Journal of Hazardous Materials 162 (2009) 386–390

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Treatment of water-based printing ink wastewater by Fenton process combined with coagulation

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ARTICLE INFO

Article history:
Received 8 April 2007
Received in revised form 9 May 2008
Accepted 12 May 2008
Available online 21 May 2008

Keywords:
Water-based printing ink
Fenton reagents
Polyaluminium chloride
Coagulation

ABSTRACT

Attempts were made in this study to examine the efficiency of Fenton process combined with coagulation for treatment of water-based printing ink wastewater. Parameters affecting the Fenton process, such as pH, dosages of Fenton reagents and the settling time, were determined by using jar test experiments. 86.4% of color and 92.4% of chemical oxygen demand (COD) could be removed at pH 4, 50 mg/l H_2O_2, 25 mg/l $FeSO_4$ and 30 min settling time. The coagulation using polyaluminium chloride (PAC) and ferrous sulfate ($FeSO_4$) was beneficial to improve the Fenton process treated effluent in reducing the flocs settling time, enhancing color and COD removal. The overall color, COD and suspended solids (SS) removal reached 100%, 93.4% and 87.2% under selected conditions, respectively. Thus this study might offer an effective way for wastewater treatment of water-based ink manufacturer and printing corporation.

1. Introduction

The printing ink industry is globally facing stringent requirements to produce new and better performing and environmentally friendly printing inks, such as water-based ink, ultraviolet curing ink and water-based UV ink. Flexography is the only printing process that consumes significant quantities of water-based ink. The estimated consumption of water-based ink used in flexography in the United Sates, Europe, Latin America and Japan, were approximately 133 333, 72 000, 11 333 and 90 000 tons in 2000, respectively [1]. The main ingredients of the conventional inks are pigments, binders, carriers and additives [2]. Compared with solvent-based ink, water-based ink uses water as carrier to substitute a majority of organic solvent, thus its development and application have led to the reduction of volatile organic compounds (VOC) emissions, as one of the main driving forces of product innovation [3]. Water-based ink is nonflammable, produces less objectionable vapors in the workplace, and does not contaminate packaged products [2]. Therefore, it has been widely used in printing the packaging of food, drug, toy, wine product and so on. However, wastewater obtained after cleaning/washing of the laboratory and industrial equipment is highly colored by the pigments and is highly contaminated with organic materials. This wastewater may also be an aesthetic concern and cannot be discharged to a wastewater system without treatment. Acrylics often used in water-based ink formulations and pigments are very difficult to break down biologically. Moreover, more stringent requirements of wastewater discharge standards have promoted recent research efforts to identify other more efficient and economic chemical treatment methods in an attempt to meet these demands. Hence, there is a need for advanced treatment process to further remove color and chemical oxygen demand (COD) from this wastewater.

The Fenton process employs ferrous ions and hydrogen peroxide (H_2O_2) under acidic pH conditions. As shown in reactions (1)–(5), strong oxidative hydroxyl radical ($HO^{\bullet}$) is produced and the ferrous ions are oxidized to ferric ions and ferric hydroxo complexes which accounts for the coagulation capability of Fenton reagents [4,5]. Then suspended solids are captured and precipitated out. The $HO^{\bullet}$ attacks organic compounds and thus causes chemical decomposition of these compounds. The Fenton process can therefore have the dual functions of oxidation and coagulation in the treatment process.

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \quad (1)$$

$$HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \quad (2)$$

$$[Fe(H_2O)_6]^{3+} + H_2O \leftrightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+ \quad (3)$$

$$[Fe(H_2O)_5OH]^{2+} + H_2O \leftrightarrow [Fe(H_2O)_4(OH)_2]^+ + H_3O^+ \quad (4)$$

$$2[Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe_2(H_2O)_8(OH)_2]^{4+} + 2H_2O \quad (5)$$

In the past few years, many experiments have been carried out to remove COD and color from industrial wastewater by Fenton's

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doi:10.1016/j.jhazmat.2008.05.068

reactions. The efficiency of Fenton process depends on the properties of the wastewater, the pH value, the Fe^{2+} concentration, the H_2O_2 dosage and the reaction time [6]. Fenton process for printing ink wastewater treatment has not yet been reported in the literature. This study attempts to explore the possibility of treating water-based printing ink wastewater by Fenton process. Experiments were conducted to examine the effects of various operating conditions on the performance of the treatment system. The experimental results can shed light on understanding the Fenton process as well as many practical aspects of its potential application.

