Effect of different carriers and operating parameters on degradation of flax wastewater by fluidized-bed Fenton process

Mengtian Chen, Hongqiang Ren, Lili Ding and Baotian Gao

ABSTRACT

This investigation evaluates the effectiveness of a fluidized-bed Fenton process in treating flax wastewater. Flax wastewater was taken from a paper-making factory in a secondary sedimentation tank effluent of a paper-making factory in Hebei. The performance of three carriers (SiO_2, Al_2O_3, Fe_2O_3) used in the reactor was compared, and the effects of different operational conditions, and Fenton reagent concentrations were studied. Experimental results indicated that SiO_2 was the most appropriate carrier in the system. The dose of Fe^{2+} and H_2O_2 was a significant operating factor in the degradation progress. The bed expansion was considered to be another factor influencing the treatment effect. Under the appropriate conditions (300 mg/L Fe^{2+}, 600 mg/L H_2O_2, and 74.07 g/L SiO_2 as the carrier, at pH = 3, 50% bed expansion), the highest removal rate of total organic carbon (TOC) and color was 89% and 94%, respectively. The article also discussed the process of the colority removal of flax wastewater and the kinetics of TOC removal.

Key words | carrier, color degradation, flax wastewater, fluidized-bed Fenton process

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INTRODUCTION

Flax wastewater, which originates from different products processing (cloth, banknote, etc.) in China, with high organic concentration, high salinity and other recalcitrant characteristics, exhibits various kinds of quality and quantity fluctuations, and leads to difficulties in treatment (Hermosilla *et al.* 2012; Salazar *et al.* 2013). The main pollutants in flax wastewater, lignin, which is a three-dimensional phenyl propanoid polymer mainly linked by ether bonds between monomeric phenylpropane units, most of which are not readily hydrolyzable (Bentivenga *et al.* 2003). After the biological treatment of flax wastewater, one interesting phenomenon was observed, that the color of effluent declined after anaerobic treatment, and increased obviously after aerobic treatment. It can be inferred that some new chromophoric or auxochrome group was generated in the biological treatment. The relatively higher colority of effluent compared to other wastewater requires effective advanced treatment.

In recent years, advanced oxidation processes (AOPs) have been used successfully to remove toxic and persistent pollutants (Mocchiutti *et al.* 2010; Liu *et al.* 2010). The Fenton process, as a common kind of AOPs, with hydrogen peroxide (H_2O_2) and ferrous ions (Fe^{2+}), generates hydroxyl radical (•OH) and converts various kinds of organic matter into CO_2 and other inorganic ions (Babuponnusami & Muthukumar 2014; Rahim Pouran *et al.* 2014).

A serious problem of the Fenton process is the production of a huge amount of ferric hydroxide ($Fe(OH)_3$) sludge which needs to be separated and further disposed of. Meanwhile, as a means of advanced treatment, the effect of the Fenton process will be limited by the secondary pollution of high salinity water. Therefore, the fluidized-bed Fenton process was developed to decrease the amount of sludge produced. The fluidized-bed Fenton process facilitates the crystallization or precipitation of the trivalent iron ions generated in Fenton reaction onto the surface of the carrier (Anotai *et al.* 2009; de Luna *et al.* 2013). The process is a combination of: (i) homogeneous chemical oxidation (H_2O_2/Fe^{2+}); (ii) heterogeneous chemical oxidation (H_2O_2/iron oxide); (iii) fluidized-bed crystallization, in which iron sludge precipitates on carrier surfaces; and (iv) reductive dissolution of FeOOH (Chou *et al.* 1999). The carriers in the fluidized-bed reactor can initiate iron precipitate through ferric crystallization on themselves. Besides, iron oxide coating on the supported carriers

doi: 10.2166/wst.2015.147

act as a heterogeneous catalyst of hydrogen peroxide to degrade the organic contaminants, reducing the ferric dosing and the sludge generation. Meanwhile, a fluidized-bed reaction system solved the problem of contact of the catalyst with the solution to improve the efficiency of catalytic oxidation (Anotai *et al.* 2012).

