

Removal of terephthalic acid in alkalized wastewater by ferric chloride

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Abstract

Terephthalic acid, which is a main component in alkali-decrement wastewater, is efficiently removed using ferric chloride in high pH solutions. About 90% removal of terephthalic acid is achieved at pH between 8 and 11. Especially, the removal reached 94.3% at pH 11. However, as the pH increased from pH 12 and 13, the low removal of terephthalic acid were found. The increasing ferric chloride dosage had a dramatic positive impact on the achieved removal of terephthalic acid. Further increase in the ferric chloride dosage did not produce better removal rate. The increase of terephthalic acid concentration also led to the increase of ferric chloride dosage in order to get the same removal of terephthalic acid. There was approximately a negative linear relationship between terephthalic acid concentration and removal of terephthalic acid. Compared with other coagulants, it can be seen that ferric chloride is more effective in a high pH solution and the amount of ferric chloride required is also less as compared with aluminum chloride, magnesium chloride and calcium chloride. Our results clearly showed that terephthalate anions strongly binds to positive Fe(OH)₃ flocs and forms insoluble complexes, probably through a mechanism involving electrostatic attraction. The electrostatic attraction may be particularly useful means of purifying wastewater in high pH solutions.

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1. Introduction

Wastewater discharged from dyeing processes can be one the biggest contributors to textile effluent, this comprises mainly residual dyes and auxiliary chemicals. Thus, wastewater from dyeing industries creates a great problem of pollution [1,2]. In dyeing processes, alkali-decrement treatment of polyester fabric is generally used for silky property, as well as to improve the dyeing capability. The alkali treatment technology was developed by Imperial Chemical Industries (England) in 1952, and it was well known that the weight of polyester could be reduced 15–30% by treating the polyester fabrics with a sodium hydroxide solution which degrade poly(ethylene terephthalate) (PET) of surface fabric into sodium terephthalate. Thus, the alkali-decrement wastewater was mainly composed of sodium terephthalate and ethylene glycol, especially containing 75 wt.% sodium terephthalate. According, a considerable amount of

sodium terephthalate contained in alkali-decrement wastewater has been discharged because a large amount of polyester fabric has been treated by alkali-decrement process. However, the alkali-decrement wastewater have a high COD concentration, high pH (pH 12–13) and bad biodegradation. So it had become a new type wastewater which was strong and difficult to treat [3].

Chemical treatment and biological treatment of alkali-decrement wastewater were investigated and developed long ago. In chemical treatment process, HCl or H₂SO₄ solutions were added to adjust pH from 12–13 to 2–4, removals of sodium terephthalate and COD can reach 99% and 90%, respectively [4–6]. However, the way must consume a great deal of acid. Biological treatment can degrade sodium terephthalate and removal of sodium terephthalate can reaches 65% [7,8]. Nevertheless, biological treatment may not always be suitable for discharge of wastewater, especially for high expense.

Recently, the interest in wastewater recycling is continuously growing because of ecological and economic consideration [9]. If the alkali-decrement wastewater were treated in high pH, the water treated can be recycled in alkali-decrement treatment of polyester fabric. Thus, the discharge of wastewater into envi-

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ronment will decrease greatly. At the mean time, consume of sodium hydroxide will be decreased in alkali-decrement process. However, little report about it was seen. Thus, it was necessary to investigate removal of terephthalic acid in alkali solutions for wastewater recycling. In recent year, adsorptive flocculation has been recognized as an effective method of removal of organic compounds in water [10]. But high-pH flocculation in alkali-decrement wastewater treatment is also little reported.

The present study focused on the removal of terephthalic acid in high-pH water by ferric chloride, the objectives were detailed information on conditions of wastes processing and the interactions of terephthalic acid and flocculations.

2. Experimental

2.1. Materials

Terephthalic acid was supplied by Acros reagent company (the degree is 99%). A stock solution was prepared by dissolving 1 g of terephthalic acid (TA) in 1 l of a NaOH solution having a concentration of 0.6 g/l. Different sample of artificial wastewater having different concentration of TA were obtained by diluting the stock solution. The pH of all samples of artificial wastewater was fixed at 12. Reagent grade ferric chloride, magnesium chloride, calcium chloride and aluminum chloride were used as coagulants.

