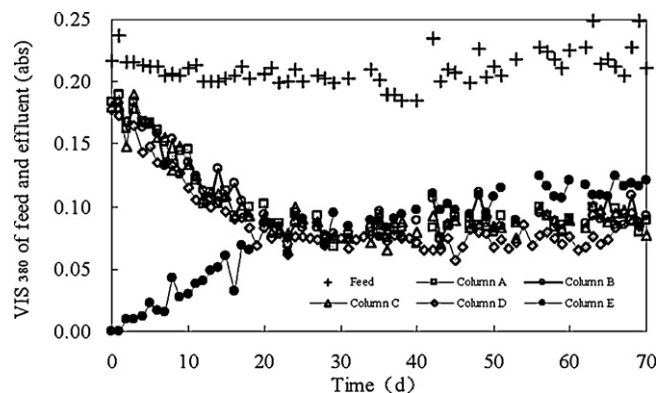


Fig. 10. Performance of the BAC treatment of the Fenton oxidized effluent sample vis₃₈₀.

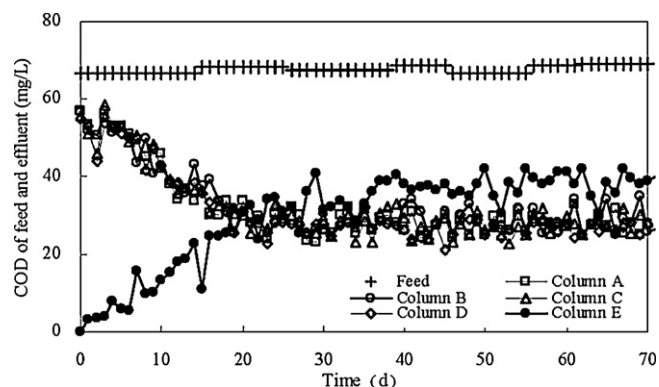


Fig. 11. Performance of the BAC treatment of the Fenton oxidized effluent sample COD.

retained in the column and began to grow resulting in the stable effluent in 35–40 days when it also functioned as a BAC adsorber.

The effect of BAC is illustrated by the large amount of total cyanide removed in Col. E (262% of the comparable adsorptive capacity) as a result of its biodegradation [23]. The long-term steady removal of organics and total cyanide in carbon columns demonstrates that the BAC function would be established naturally although the inoculation made it happened faster [24].

Although total cyanide was not well adsorbed on activated carbon as the residual organics (Table 4) and had indeed broke through the carbon column much faster, its concentration of Col. E effluent remained significantly below the discharge limit of 0.5 mg/L as

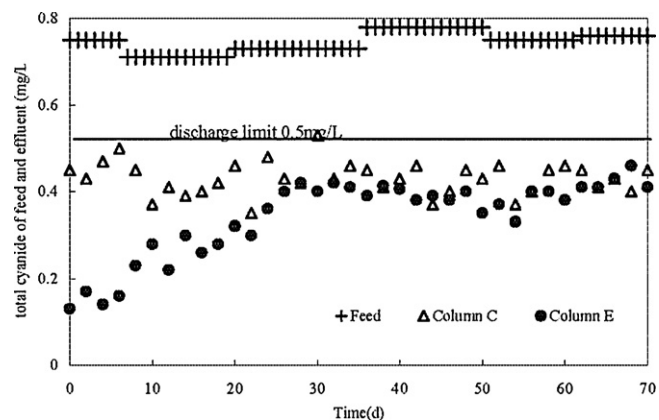


Fig. 12. Performance of the BAC treatment of the Fenton oxidized effluent sample total cyanide.

Table 5

Summary of the BAC treatment performance. Flow rate = 0.78 mL/min (EBCT = 40 min), run time = 70 day; Col. A–D were inoculated^a columns charged with presaturated carbons^b. Feed: H₂O₂ (40 mg/L) supplemented Fenton oxidized coking plant effluent, COD = 68 mg/L, UV₂₅₄ = 1.08, vis₃₈₀ = 0.217 abs, CN = 0.75 abs. Total amount fed: COD = 5480 mg, UV₂₅₄ = 87.3 abs L, vis₃₈₀ = 17.0 abs L, total CN = 60.5 mg.