As an important factor in the Fenton-fluidized-bed reactor (FBR) system, many kinds of carriers have been reported that are used in Fenton reaction, for example, inorganic oxide particles, iron or other metal compounds, carbon nano-particles, etc. Huang & Huang (2008) compared four kinds of carriers used in fluidized-bed reactors, including three kinds of immobilized iron oxides on silica matrix and the commercial catalyst FeOOH, and studied the effects of the carriers during the degradation progress of phenol. Chou *et al.* (2001) used supported γ-FeOOH in a circulating fluidized-bed reactor to oxidize benzoic acid and focused on the operating factors affecting the oxidation process. Pukdee-Asa *et al.* (2012) reported the degradation of azo-dye by FBR-Fenton process with alumina (Al_2O_3) and silica oxide (SiO_2) and compared the removal performance with these two different carriers. FBR-Fenton process has been applied into the treatment of effluent such as dyeing wastewater, benzene class wastes and many kinds of simulation wastewater (Muangthai *et al.* 2010; Anotai *et al.* 2011). However, advanced treatment of effluent of paper-making wastewater at low concentration (flax wastewater, for example) with FBR-Fenton was barely reported, and most reports with paper-making wastewater were focused on the pretreatment by traditional Fenton reaction (Bentivenga *et al.* 2003; Torrades *et al.* 2011).

This study used the fluidized-bed Fenton process (Fe^{2+}/H_2O_2/carrier) to treat flax wastewater. Experiments were performed to establish the optimal conditions for the treatment of the lignin in an aqueous medium. Color, mineralization rates, iron concentration and other indicators were used to evaluate the treatment effect. Conversely, the effects of carriers were investigated using silica oxide (SiO_2)/alumina (Al_2O_3)/iron oxide (Fe_2O_3)/covered silica oxide as supports. Bed expansion was studied as another influencing operation factor of the system.

MATERIALS AND METHODS

Source of wastewater

The flax wastewater was taken from a paper-making factory which was used for banknote production. Samples were collected in the secondary sedimentation tank effluent after A/O treatment. Raw water quality analysis is shown in Table 1.

Table 1 | Conventional indicators of water quality

CODcr (mg/L)	TOC (mg/L)	pH	Color
800 ± 10	350 ± 5	8.0 ± 0.2	256 ± 5

Fenton reactor

A 1.0 L FBR, as shown in Figure 1, was utilized in all experiments. The FBR is a cylindrical vessel (5.20 cm $\phi \times 50$ cm) consisting of an outlet, inlet and recirculation sections. H_2O_2 and $FeSO_4$ were fed continuously into the bottom of reactor. Carriers were fluidized by adjusting internal circulation at 50% bed expansion. Batch recirculation mode was used in this study. All experiments were conducted at room temperature.

Carriers

Table 2 shows the physical and chemical properties of three carriers used in the reactor. Three kinds of carriers used in the experiments were achieved from Yuanheng water

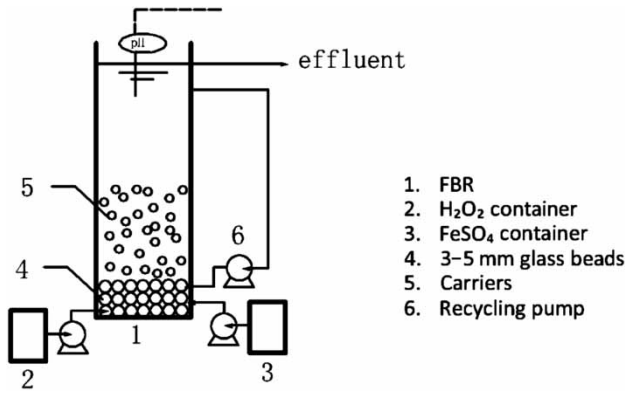

Figure 1 | The schematic diagram of a FBR.

Table 2 | Physico-chemical properties of the a carriers

Sample ID	Apparent density (g/cm³)	Specific surface area (m²/g)	Specific intruded volume (mL/g)	Total porosity (%)
Al_2O_3	3.734	0.067	0.009	3.41
SiO_2	2.541	0.155	0.0225	5.41
Fe_2O_3	2.694	0.165	0.0391	9.52

purification material plant in Gongyi City. Hydrogen peroxide (H_2O_2, 30%, w/w), ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$) were provided by Nanjing Chemical Reagents Co., Ltd (Nanjing, China), which were reagent grade and used without further purification.

