



Enhanced carbon adsorption treatment for removing cyanide from coking plant effluent

Wei Zhang, Wandong Liu, Yan Lv, Bingjing Li, Weichi Ying*

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

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ABSTRACT

Batch experiments were conducted to determine the effects of metal loading and fixing methods on the capacity of granular activated carbon (GAC) for removing cyanide from KCN (pH 11), $K_3Fe(CN)_6$ solutions and several SCP effluent samples. KI fixed carbon (Cu/KI-GAC) was the most effective among the GAC samples tested. Adsorption was the primary mechanism of cyanide removal; catalytic oxidation of the adsorbed cyanide on carbon surface contributed a minor amount of the observed removal. Four small adsorbers containing the base GAC and 0–100% of Cu/KI-GAC were employed for treating a Fenton oxidized/precipitated SCP effluent sample. After the start-up period (<3-week) to establish the effective biological activated carbon (BAC) function in the adsorbers, the effluents became stable and met the discharge limits ($COD_{Cr} < 50$ mg/L and $TCN < 0.5$ mg/L); with >30% Cu/KI-GAC in the adsorber, the effluent would meet the discharge limits during the start-up phase.

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1. Introduction

In China today, most existing chemical industry wastewater treatment plants are hard pressed to meet increasingly more stringent effluent discharge limits. There are also urgent needs 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 for reuse. Shanghai Coking Plant (SCP) is one of the largest chemical plants in the city with capacities to produce 3.2 million m^3/a of manufactured gas, 1.9 million ton/a of coke, 350,000 ton/a of methanol and more than 100 additional products. About 7000 m^3/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. The SCP biotreated effluent does not meet the existing discharge limits for residual organic constituents and total cyanide ($COD_{Cr} < 50$ mg/L and $TCN < 0.5$ mg/L) [1]. Cost effective post treatment of the SCP effluent is desired to produce a final effluent that may be directly discharged and/or recycled for many reuse functions.

Alkaline chlorination, ozonization, and wet-air oxidation are chemical oxidation methods effective for treating cyanide containing wastewater [2,3]. The high degree of chlorination required to meet the effluent objectives needs excessive doses of caustic and chlorine or sodium hypochlorite [4] which, in addition to the need

for neutralization, would create a safety concern due to the large amounts of residual chemicals and by products [5]. Ozonization is expensive because it is not selective, while wet-air oxidation is only a viable alternative for small-scale applications because of the high temperature and pressure requirements. Other reported treatment methods, such as Caro's acid, copper-catalyzed hydrogen peroxide, electrolytic oxidation, ion exchange, acidification, AVR (acidification, volatilization, and re-neutralization) process, lime-sulfur, reverse osmosis, thermal hydrolysis, and INCO process (by SO_2/air) [2,3,6,7] are either too costly or unable to produce an effluent that would meet the discharge limits on both cyanide and organic.

Depending on the influent composition and season of the year, the SCP effluent contains variable concentrations COD_{Cr} (100–200 mg/L) and TCN (2–7 mg/L), which are all complex cyanides since any free cyanide would have been stripped by aeration (pK_a of $HCN = 9.3$). Granular activated carbon (GAC) adsorption has been employed for removing both free and complex cyanides present in many industrial wastewaters and that its adsorptive capacities for $Cu(CN)_4^{2-}$ was much greater than for CN^- [8,9]. Activated carbon functioned both as an adsorbent and as a carrier of catalyst for cyanide oxidation [10–13]. In the presence of dissolved oxygen (DO), the adsorbed cyanide may be oxidized to CNO^- (Eq. (1)) which was hydrolyzed to NH_4^+ (Eq. (2)); further oxidation of CNO^- to form N_2 (Eq. (3)) is not expected since about the same total nitrogen concentrations were found in a SCP effluent before and after the copper/sulfite catalyzed oxidation treatment [14]:



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

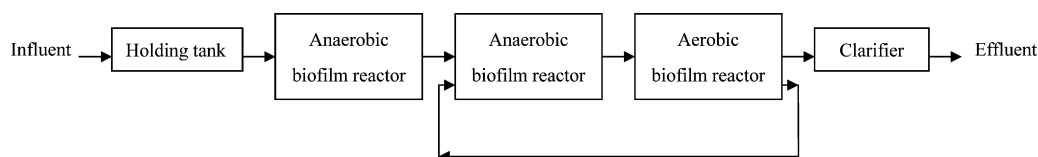
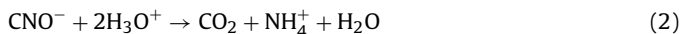


Fig. 1. Flow diagram of SCP wastewater treatment plant.