No.	Carbon/weight (g)	Amount removed ^c COD/UV ₂₅₄ /vis ₃₈₀ /CN (mg or abs L)	Total capacity ^d COD/UV ₂₅₄ /vis ₃₈₀ /CN (mg or abs L)	Removal ^e COD/UV ₂₅₄ /vis ₃₈₀ /CN (%)	Capacity utilization ^f COD/UV ₂₅₄ /vis ₃₈₀ /CN (%)
A	Fruit, 14.1	2840/41.1/8.37/		51.9/47.0/49.2/-	
B	Coconut, 10.5	2860/43.6/8.01/		52.1/49.9/47.1/-	
C	Coal, 14.0	2780/42.4/8.37/25.7		50.7/48.4/49.2/42.5	
D	Spent coconut, 10.7	2780/40.8/8.24/		50.6/46.8/48.5/-	
E	New coal, 13.7	3370/61.6/11.3/41.0	9020/79.0/21.4/15.7 ^g	61.6/70.5/66.5/67.8	37.4/77.9/53.9/262

^a Presaturated by the Fenton oxidized effluent.

^b Inoculated with the acclimated culture.

^c Calculated from the BAC data (Figs. 9–12).

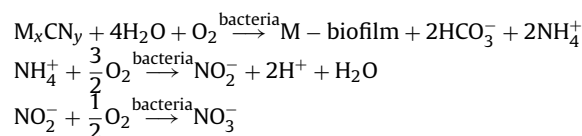
^d Adsorptive capacity (Table 2 and g) × carbon weight.

^e Amount removed/amount fed.

^f Amount removed/total capacity.

^g Capacity for CN in K₃Fe(CN)₆, X/M (mg/g) = 1.346C_f^{0.569} (R² = 0.949).

the result of biodegradation. The findings of cyanide biodegradation are consistent with the literature reports [25]; the following mechanism has been proposed [26]:



In actual treatment operations, both adsorption and biodegradation are active in the BAC adsorbers. The available adsorptive capacity of the BAC columns will ensure the desired degree of pollutant removal in the cases of shock loadings and occasional presence of more persistent organic compounds [27,28]. Although GAC's adsorptive capacity does not affect the long-term treatment performance of a BAC system, the higher capacity carbon is desirable in such occasions and also for removing persistent compounds that require a long time for acclimation [29].

4. Summary

Coagulation, flocculation and sedimentation and Fenton oxidation (Fenton) are both effective for removing organic constituents of the biotreated Shanghai coking plant effluent. In addition, Fenton and CFS + Fenton removed most of total cyanide present in the SCP effluent samples. After the CFS or Fenton, the residual organic constituents of the treated SCP effluent were more effectively removed by carbon adsorption. The combined Fenton and BAC treatment of the biotreated SCP effluent produced a high quality final effluent of <50 mg/L in COD_{Cr} and <0.5 mg/L in total cyanide during the 70-d study without no need for new activated carbon in the near future. Fenton oxidation followed by the BAC treatment is an attractive, cost effective process for treating the SCP coking plant effluent to produce a final effluent that can be recycled for many beneficial purposes while meeting more stringent discharge limits of the future.

Acknowledgements

A major part of this study was supported by the grant 2007AA06Z331 from the National High Technology Research and Development Program of China (863 Program). We are grateful to Mei-ling Li, Yuan Yu and Yin-mei Cheng of Shanghai Coking Co. for providing information on wastewater treatment plant and the effluent samples. You-liang Liu of Xingchang Activated Carbon Company for providing activated carbon samples. Li-jun Fu of our lab assisted in the experimental program of this study.