Experiment design

In this investigation, carriers (74.07 g/L) were first added to the FBR (Figure 1), then flax wastewater was pumped into the FBR. The pump was turned on to suspend the carriers and mix the solution. The solution pH was adjusted to 3.0 ± 0.2 by adding H_2SO_4 or NaOH. After the pH reading stabilized, the ferrous (Fe^{2+}) solution was added. The reaction began when H_2O_2 solution was added. Samples extracted at selected intervals were immediately sampled into tubes containing NaOH solution to stop the reaction. Thereafter, solutions were filtered through 0.45 μm syringe micro-filters (Su *et al.* 2013).

The total organic carbon (TOC) concentrations in a sample were detected by TOC 5000A analyzer (Shimadzu Corporation, Japan). Total iron concentrations were determined using atomic absorption spectrometer (thermo, ice 3,500) after passing through the 0.45-μm filter membrane and acidified to pH <2 by nitric acid. Colority was determined by dilution and colorimetric methods.

RESULTS AND DISCUSSION

Effect of different carriers and dosage of Fe^{2+}

In Figure 2, different carriers ($SiO_2/Al_2O_3/Fe_2O_3$) were investigated on the efficiency of discoloration, mineralization of flax wastewater under different concentrations of Fe^{2+}, and iron ion concentration in effluent was also detected. The systems containing each carrier were kept under 600 mg/L H_2O_2 at pH = 3. Both the TOC and color had a steep decrease in the first 10 minutes and continued to lessen in the next 90 minutes. This was consistent with the 'two-stage' theory that had been reported in other literature (Anotai *et al.* 2011). The degradation rate increased as Fe^{2+} concentration increased obviously from 200 to 300 mg/L. However, when Fe^{2+} concentration continued to grow to 400 mg/L, the TOC and color removal rate did not change too much for Fe^{2+} starting to compete •OH with organic pollutions (Cao *et al.* 2014).

Meanwhile, the efficiency of discoloration and mineralization in Al_2O_3 system was less than that of other two systems. The specific surface area, specific intruded volume and total porosity of Al_2O_3 were the smallest among the three carriers (Table 2), therefore, organic particles were less likely to be adsorbed onto it. This could affect the degradation of flax wastewater in fluidized-bed system. The differences between the SiO_2 and Fe_2O_3 were not significant for the TOC and color degradation progress, however, the degradation rate in Fe_2O_3 system was slightly faster when Fe^{2+} concentration was at a low level, because of the dissolution of a small amount of iron ion from the carrier surface during the reaction. At the end of the reaction, the highest efficiency of discoloration and mineralization of flax wastewater in SiO_2 and Fe_2O_3 system was above 89% while in Al_2O_3 system it was around 75–85%.

Table 3 shows the total iron ion concentration in the effluent after being neutralized to $pH = 8 \pm 0.1$ and precipitated for half an hour. The salinity of the effluent after the fluidized-bed process had decreased by 80–90% compared to the homogeneous phase. The iron ion concentration was even lower when Fe^{2+} concentration was at 300 mg/L. This is because the neutralization after Fenton reaction functioned as a coagulation and sedimentation process, and Fe^{2+} with 300 mg/L is a better reagent dosage for coagulation, while 400 mg/L led to an elevation of iron concentration although it also brought a satisfactory coagulation effect. Conversely, the iron ion concentration in SiO_2 system was a bit lower than that in Fe_2O_3 due to the iron dissolution from the surface of Fe_2O_3. Considering the above along with the costs of carriers, the SiO_2 carrier was utilized to explore the degradation of flax wastewater under various experimental conditions in the fluidized-bed Fenton process.