Fenton oxidation (Fe^{2+} catalyzed oxidation by H_2O_2) is effective for breaking up large organic molecules and complex cyanides of the SCP effluent [15–17] making it possible for their long-term removal in GAC adsorbers which in effect function as biological activated carbon (BAC) systems, capable of removing both residual organic (COD and UV_{254}) and TCN, in the SCP effluent [18]. Recently, Dash et al. have found the BAC process is more effective than adsorption and biodegradation alone for removing iron cyanide in batch reactors [19].

Loading a transitional metal, such as copper and silver, on the GAC has improved its adsorptive for cyanide due to chemisorption resulting from the interaction between complex ions and the surface groups of GAC and the catalytic oxidation of cyanide by adsorbed oxygen with metal compounds adsorbed on carbon surface as the catalyst [20–22]. To further improve the capacity of Fenton-BAC system in removing TCN, metal impregnation (loading) of GAC is investigated in this study.

The objectives of this study were to: (1) compare the cyanide removal effectiveness of a coal base activated carbon relative to several metal loaded carbons, (2) identify the best metal fixing method, (3) determine the effects of contact time and dissolved oxygen (DO) on the observed cyanide removal capacities of the batch treatment experiments, (4) validate the micro column rapid breakthrough (MCRB) method for simulating the breakthrough curve of a small carbon adsorber employed for removing TCN from $\text{K}_3\text{Fe}(\text{CN})_6$ solution and effluent samples, (5) demonstrate that the Fenton oxidation/precipitation enhanced carbon adsorption treatment of SCP effluent will produce a high quality effluent that may be directly discharged and/or recycled for beneficial reuses, and (6) illustrate that using some metal impregnated GAC will ensure the adsorber effluent will ensure meeting the effluent discharge limits during the start-up phase of the BAC system for long-term treatment of the SCP effluent.

2. Materials and methods

2.1. Materials, instruments and equipment

Since $\text{K}_3\text{Fe}(\text{CN})_6$ is likely the major TCN constituent of a coking plant effluent [23], it was employed to prepare the test solutions and also to maintain a desired TCN concentration of the SCP effluent in the long-term treatment runs. Several batches of SCP effluent samples (pH 6–7, $\text{COD}_{\text{Cr}} = 100\text{--}150\text{ mg/L}$, $\text{TCN} = 1.0\text{--}6.5\text{ mg/L}$) were brought in from the plant during the study period and employed as the feed to the carbon adsorbers after pretreatment by coagulation/flocculation using polymeric ferric sulfate ($\text{Fe}^{3+} = 58\text{ mg/L}$ at pH 7.0 maintained by NaOH) or Fenton oxidation/precipitation using hydrogen peroxide, FeSO_4 and NaOH solutions (oxidation: $\text{Fe}^{2+} = 56\text{ mg/L}$, $\text{H}_2\text{O}_2 = 27.2\text{ mg/L}$, followed by neutralization with NaOH to pH 7.0).