2. Materials and methods

2.1. Wastewater

The water-based printing ink wastewater was obtained from an ink chemical company located in Hangzhou, China. According to the company, the main components of the wastewater sample were water, acrylics, ammonia, 1,2-propylene glycol, isopropanol, monoethanolamine, carbon black, water-based wax, and defoamer agent. This wastewater was neutral (pH 7) and black. Its concentration of COD ranged 4350–5200 mg/l, and its color ranged 1000–2000 times based on dilution method. The transmittance value was 0, and the suspended solids (SS) concentration was 195 mg/l. The efficiency of wastewater treatment process was mainly evaluated in terms of the color and COD removal.

2.2. Fenton process

The Fenton process experiments were conducted by using jar test method. The operating parameters included dosages of H_2O_2 and $FeSO_4$, pH value and settling time. Every beaker was first filled with 1000 ml of wastewater sample, and the pH was adjusted to the designed value with 0.1N H_2SO_4 solution. Then $FeSO_4$ and H_2O_2 (30%, w/w) were added and the process was proceeded with rapid mixing of wastewater sample at 120 rpm for 10 min, slow mixing at 95 rpm for 10 min, and then maintaining standstill for 30 min. The supernatant was withdrawn for COD and color analyses.

2.3. Coagulation process

The Fenton process treated effluent was further subjected to chemical coagulation. Based on the preliminary experiments, polyaluminium chloride (PAC) and $FeSO_4$ were chosen as the efficient coagulant and coagulant aid, respectively. Jar test experiments were carried out in order to determine the optimal dosage of each coagulant to shorten the flocs settling time and further reduce the color and COD. PAC was added first and mixed for 10 min under rapid mixing conditions (120 rpm) and then ferrous sulfate was added and slow mixing was applied (95 rpm) for 10 min. Finally, the solution maintained standstill for 30 min to settle out the flocs. The pH was adjusted to the desired value with 0.1N H_2SO_4 and NaOH solutions before the coagulant was added.

The Fenton process and coagulation were performed with jar test equipments (TA6-4, Wuhan, China) comprising six paddle rotors (24.5 mm × 63.5 mm), equipped with six beakers of 1 l each. During the experiment, all the chemicals used were of analytical grade and supplied from Huadong Medicine Group Co. Ltd.

2.4. Chemical analyses

Prior to and after treatment, samples were withdrawn from the sampling port located about 2 cm below the liquid level for the determination of COD, color and SS. Analyses were undertaken in triplicates. COD was determined in accordance with the method 508C (closed reflux, colorimetric method) in standard methods [7]. The pH was measured using portable pH meter (pHB-2, China). The color value of each sample was based on the transmittance value using the 721-spectrophotometer (Shanghai, China) equipped with glass cuvette with an optical way length 1 cm at wavelength of 630 nm. The initial color value was also determined using dilution method [8]. The initial and final SS of wastewater were measured using gravimetric method [9].

3. Results and discussion

3.1. Factors affecting the performance of Fenton process

3.1.1. Effect of pH

The pH has been observed to be a highly important factor for the effective Fenton treatment [10]. Fig. 1 demonstrates the pH effect on the color and COD removal of the wastewater treated by Fenton process with a fixed amount of 50 mg/l H_2O_2 and 25 mg/l $FeSO_4$. As the pH increased from 1 to 6, the COD removal remained in the range of 91.6–92.4%, and the maximum value of COD removal was 92.4% at pH 4. The COD removal started to decrease slightly at pH 5, due to the increasing rate of autodecomposition of H_2O_2, deactivation of iron ion into iron oxyhydroxides, the increased scavenging effect of $HO^{\bullet}$ resulting in the decreased oxidation potential of $HO^{\bullet}$ [11]. The results show that high COD removal could be achieved at wide range of pH, whereas, the color removal varied from 70.8% to 84.0%. This is related with the characteristics of this type wastewater, some organics, such as 1,2-propylene glycol, isopropanol, monoethanolamine, could be easily oxidized, but carbon black, mainly contributed to the color, was removed by coagulation. In addition, destabilization is a primary driving force in flocculation of water-based printing ink wastewater and the suspension stability is related with pH according to the zeta potential–pH relationship, as the decreasing of pH (<6), destabilization is easily achieved and particles are prone to aggregation [12]. This process could also be beneficial to improve the efficiency of Fenton process. Taking both COD and color removal into consideration, pH 4 was chosen for all Fenton process experiments in this study.