References

- W. Fu, Q. Wang, X. Xiang, Technologies for recycling industrial wastewaters, *Technol. Water Tr. (Chin.)* 30 (2004) 185–186.
- W. Ying, E. Dietz, G. Woehr, Adsorptive capacities of activated carbon for organic constituents of wastewaters, *Environ. Prog.* 9 (1990) 1–9.
- G. Franklin, H. Stensel, *Wastewater Engineering: Treatment and Reuse*, 4th ed., Metcalf & Eddy, 2004.
- C.P. Huang, C. Dong, Z. Tang, Advanced chemical oxidation: its present role and potential future in hazardous waste treatment, *Waste Manag.* 13 (1993) 361–377.
- A. Guedes, L. Madeira, R. Boaventura, C. Costa, Fenton oxidation of cork cooking wastewater—overall kinetic analysis, *Water Res.* 37 (2003) 3061–3069.
- M. Lapertot, C. Pulgarín, P. Fernández-Ibáñez, M. Maldonado, L. Pérez-Estrada, I. Oller, W. Gernjak, S. Malato, Enhancing biodegradability of priority substances (pesticides) by solar photo-Fenton, *Water Res.* 40 (2006) 1086–1094.
- J.J. Pignatello, Dark and photoassisted iron(3+)-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide, *Environ. Sci. Technol.* 26 (1992) 944–951.
- W. Ying, J. Duffy, E. Tucker, Removal of humic acid and toxic organic compounds by iron precipitation, *Environ. Prog.* 7 (1998) 262–269.
- L. Clesceri, A.E. Greenberg, A.D. Eaton, *Standard Methods for the Examination of Water and Wastewater*, United Book Press, Inc., Baltimore, Maryland, 1998.
- L. Fu, B. Li, W. Jiang, Z. Lin, W. Ying, Efficient and cost effective methods for measuring COD of water samples, *Environ. Pollut. Control (Chin.)* 30 (2008) 57–61.
- L. Fu, Optimization study of the coagulation/flocculation step of the integrated activated carbon adsorption process for advanced treatment of coking plant wastewater, MS Thesis, East China University of Science and Technology, Shanghai, PR China, 2008.
- W. Ying, W. Zhang, Q. Chang, W. Jiang, G. Li, Improved methods for carbon adsorption studies for water and wastewater treatment, *Environ. Prog.* 25 (2006) 110–120.
- H. Gallard, J. Laat, B. Legube, Effect of pH on the oxidation rate of organic compounds by Fe-III/H₂O₂, mechanisms and simulation, *New J. Chem.* 22 (1998) 263–268.
- C. Walling, Fenton's reagent revisited, *Acc. Chem. Res.* 8 (1975) 125–131.
- P. Wang, W. Lau, H. Fang, D. Zhou, Landfill leachate treatment with combined UASB and Fenton coagulation, *J. Environ. Sci. Health* 35 (2000) 1981–1988.
- Y. Kang, K. Hwang, Effects of reaction conditions on the oxidation efficiency in the Fenton process, *Water Res.* 34 (2000) 2786–2790.
- Y. Deng, J.D. Englehardt, Treatment of landfill leachate by the Fenton process, *Water Res.* 40 (2006) 3683–3694.
- J. Sun, S. Sun, M. Fan, H. Guo, L. Qiao, R. Sun, A kinetic study on the degradation of p-nitroaniline by Fenton oxidation process, *J. Hazard. Mater.* 148 (2007) 172–177.
- T. Mudder, *The Cyanide Guide (Mining Environmental Management, Special Issue)*, The Mining Journal, London, England, 2001, p. 45.
- H. Hidaka, T. Nakamura, A. Ishizaka, M. Tsuchiya, J. Zhao, Heterogeneous photocatalytic degradation of cyanide on TiO₂ surfaces, *J. Photochem. Photobiol. A* 66 (1992) 367–374.
- W. Jiang, W. Zhang, Q. Chang, H. Zhang, L. Fu, W. Ying, M. Li, Y. Yu, Enhanced activated carbon adsorption process for advanced treatment of biotreated coking plant wastewater, *Environ. Pollut. Control (Chin.)* 29 (2007) 265–270.
- W. Zhang, Q. Chang, W. Liu, B. Li, W. Jiang, L. Fu, W. Ying, Selecting activated carbon for water and wastewater treatability studies, *Environ. Prog.* 26 (2007) 289–298.
- Y.B. Patil, K.M. Paknikar, Removal and recovery of metal cyanides using a combination of biosorption and biodegradation processes, *Biotechnol. Lett.* 21 (1999) 913–919.
- D.W. McLeod, C. Lin, W. Ying, Biological activated carbon process for removing sulfonate from groundwater, in: *Proceeding of 46th Industrial Waste Conference*, Purdue University, Indiana, 1991.

- [25] A. Akcil, A.G. Karahan, H. Ciftci, O. Sagdic, Biological treatment of cyanide by natural isolated bacteria (*Pseudomonas* sp.), *Miner. Eng.* 16 (2003) 643–649.
- [26] J. Whitlock, T. Mudder, The Homestake wastewater treatment process. Part I: design and startup of a full scale facility, in: T.I. Mudder, M. Botz (Eds.), *The Cyanide Monograph*, second ed., Mining Journal Books Limited, London, England, UK, 1998.
- [27] W. Ying, W. Weber, Bio-physicochemical adsorption system models for wastewater treatment, *J. Water Pollut. Control Federation* 51 (1997) 2661–2667.
- [28] W. Zhang, Biological activated carbon process for removing BTEX and MTBE from groundwater, PhD Dissertation, East China University of Science and Technology, Shanghai, PR China, 2008.
- [29] W. Jiang, Enhanced activated carbon adsorption process for advanced treatment of coking plant effluent, PhD Dissertation, East China University of Science and Technology, Shanghai, PR China, 2008.