Cyanide removal effectiveness of 11 different activated carbons was compared in the batch treatment runs. The activated carbon samples included base coal activated carbon (Coal) and 10 metal loaded activated carbons of which 7 were prepared in the lab: Ag-

GAC-1 (1.62% Ag), Ni-GAC (0.89% Ni), Fe-GAC (0.84% Fe), Cu-GAC-1 (0.96% Cu) and 3 Cu loaded and fixed carbon: Cu/ NaHCO_3 -GAC, Cu/ Na_2CO_3 -GAC, Cu/KI-GAC-1, and 3 others provided by Shanghai Activated Carbon Co.: Ag-GAC (0.1% Ag), Cu-GAC (3.1% Cu) and Cu/KI-GAC (3.1% Cu and fixed by KI). The home made metal loaded carbons were prepared by mixing a fixed amount of Coal with an aliquot of metal sulfate/nitrate solution enough to cover the carbon and then drying the mixture in an oven (at $105\text{ }^\circ\text{C}$) to remove the water. Cu/KI-GAC was prepared by mixing Cu-GAC with KI solution and then dried; NaHCO_3 and Na_2CO_3 solutions were employed in place of KI for preparing the other two Cu fixed carbons. All carbon samples were crushed using a coffee grinder, sieved for the proper size fractions, washed, dried and stored before the test.

Temperature programmed reduction (TPR) runs to obtain the intensity profile were performed by an external service group employing AutoChem II TPR instrument (Micromeritics). Unico UV2000 UV-vis Spectrophotometer (Unico Shanghai Instrument), DO probe/meter (Shanghai Precision & Scientific Instrument), auto sampler (modified BSZ-160, Shanghai Huxi Analytical Instrument), coffee grinder (4041/KSM2, Braun Co. USA). The rotating shaft and drum employed for the isotherm experiments and the carbon columns for the breakthrough experiments were home made for previous adsorption treatability studies [24,25].

2.2. Analytical methods

The standard methods [26] were employed for measurements of COD_{Cr} (the modified Hach COD_{Cr} Method [27]), total cyanide (the isonicotinic acid-pyrazolone colorimetric methods [28–32]) and H_2O_2 (the KMnO_4 method). The DO probe/meter was calibrated each time before the DO measurements.

2.3. Batch experiments of cyanide removal

Five series of batch experiments were conducted to determine the effects of metal loading, the metal fixing method, contact time and DO on the removal of free and complex cyanides by adsorption and/or catalytic oxidation on carbon surface. A series of 640-mL glass bottles were filled with 20–100 mg of pulverized (45–75 μm) carbon and the cyanide containing sample; the bottles were then capped with no headspace and mixed in a rotating drum for 1–6 h. The amount of cyanide removed was calculated for each test sample: $X/M\text{ (mg/g)} = (C_0 - C_f) \times V/m$, where C_0 : the initial cyanide concentration (mg/L), C_f : the residual cyanide concentration (mg/L), V : sample volume (0.04 L), and m : carbon weight (g). The pairs of X/M & C_f were correlated by the Freundlich adsorption isotherm model: $X/M = kC_f^{1/n}$. The experimental data and the model best-fit straight lines were plotted as the isotherms in log–log scale [24,33].

2.4. Continuous flow carbon column breakthrough experiments

Three series of continuous flow carbon column breakthrough experiments were conducted for removing TCN from $\text{K}_3\text{Fe}(\text{CN})_6$ solution, coagulated/precipitated SCP effluent, and Fenton oxidized/precipitated SCP effluent samples. The breakthrough experiments employing both the conventional method (using

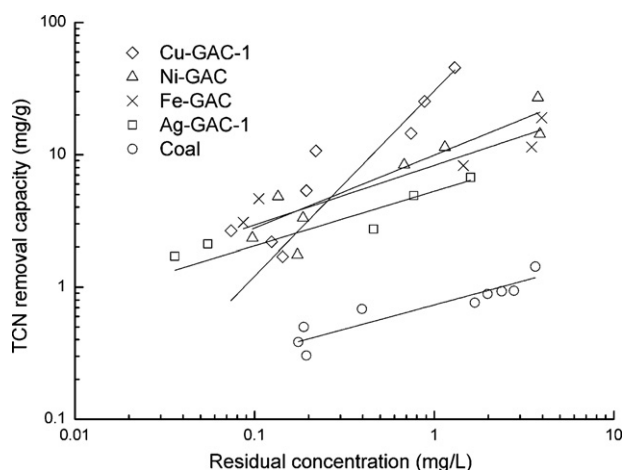


Fig. 2. Effect of metal loading on TCN removal.