3.1.2. Effect of ferrous dosage

Fig. 2 presents the effect of ferrous dosage on the color and COD removal with a fixed amount of 50 mg/l H_2O_2 for the wastewater. In the presence of H_2O_2 only, the color and COD removal were 73.9% and 80.6%, respectively. As the dosage of $FeSO_4$ increased

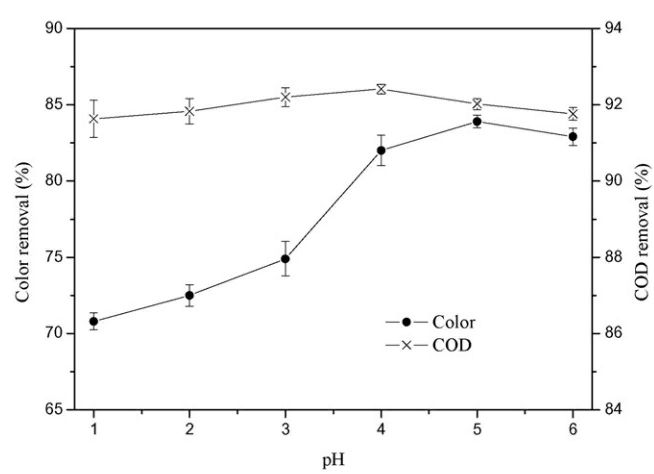

Fig. 1. Effect of pH on color and COD removal by Fenton process (H_2O_2 = 50 mg/l; $FeSO_4$ = 25 mg/l).

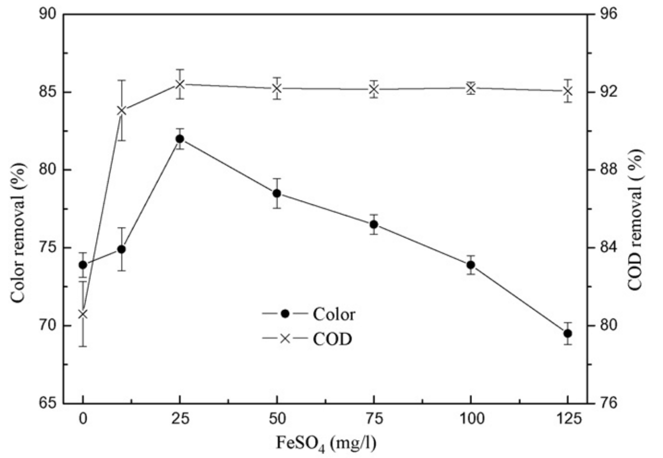

Fig. 2. Effect of $FeSO_4$ dosage on color and COD removal by Fenton process (H_2O_2 = 50 mg/l; pH 4).

from 10 mg/l to 25 mg/l, the color removal increased from 74.9% to 82.0%, but COD removal increased slightly from 91.1% to 92.4%. When increasing the $FeSO_4$ dosage from 25 mg/l to 125 mg/l, the COD removal remained in the range of 92.1–92.4%, while the color removal decreased obviously from 82.0% to 69.5%. Meanwhile, it had been observed that large amounts of small flocs were suspended in the supernatant and difficult to settle down. Hence, the increasing dosage of ferrous sulfate significantly improved the color and COD removal in the range of 0–25 mg/l. This was due to the increasing amount of ferric hydroxo complexes and $HO^{\bullet}$ generated by the redox reaction with the increasing dosage of ferrous sulfate. Then the pigments and other organics suspending in wastewater were oxidized, coagulated, and precipitated out. Such a coagulation/precipitation action perhaps constitutes an important part of color and COD reduction of the Fenton process for this type of wastewater. Therefore, the dosage of $FeSO_4$ was fixed at 25 mg/l for Fenton process experiments.

3.1.3. Effect of H_2O_2 dosage

Fig. 3 shows the removal of color and COD at different H_2O_2 dosages. The pH was controlled at 4 and the $FeSO_4$ dosage was fixed at 25 mg/l. When the dosage of H_2O_2 increased from 0 mg/l to 17 mg/l, the COD removal increased from 82.8% to 91.8%. However, the dosage of H_2O_2 varied from 17 mg/l to 133 mg/l, the COD removal was within the range of 91.7–92.4%, indicating that most of organics, such as 1,2-propylene glycol, isopropanol, monoethanolamine, could be oxidized by $HO^{\bullet}$.