Effect of H_2O_2 dosage

Figure 3 shows the effect of the H_2O_2 concentration on the removal efficiencies of color and TOC for flax wastewater in SiO_2 fluidized-bed system. The reaction was carried out under 300 mg/L Fe^{2+} at pH = 3. There was an increase in TOC removal when the dose of H_2O_2 increased from 200 to 600 mg/L. However, when the dose increased to 800 mg/L, the removal rate of TOC met a decrease after 50 minutes, despite the relatively high removal rate in the first 50 minutes. This was because excessive hydrogen peroxide led to side effects and could cause the loss of oxidant. At the end of the reaction, the highest color removal reached 94% while TOC removal was 89% when H_2O_2 concentration was 600 mg/L compared to other dosages. The results of the effect under different dosages

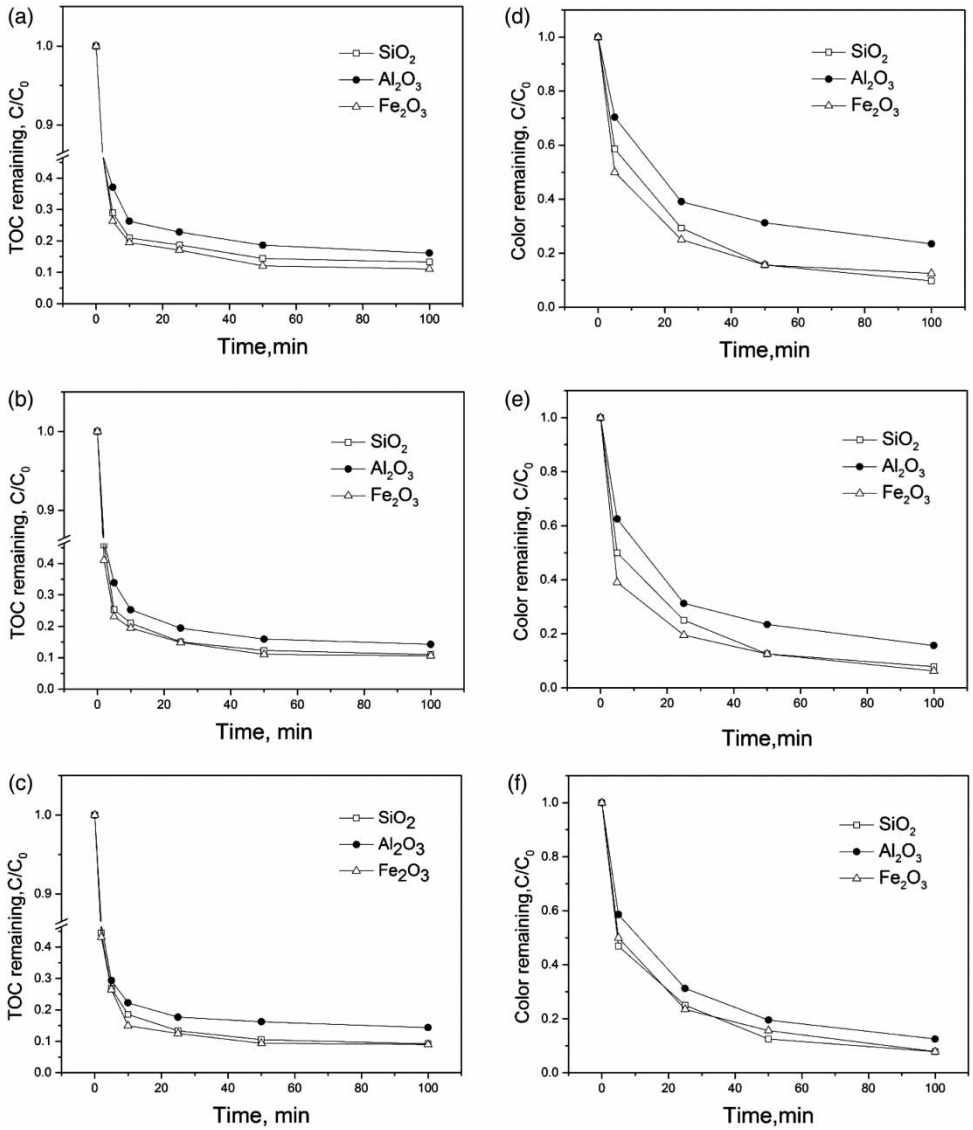

Figure 2 | Effect on mineralization of different carriers on different concentrations of Fe^{2+}: (a) 200 mg/L, (b) 300 mg/L, (c) 400 mg/L; and effect on discoloration of different carriers on different concentrations of Fe^{2+}: (d) 200 mg/L, (e) 300 mg/L, (f) 400 mg/L in fluidized-bed Fenton process (H_2O_2: 600 mg/L, carrier: 74.07 g/L, at pH = 3).