2.2. Procedures

A jar test was used in this study. Each beaker contained 100 ml of the wastewater. A period of 3 min was allowed for the mixing of the coagulant, and the sample at 80–85 rpm, followed by a period of 10 min of slow agitation at 30–35 rpm after adding of coagulant. The solution was then allowed to settle and the time of settlement was recorded, the supernatant was taken for analysis. The study of the influence of pH on terephthalic acid removal was performed by mixing ferric chloride solution with 100 ml of 500 mg/l terephthalic acid solution. One series of experiments was performed keeping the pH constant with 0.1 M HCl acid or 0.1 M sodium hydroxide solutions.

The concentration of sample was carried out using reversed phase HPLC system. The reversed phase HPLC system consisted of an SPD-M10A photodiode array detector set to 240 nm, a SIL-10AD automatic sampler, two LC-10AD pumps, a CTO-10A oven and SCL-10A system control box, Class-VIP data collection system. The separation column was Kromstar (C₁₈, 250 mm × 4.6 mm i.d., 5 μm). The mobile phase was degassed solution of 80/20 methanol/water (80/20, v/v) with flow rate of 0.80 ml/min.

3. Results and discussion

3.1. The comparison of the application of different coagulants

Different coagulants such as ferric chloride, aluminum chloride, magnesium chloride and calcium chloride were used in

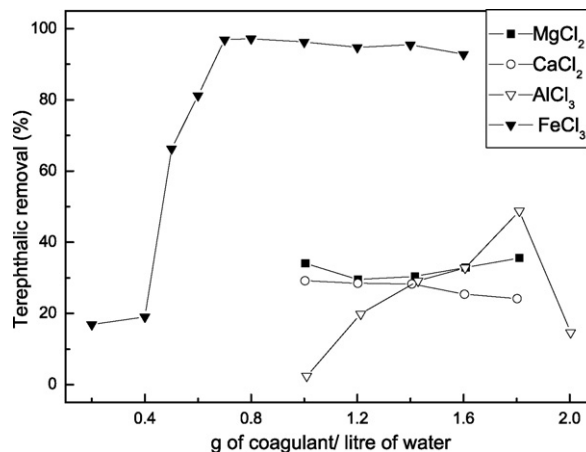


Fig. 1. Effect of coagulants on terephthalic acid removal.

order to compare coagulant effects in high pH solutions. Fig. 1 shows the plot of the rate of removal of terephthalic acid at pH 11 for different coagulants. It can be seen that ferric chloride is more effective in a high pH solution and the increasing ferric chloride dosage had a dramatic positive impact on the achieved removal of terephthalic acid. It is evident that for the removal of more 90% of 500 mg/l terephthalic acid solution, a dosage of ferric chloride of 0.7 g/l is required. It may be attributed to the following reasons: (1) the increase of adsorptive surface due to increase of ferric hydroxide precipitates and (2) the formation of floc and terephthalic acid anion complexes by electrostatic interaction. The complexes led to an enhancement of removal of terephthalic acid.

However, further increase in the ferric chloride dosage did not produce better removal rate, as almost all the terephthalic acid had been removed at this stage. Also, the presence of excessive ferric chloride will form too much flocs which may result in longer settling time.

In the mean time, the amount of ferric chloride required is also less as compared with aluminum chloride, magnesium chloride and calcium chloride for removal of sodium terephthalate. Fig. 2 shows the plot of the rate of COD removal at pH 11 for different coagulants. This result is similar to Fig. 1, 90% removal

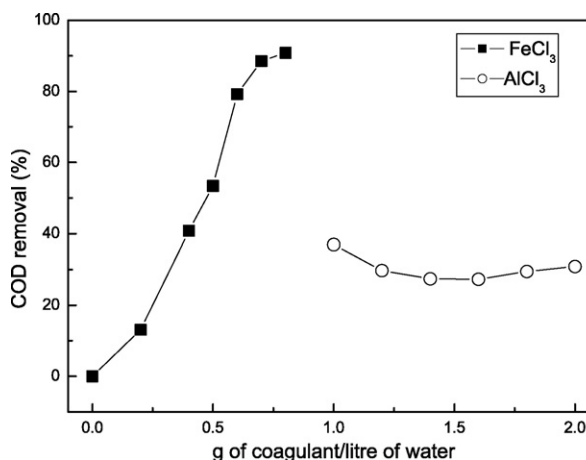


Fig. 2. Effect of coagulants on COD removal.