From Fig. 3, it can be seen that the color removal increased from 73.1% to 82.0% as the H_2O_2 dosage ranged from 0 mg/l to 50 mg/l. This is due to the increasing amount of ferric ion and its hydroxo complexes generated by the redox reaction as shown in reactions (1)–(5), and this was beneficial to the coagulation of carbon black. When H_2O_2 dosage was increased from 50 mg/l to 133 mg/l, the color removal decreased from 82.0% to 75.9%. This may be caused by the regeneration of Fe^{2+} in the solution resulting in decrease of Ferric ion and color removal [13], as shown in reactions (6) to (7). 50 mg/l H_2O_2 was enough for Fenton process experiments.

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + {}^{\bullet}OOH + H^+ \quad (6)$$

$${}^{\bullet}OOH + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \quad (7)$$

3.1.4. Effect of settling time

Fig. 4 shows the removal of color and COD at different settling time (0–2 h) after Fenton process. The dosages of H_2O_2 and $FeSO_4$ used were 50 mg/l and 25 mg/l. The pH was controlled at 4. After the rapid and slow mixing, large amounts of small flocs were consistently observed and would take a very long time to settle down. Furthermore, these small flocs frequently interfered with color and COD measurement. As the settling time increased, the color and COD removal increased sharply during the first 30 min and increased slowly afterwards. In order to shorten the flocs settling time, chemical coagulation process was designed to treat the Fenton treated effluent and further to reduce the color and COD. Thus the settling time was chosen as 30 min.

3.2. Factors affecting the coagulation efficiency

To shorten the flocs settling time and to further reduce the color and COD, coagulation process was necessary. Compared with the traditional coagulants, aluminium salt coagulant has the advantages of higher efficiency and relatively lower cost. PAC is commonly used as flocculant for water treatment [14] and was found to be the most efficient coagulant for pretreatment of currency printing ink wastewater, achieving color, SS, biochemical oxygen demand (BOD) and COD removals of 95.9–96.0%, 96.5–97.0%, 61.3–65.8% and 54.8–61.8%, respectively, at an optimum concentration of 1500 mg/l PAC [15,16]. To optimize the parameters affecting the efficiency of coagulation, an orthogonal experiment designed with three-level

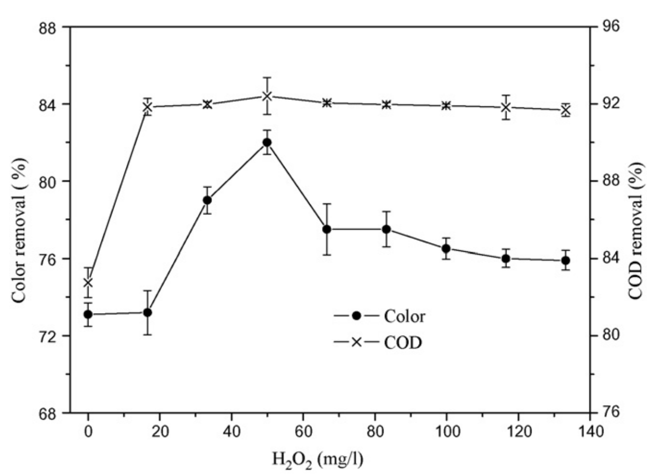

Fig. 3. Effect of H_2O_2 dosage on color and COD removal by Fenton process ($FeSO_4$ = 25 mg/l; pH 4).

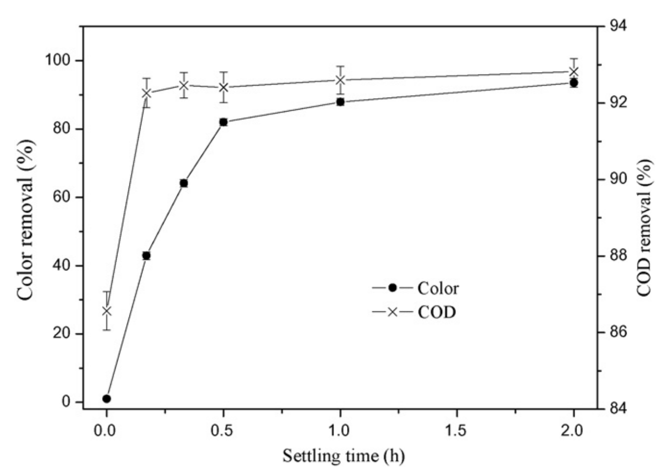

Fig. 4. Effect of settling time on color and COD removal after Fenton process (H_2O_2 = 50 mg/l; $FeSO_4$ = 25 mg/l; pH 4).