Table 3 | Iron concentration of the supernatant in aqueous environment (mg/L)

	Fe^{2+} concentration		
Carriers	**200 mg/L**	**300 mg/L**	**400 mg/L**
SiO_2	0.65 ± 0.04	0.32 ± 0.05	0.67 ± 0.09
Al_2O_3	0.70 ± 0.07	0.43 ± 0.01	0.75 ± 0.05
Fe_2O_3	0.62 ± 0.06	0.42 ± 0.07	0.71 ± 0.01

of Fe^{2+} could be achieved in the previous section. Analysis of the effect of reagent or ratio between reagents was established in the discussion of kinetics.

Effect of bed expansion of the fluidized-bed system

In this section, the effect on iron removal and discoloration with different bed expansion was investigated, besides, SiO_2 was repeatedly used in the fluidized-bed Fenton system for up to five cycles. Figure 4 shows the impact of crystallized iron that coated upon the surface of carrier on discoloration and mineralization. At the end of the first circle, the circulation pump was stopped and the solution was drained through the SiO_2 bed of the reactor via the bottom outlet. Then, the fresh flax wastewater was poured into the reactor and the Fe^{2+} and H_2O_2 were added chronologically to start the second cycle and so on. It was found that the number of

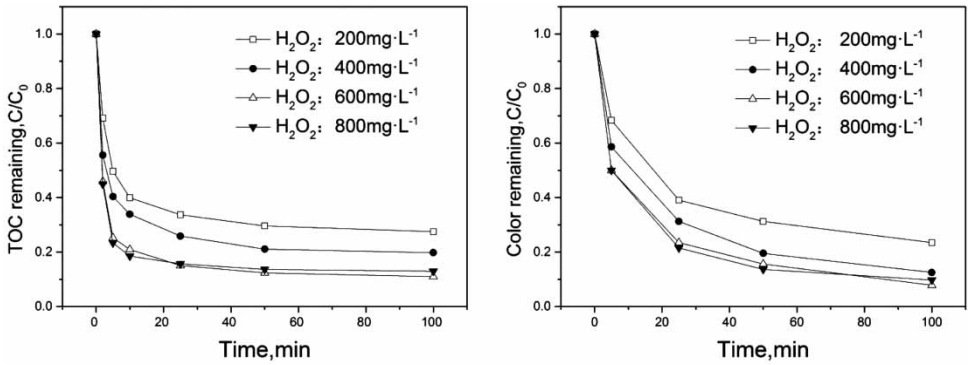

Figure 3 | Effect on discoloration and mineralization of carrier SiO_2 under different concentrations of H_2O_2 in fluidized-bed Fenton process (Fe^{2+}: 300 mg/L, SiO_2: 74.07 g/L, at pH = 3).

reuse cycles did not have substantial impact on TOC removal, similar to previous observations affirming that carriers played a secondary role on the mineralization. Meanwhile, in the 20% of bed expansion series, the discoloration was obviously lower than for the other two systems. Perhaps lower bed expansion could not prompt iron crystallization, which was reported in the literature (Chou *et al.* 2004). In the 100% of bed expansion series, the later 2 cycles showed a 2% decrease of color removal rate, as shown in Figure 4. The reason was that high bed expansion could lead to drastic friction between particles, which resulted in the desorption of color from carriers as the reaction went further.

KINETIC MODELING

Table 4 summarized kinetic modeling data for each test. The knowledge of oxidation kinetics is a key feature for accurate design of a wastewater treatment process. Available kinetic models for the Fenton process vary in complexity. Kinetic modeling has been applied in calculating the constant rate of TOC value by many researchers, which is considered deriving from the Langmuir–Hinshelwood equation (Inchaurrondo *et al.* 2012). Lin & Gurol (1998) described the heterogeneous catalytic reactions of H_2O_2 with several kinds of particles in aqueous solution, which followed the Langmuir–Hinshelwood mechanism. The intrinsic reactions on the oxide surfaces were expected to be the rate-limiting steps. The proposed kinetic model of H_2O_2 decomposition process was reduced to zero-order or first-order expressions in this paper. However, in the FBR system, second-order kinetics expression obtained on the basis of observations was validated by the kinetic model in many previous studies (Su *et al.* 2011). Anotai *et al.* (2009) reported the concentration of Fenton reagents and reaction conditions (such as pH) affected the kinetics expression. The mineralization of flax wastewater and discoloration rate were >80% under different Fe^{2+} concentrations (range from 200 to 400 mg/L) in all three carriers reaction system. The rate constants (k) of TOC removal for the flax wastewater under various Fe^{2+} concentrations with different kinds of carriers were calculated (Table 4). All reaction rate constants (k) of TOC values were calculated from the linear regression of