10–13 g of un-sieved carbon) and the efficient MCRB (0.5 g of 80–120 μm carbon) to verify the TCN removal capacities of Coal and Cu/KI-GAC, to confirm the effectiveness of the MCRB technique, and to obtain long-term treatment performance of the small Coal column in removing TCN from the SCP effluent. The MCRB method is described in earlier papers [24,25].

3. Results and discussion

3.1. Batch experiments of cyanide removal

3.1.1. Effects of metal loading and fixing method on TCN removal

Fig. 2 presents the 1-h TCN removal capacities of 5 carbons (Coal, Ag-GAC-1, Cu-GAC-1, Ni-GAC and Fe-GAC); the data clearly show that metal loading significantly enhanced the TCN removal capacity of the base carbon, consistent with literature reports [10,20,21,34] and that, considering the % loading and cost of metal, copper was the best metal of the four studied. Fig. 3 presents the same comparative removal capacities of 6 Cu loaded carbons with and without chemical fixing; the data have demonstrated that fixing loaded Cu on the carbon enhanced its TCN removal capacity and that KI was the best fixing chemical, as CuI was less water soluble than CuCO_3 and $\text{Cu}(\text{HCO}_3)_2$ [35,36]. Similar batch runs were performed on KCN solutions; the results show the GACs' removal capacities for free cyanide were much less than those for $\text{K}_3\text{Fe}(\text{CN})_6$ based TCN.

The TPR intensity profiles (Fig. 4) show a peak at 288 $^\circ\text{C}$ for the Cu-GAC sample and a delayed peak at 510 $^\circ\text{C}$ for the Cu/KI-GAC sam-

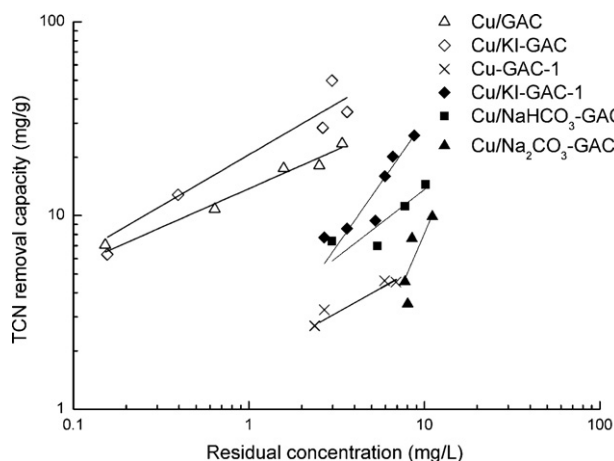


Fig. 3. Effect of Cu fixing on TCN removal.

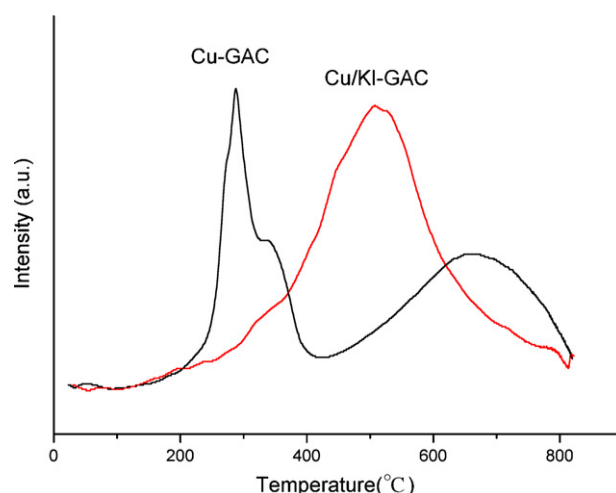


Fig. 4. TPR intensity profiles of the two copper impregnated GAC samples.

ple; such a shift suggests that the KI fixing treatment enhanced the interaction of CuO and GAC, making the loaded copper more difficult to be reduced in the TPR procedure which might have been the reason for the higher TCN removal capacity of Cu/KI-GAC, relative to Cu-GAC, because its loaded copper is more tightly bound and thus less likely to be removed from GAC. Higher copper loading of Cu-GAC and Cu/KI-GAC and more effective loading/fixing procedures employed in the preparation of the commercial copper loaded carbon (Cu-GAC and Cu/KI-GAC) were the reasons for their higher TCN removal capacities relative to those of the home made Cu loaded carbons.