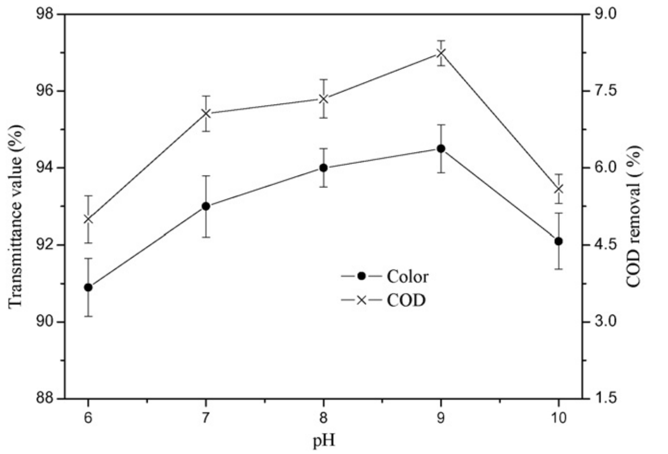

Fig. 5. Effect of pH on COD removal and transmittance value of treated water in coagulation process (PAC = 700 mg/l; $FeSO_4$ = 300 mg/l).

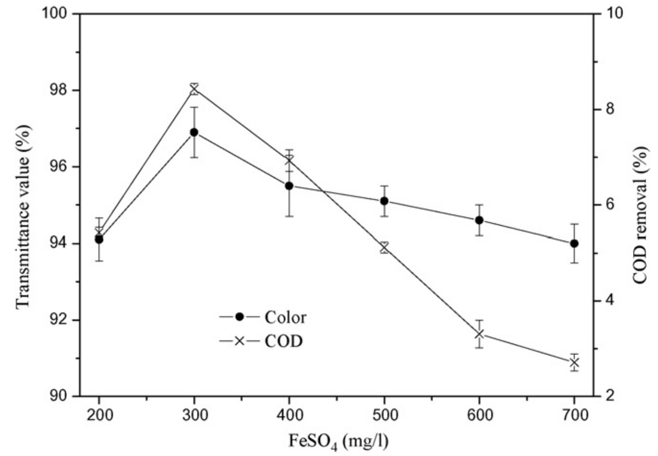

Fig. 7. Effect of $FeSO_4$ dosage on COD removal and transmittance value of treated water in coagulation process (PAC = 700 mg/l; pH 9).

and three-variable was carried out, the variables were pH, PAC dosage, and $FeSO_4$ dosage.

3.2.1. Effect of pH

Fig. 5 shows the efficiency of coagulation with PAC and $FeSO_4$ (700 mg/l and 300 mg/l, respectively) at different pH. It indicated that COD and color removal were not so dependent on pH. The COD removal was 5.0% and 8.2% in pH 6 and 9. The transmittance value of the treated water after coagulation process increased from 90.9% to 94.5% when the pH increased from 6 to 9. The quality of the treated water was reduced when the pH was above 9. Thus pH 9 was selected in the following experiments.

3.2.2. Effect of PAC dosage

Fig. 6 shows the effects of PAC dosage on COD removal and the transmittance value of the coagulation treated water at pH 9 and the dosage of $FeSO_4$ was 300 mg/l. When the dosage of PAC increased from 500 mg/l to 700 mg/l, the transmittance value of the treated water after coagulation process increased from 92.0% to 97.2% and the COD removal increased from 5.0% to 8.3%. The COD removal was not high and this may be explained by the fact that most of particles (pigments and binders) contributed to color and SS are removed in Fenton process and the residual dissolved COD is difficult to be removed through destabilization and cross-linking mechanism in coagulation. But it could be observed that the small flocs were easily settled to the bottom of the jar under the operational conditions of 700 mg/l PAC, pH 9 and 300 mg/l $FeSO_4$. Thus this coagulation process could improve the settlement of flocs.