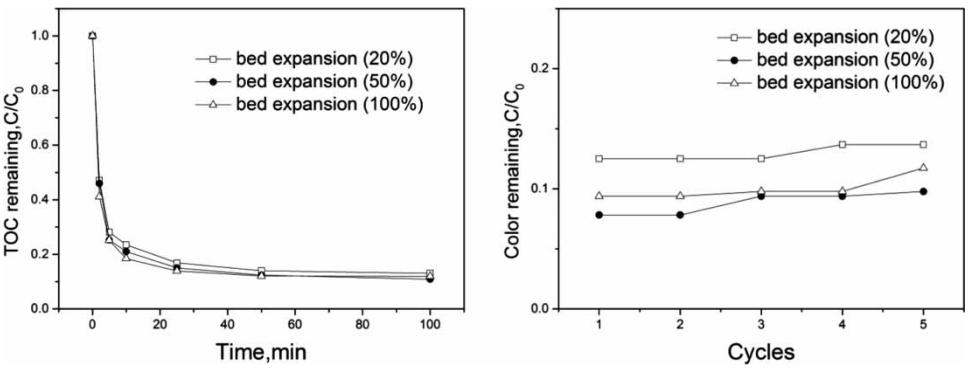

Figure 4 | Effect on mineralization and discoloration of carrier SiO_2 under different bed expansions in fluidized-bed Fenton process (Fe^{2+}: 300 mg/L, H_2O_2: 600 mg/L, SiO_2: 74.07 g/L, at pH = 3).

Table 4 | Pseudo second-order rate constants (k) of TOC removal, color and TOC removal efficiencies under various Fe^{2+} concentrations in three carrier systems

Carriers	Concentration (mg/L) $[Fe^{2+}]$	$[H_2O_2]$	$\frac{H_2O_2}{FE^{2+}}$	Second order K, $(mg \cdot L^{-1})^{-1} \cdot min^{-1}$	Color removal,%	TOC removal,%	R^2 of second order
SiO_2	200		8.1	18.43	90.2	86.7	0.929
	300	600	5.5	20.28	92.2	89.1	0.949
	400		4.0	20.78	92.2	90.9	0.968
Al_2O_3	200		8.1	15.62	76.6	83.9	0.886
	300	600	5.5	17.48	84.4	85.7	0.903
	400		4.0	18.72	87.5	85.6	0.911
Fe_2O_3	200		8.1	20.02	87.5	89.0	0.947
	300	600	5.5	22.03	93.8	89.4	0.948
	400		4.0	21.68	92.2	91.1	0.975
SiO_2		200	1.8	10.34	76.5	72.5	0.706
	300	400	3.6	14.00	87.5	80.2	0.812
		600	5.4	20.28	92.2	89.1	0.949
		800	7.2	21.01	90.1	87.0	0.933

the pseudo second-order kinetic model (R^2 of second order was shown in the table; R^2 of first order <0.90, not shown). The pseudo second-order reaction kinetic equation (period: 0–100 minutes) was as follows:

$$[1/C] = [1/C_0] + kt$$

where [C] and [C_0] are the TOC value at reaction time t and 0 minutes, respectively, and k is the rate constant. The rate constant (k) of TOC removal increased when the Fe^{2+} concentration increased and did not change too much when Fe^{2+} dosage exceeded 300 mg/L (Table 4); however, the rate constant (k) of TOC removal at various H_2O_2 concentrations decreased when H_2O_2 dosage was over 600 mg/L. Table 4 also suggested that rate constant decreased obviously when ratio of Fe^{2+} and H_2O_2 was over 5.5 in SiO_2 system. Therefore, the ratio of $[Fe^{2+}]$: $[H_2O_2]$ was another important operational factor of FBR.