3.1.2. Effects of contact time and DO on cyanide removal

Fig. 5 illustrates the effects of contact time (1 and 5 h) and DO (2 and 7 mg/L) on TCN removal capacities of Coal and Cu/KI-GAC from a SCP effluent. The higher removal capacities observed with a longer contact time and a higher DO were the result of catalytic oxidation of adsorbed cyanide on carbon surface. The catalytic oxidation was not strongly dependent on cyanide concentration and that its contribution to the total observed cyanide removal was not as noticeable for Cu/KI-GAC due to its much higher TCN removal capacity relative to Coal. Such results have suggested that adsorption of cyanide species is fast and that the observed 1-h removal capacity of a carbon may be considered as its adsorptive capacity for cyanide.

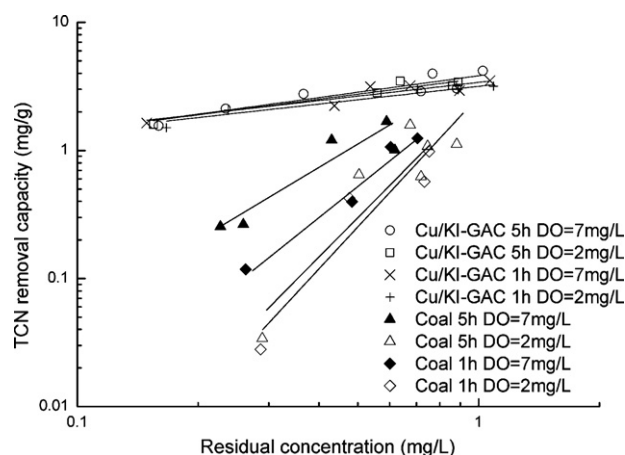


Fig. 5. Effects of contact time and DO on TCN removal.

Table 1
Summary of breakthrough runs for treating $K_3Fe(CN)_6$ solution and coagulated SCP effluent (Feed: Col. a–b: $K_3Fe(CN)_6$ solution, Col. c–f: coagulated effluent; pH 6.5, DO = 7 mg/L).

Carbon/column (Fig. 7)	Flow rate (mL/min)	Carbon charged (g)	EBCT (s)	Feed TCN (mg/L)	Contact (run) time (h)	Batch removal capacity (mg/g) ^a	TCN removed (mg/g) ^b	Removal ratio (%) ^c
Coal (a) ^d	3.1	0.51	17	2.5	15	2.3	2.5	109
Coal (b) ^e	1.0	10.3	1530	2.1	551	2.0	3.2	160
Coal (c) ^d	3.1	0.51	17	1.9	9	2.4	2.5	104
Coal (d) ^e	0.9	10.2	1668	1.9	254	2.4	1.6	67
Cu/KI-GAC (e) ^d	3.3	0.50	15	1.9	9	5.8	3.8	66
Cu/KI-GAC (f) ^e	0.9	11.7	1608	1.9	383	5.8	3.2	55

^a 1-h removal capacity at the feed concentration from Figs. 5 and 6.

^b Cumulative TCN removal at the end.

^c b/a.

^d MCRB runs.

^e Small column conventional breakthrough runs.

Fig. 6 presents the adsorptive capacities of 4 carbons for TCN in $K_3Fe(CN)_6$ solution, showing the expected order of Cu/KI-GAC > Cu-GAC > Ag-GAC > Coal. The observed cyanide removal capacities were dependent on factors that affect adsorption and catalytic oxidation, such as carbon type, cyanide form/source (free and total cyanides of a solution and effluent), contact time and DO.