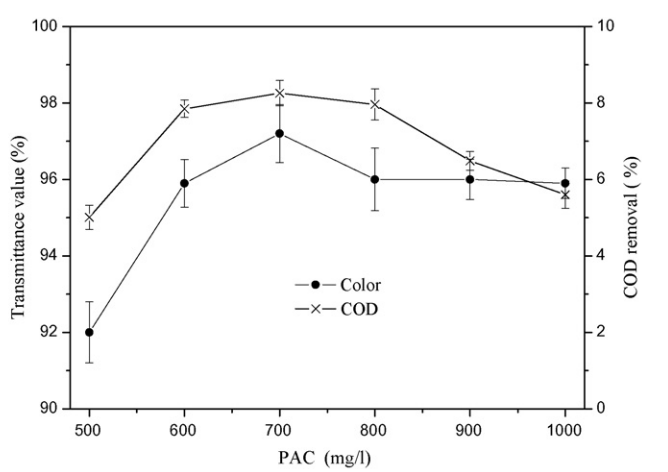

Fig. 6. Effect of PAC dosage on COD removal and transmittance value of treated water in coagulation process ($FeSO_4$ = 300 mg/l; pH 9).

3.2.3. Effect of $FeSO_4$ dosage

Fig. 7 shows the effects of $FeSO_4$ dosage on COD removal and the transmittance value of the coagulation treated water at pH 9 and the dosage of PAC was 700 mg/l in coagulation process. It can be seen that the COD removal significantly increased when the $FeSO_4$ dosage increased from 200 mg/l to 300 mg/l and declined as the $FeSO_4$ dosage was over 300 mg/l. The removal of color had the similar trend to COD. Therefore, the optimum $FeSO_4$ dosage was 300 mg/l.

3.3. Fenton process combined with coagulation

Based on the optimization of Fenton and coagulation processes, the initial wastewater was firstly subjected to Fenton process, and subsequently the supernatant water was withdrawn and treated by coagulation. Experimental parameters were controlled at individual selected conditions. The initial values of transmittance, COD and SS were 0%, 4750 mg/l and 195 mg/l, respectively. The characteristics of Fenton process treated and coagulation treated effluent and the overall treatment efficiency are summarized in Table 1. In Fenton process, 86.4% of color and 92.4% of COD could be removed under pH 4, 50 mg/l H_2O_2, 25 mg/l $FeSO_4$ and 30 min settling time. Because of the existence of large amounts of small unprecipitated flocs, the SS removal of wastewater treated by Fenton process was only 45.6% after 30 min

Table 1
Overall treatment efficiency of Fenton process combined with coagulation

Parameter	Fenton treated effluent	Removal efficiency (%)	Coagulation treated effluent	Removal efficiency (%)	Overall efficiency (%)
Color	86.4%	86.4	100%	13.6	100
COD (mg/l)	361	92.4	314	13.0	93.4
SS (mg/l)	106	45.6	25	76.4	87.2

settling time, but the coagulation process significantly enhanced the color and SS removal. The final color, COD and SS removal reached 100%, 93.4% and 87.2%, respectively. Thus the coagulation was beneficial to improve the Fenton process treated effluent in reducing the flocs settling time, enhancing color and COD removal.

4. Conclusion

Treatment of the actual water-based printing ink wastewater by Fenton process combined with coagulation was conducted in this study. In Fenton process, 92.4% of COD and 86.4% of color removal could be obtained after 30 min settling time at the following conditions: pH 4, dosages of H_2O_2 and $FeSO_4$ were 50 mg/l and 25 mg/l, respectively. Large amounts of small flocs generated in Fenton process took much longer time to settle down. In this respect, coagulation was found highly beneficial in reducing the floc settling time. Furthermore, coagulation using 700 mg/1 PAC and 300 mg/1 $FeSO_4$ at pH 9 was helpful to enhance decolorization of this wastewater. The overall color, COD and SS removal reached 100%, 93.4% and 87.2%, respectively, indicating that the Fenton process combined with coagulation was effective for wastewater treatment of water-based printing ink manufacturer and printing corporation. It might offer potential application of reusing the treated water for cleaning machines (either after a single production or for a final cleaning) and will significantly contribute to reducing freshwater consumption.

Acknowledgement

The financial support from the Education of Zhejiang Province of China (Grant No. 20061080) is gratefully acknowledged.

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