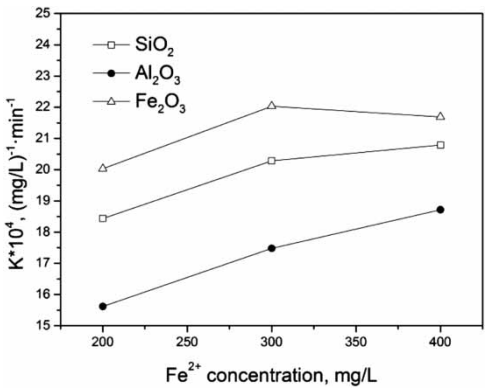

Figure 5 | Effect of carrier and Fe^{2+} concentration on pseudo second-order rate constants (k) under H_2O_2: 600 mg/L, carrier: 74.07 g/L, at pH = 3.

Another notable observation was the effect of different carriers on mineralization in the fluidized-bed Fenton system. Figure 5 suggested that the rate constant (k) of TOC removal was in the following order: $Fe_2O_3 > SiO_2 > Al_2O_3$. The removal efficiencies for color and TOC with the Al_2O_3 system were particularly lower than other two carriers because of its poor physico-chemical properties. The constant rate (k) of the Fe_2O_3 system had advantages over the other two carriers especially when Fe^{2+} concentration was low due to the iron dissolution.

Furthermore, the process of color removal was discussed and speculated. At the beginning of the reaction, the effect of •OH led to products deriving from a carbon–carbon bond cleavage. The cleavage of conjugated double bond might explain the color loss during the first several minutes and the products were further degraded as the reaction went on. The flax wastewater gradually formed phenolic compounds and double-bonded long chain compounds. Some auxochrome groups, for example, -OH/-SO_3H, etc., generated during the reaction as well, as Otto Witt's theory in 1876. These facts all contributes to the fluctuation of the colority. Compared with the degradation of some dyeing wastewater (Su *et al.* 2011), the degradation speed of color was slower than that of TOC. The color removal process was quite different from the cleavage of N = N bond (Pukdee-Asa *et al.* 2012) which was the key step of degradation of dyes. In contrast, some colority which was not available before might be brought about into the system during the lignin degradation.

At the end of the reaction, removal rate of color was higher than that of TOC, which indicates that the chromophoric group was destroyed during wastewater degradation

and partly mineralized to CO_2 and H_2O (Xu *et al.* 2004). Although the chromophoric structure of flax wastewater molecules is destroyed by •OH radicals, some colorless intermediates during the degradation formed in the solution as the reaction went further.

CONCLUSIONS

The discoloration and mineralization of flax wastewater in an aqueous medium by the fluidized-bed Fenton process under various operating conditions were investigated. The process with pollutants being adsorbed on the surface of carriers, could further help degradation of the wastewater with lower iron concentration in the effluent. SiO_2 was the most appropriate carrier used in the fluidized-bed system and the process was also influenced by the dose of Fe^{2+} and H_2O_2 reagent. Under 300 mg/L Fe^{2+} and 600 mg/L H_2O_2, maximum mineralization was achieved by the fluidized-bed Fenton process with 89% TOC removal, while TOC of raw water was 350 ± 5 mg/L and the color removal efficiency for flax wastewater was 94%. The TOC removal efficiency was increased by increasing the Fe^{2+} concentration. Conversely, removal efficiencies of color and TOC were hindered by excess H_2O_2 scavenging the •OH radicals usable in the process. The removal efficiencies of color and TOC were also affected by the bed expansion in batch studies. Flax wastewater mineralization follows a pseudo second-order kinetics law and mineralization kinetics was influenced significantly by $[Fe^{2+}]$:$[H_2O_2]$ concentration ratio. It could be inferred that the degradation and generation of the chromophoric and auxochrome groups leads to the change of the colority during the whole treatment process.

ACKNOWLEDGEMENT

The authors would like to thank Jiangsu union innovation funds (BY2012189).

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First received 24 October 2014; accepted in revised form 18 March 2015. Available online 30 March 2015