3.2. Breakthrough experiments

Fig. 7 presents TCN breakthrough curves of 6 columns employing both the conventional method (b, d and f) and the MCRB method (a, c and e); Col. a and Col. b were fed by $K_3Fe(CN)_6$ solutions while other columns were fed by the coagulated/precipitated SCP effluents. Table 1 summarizes the performance data of those columns. The results demonstrate that Cu/KI-GAC had a much larger TCN removal capacity than Coal and that catalytic oxidation of adsorbed TCN on Coal resulted in >100% removal ratio of Col. a and Col. b where the longer contact time enhanced removal even more [21]. The MCRB curves of Col. c and Col. e are similar to the corresponding small conventional columns (Col. d and Col. f) in the common ranges of bed volumes treated; such results have validated using the MCRB method to obtain a full breakthrough curve in a small fraction of time that would be necessary for the conventional method using a small carbon column.

The third series of breakthrough experiments involved the long-term treatment of a SCP effluent sample containing higher than usual TCN (6.5 mg/L). To ensure the GAC treatment would produce a dischargeable final effluent, the SCP effluent was first pretreated by Fenton oxidation/precipitation to produce the feed

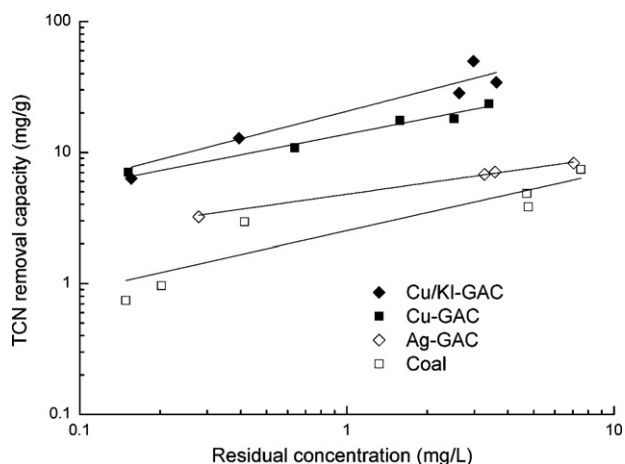


Fig. 6. Effect of Cu fixing on TCN removal.

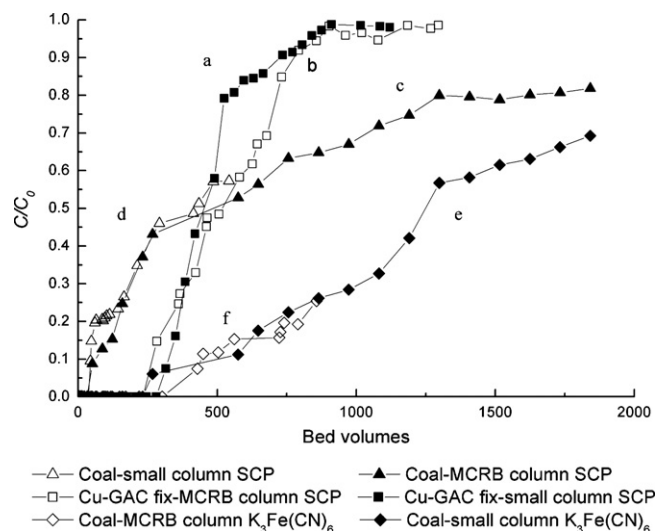


Fig. 7. Breakthrough curves for GAC adsorbers.

($COD_{Cr} < 80$ mg/L and TCN < 3.5 mg/L) to the four small conventional adsorbers filled with the base coal and varying account of Cu/KI-GAC (0%, 10%, 30%, and 100% in Col. g, h, i, and j, respectively). Fig. 8 presents their TCN breakthrough curves and that Fig. 9 shows their COD removal performance of the last 4 days of the 57-day study.

TCN concentration of the Col. g–i effluent samples increased quickly, exceeding the discharge limit (0.5 mg/L) in 2–5 days. While

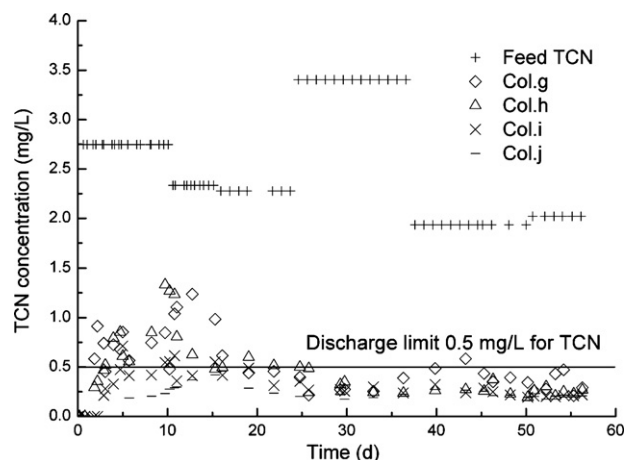


Fig. 8. Performance of the Fenton-BAC treatment of the SCP effluent TCN removal.

Table 2

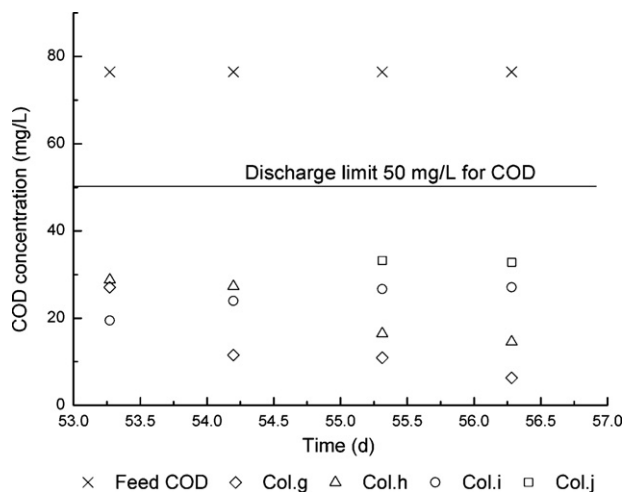
Summary of 57-day breakthrough runs for Fenton pretreated SCP effluent samples (Feed pH 6.5, DO = 7 mg/L).

Carbon/column (Fig. 8)	Flow rate (mL/min)	Carbon charged (g)	EBCT (min)	Batch removal capacity (mg/g) ^a	TCN removed (mg/g) ^b	Removal ratio (%) ^c
100%Coal (g)	0.94	10.0	26	3.9	14.0	359
10%Cu/KI-GAC	1.00	10.2	25	4.1	15.7	383
+90%Coal (h)	0.92	10.2	26	4.6	15.3	333
30%Cu/KI-GAC	0.92	10.2	26	4.6	15.3	333
+70%Coal (i)	0.98	10.1	22	6.1	17.1	280
100%Cu/KI-GAC (j)	0.98	10.1	22	6.1	17.1	280

^a 1-h removal capacity at the feed concentration from Fig. 5.^b Cumulative TCN removal at the end.^c b/a.

TCN of Col. j, the column with all Cu/KI-GAC, effluent samples were well below <0.5 mg/L during the entire 57-day study. After 10 days, the TCN concentrations of Col. g–i effluent samples began to decrease gradually and dropped below the discharge limit by the 20th day. After this start-up period (the first 3–4 weeks of the column runs), the treatment performance of all columns became stable; TCN of all effluent samples remained below 0.5 mg/L even when the feed concentration was increased to 3.5 mg/L (with less intensive Fenton pretreatment). Fig. 9 shows that Col. g–j were still effective for COD removal that COD of all effluent samples were below the discharge limit of 50 mg/L.

Table 2 summarizes the performance data of TCN removal in the four columns. The cumulative TCN removals in the four columns were 280–383% of their respective TCN adsorptive capacities, and furthermore, there was no sign of needing carbon replacement for any of them. The activated carbon columns exhibited such long-term TCN and COD removal capabilities because they became fully functional biological activated carbon (BAC) systems which resulted from the facts that organic and TCN constituents of the feed were made more biodegradable by the Fenton oxidation pretreatment and that the carbon columns were ideal for establishing highly acclimated biomass during the started up period [19,23,37–39]. The data of this study have demonstrated that partial filling of Cu/KI-GAC did not prevent the BAC function and that a sizable amount of it (>30% in this study) would ensure the final effluent meeting the stringent TCN discharge limit at all times. These results suggest that Fenton oxidation pretreatment followed by the BAC treatment in the adsorber is a cost effective advanced treatment of the SCP effluent for direct discharge and/or reuse and that partial filling of the adsorber with Cu/KI-GAC will furthermore ensure meeting the effluent discharge limits during the start-up phase of the adsorber operation [23,37,39–41].

**Fig. 9.** Performance of the Fenton-BAC treatment of the SCP effluent: COD removal.

4. Conclusions

- Adsorption of cyanide on pulverized activated carbon (45–75 μm) was rapid; the removal in 1 h was a good estimate of its adsorptive capacity.
- Metal impregnation (loading) of activated carbon enhanced its capacity for cyanide; chemical fixing of the loaded carbon further enhanced the capacity. Both the loading and fixing method affected the capacity enhancement. Copper loaded and KI fixed coal-based activated carbon (Cu/KI-GAC) was the most cost effective of all carbons studied.
- The observed cyanide removal capacities were dependent on factors that affect adsorption and catalytic oxidation, such as carbon type, cyanide form/source (free and complex cyanide of the test sample), contact time and DO. The base activated carbon (Coal) and Cu/KI-GAC had greater capacities for TCN of $\text{K}_3\text{Fe}(\text{CN})_6$ solution and, to a less degree, SCP effluent than CN^- of the basic KCN solution.
- In the presence of dissolved oxygen ($\text{DO} > 3 \text{ mg/L}$), adsorbed cyanide was slowly oxidized on the surface of activated carbon. The effect of slow catalytic oxidation was more noticeable in the Coal adsorbers over a longer time period as evidenced by its higher batch removal capacity of longer contact times (Fig. 5) and >100% removal ratio observed in several breakthrough runs (Table 1). The enhanced removal due to catalytic oxidation was small for Cu/KI-GAC due to its much higher (>10 \times) adsorptive capacity.
- The breakthrough curves of the micro size MCRB and the small conventional carbon columns were nearly identical in the common range of bed volumes of feed ($\text{K}_3\text{Fe}(\text{CN})_6$ solution and the coagulated/precipitated SCP effluent) treated. Such results provided the basis for employing the efficient MCRB method to simulate the treatment performance of a full-scale carbon adsorber in a small fraction of time that would be required employing the conventional breakthrough method.
- With Fenton oxidation/precipitation to lower the feed concentration ($\text{COD}_{\text{Cr}} < 80 \text{ mg/L}$ and $\text{TCN} < 3.5 \text{ mg/L}$), the small adsorbers filled with the base coal carbon and 0–100% of Cu/KI-GAC produced a stable and high quality effluent ($\text{COD}_{\text{Cr}} < 50 \text{ mg/L}$ and $\text{TCN} < 0.5 \text{ mg/L}$) after the start-up period of about 3 weeks.
- The activated carbon columns exhibited stable long-term TCN and COD removal capabilities because they became fully functional biological activated carbon (BAC) systems which resulted from the facts that the organic and TCN constituents of the feed were made more biodegradable by the Fenton oxidation pretreatment and that the carbon columns were ideal for establishing highly acclimated biomass during the started up period.
- The Fenton oxidation/precipitation pretreatment followed by the BAC treatment in the activated carbon adsorber is a cost effective advanced treatment of the SCP effluent for direct discharge or reuse and that partial filling the adsorber with Cu/KI-GAC will furthermore ensure meeting the effluent

discharge limits during the start-up phase of the adsorber operation.

Additional studies to address such important issues as the potential Cu leaching and durability of the cyanide degradation bacteria in the adsorbers are necessary before conducting the pilot demonstration or full-scale application of the Fenton enhanced BAC process, with possible further enhancement of employing Cu/KI-GAC in the adsorber. Furthermore, economics analysis should be performed on this innovative integrated process relative to alternatives to ensure its cost effectiveness for the intended applications.

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