of terephthalic acid is accompanied by the 90% COD removal and the COD removal using AlCl_3 is also low. It maybe attribute to the various optimum pH of aluminum chloride, magnesium chloride and calcium chloride. The removal of terephthalic acid will decrease due to the solubility of precipitate at the pH beyond their optimum values. Also, it maybe attribute to the differences in the specific surface of metal hydroxide precipitates, $\text{Fe}(\text{OH})_3$ flocs maybe have bigger adsorptive surface than other metal hydroxide flocs, such as $\text{Ca}(\text{OH})_2$ flocs. Thus, aluminum chloride, magnesium chloride and calcium chloride were not effective for removal of terephthalic acid in high pH solutions.

3.2. Effect of pH on removal of terephthalic acid

The removal of terephthalic acid from a 500 mg/l solution by ferric chloride has been conducted at various pH values. The results were presented in Fig. 3. About 90% removal of terephthalic acid is achieved at pH between 8 and 11. Especially, the removal reached 94.3% at pH 11. However, as the pH increased from pH 12 and 13, the low removal of terephthalic acid were found, and the removals of terephthalic acid were 53.5% and 25.9%, respectively. This is probably due to the formation of ferric hydroxide precipitate at pH greater than 8. When pH increased, the ferric hydroxide precipitates were formed easily



When the pH value falls in the range 8–11, good flocculation occurs, almost all the ferric ions are converted into ferric hydroxide. The ferric hydroxide precipitates maybe act through an adsorptive coagulating mechanism. Its structure provides a large adsorptive surface area and its positive electrostatic surface charge enables it to act as a powerful and efficient coagulant. However, at the pH beyond 11.0, the results show lower removal rate. This phenomenon is probably due to the increase in the solubility of ferric hydroxide precipitate. The concentration of $\text{Fe}(\text{OH})_4^-$ increased with increase of pH values from 12 to 13. This result showed that electrostatic interaction between flocs and terephthalic acid played an important role in removal of terephthalic acid. The solubility studies on the magnesium, alum

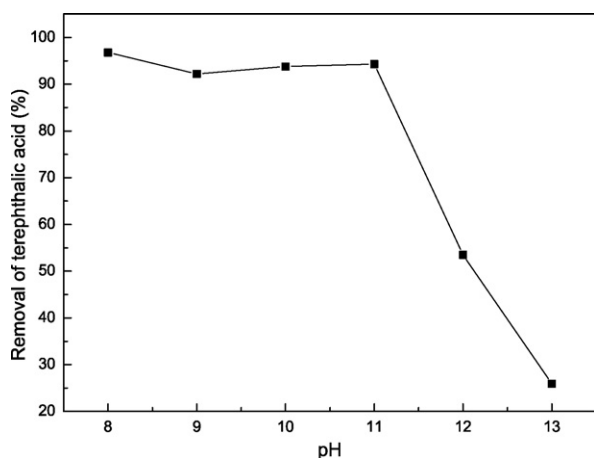


Fig. 3. Effect of pH on the removal of terephthalic acid using FeCl_3 .

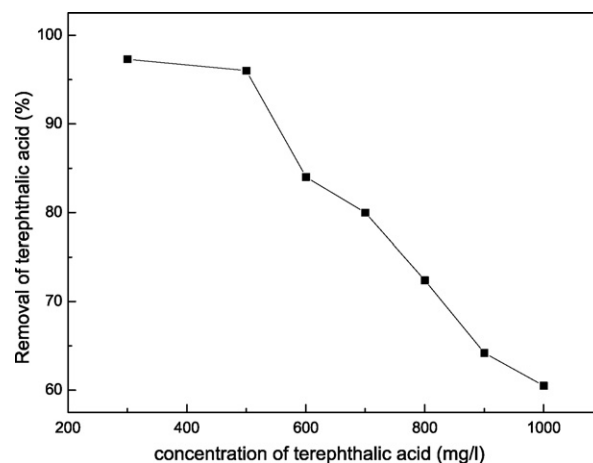


Fig. 4. Effect of terephthalic acid concentration on terephthalic removal at pH 11.

and PAC also show this phenomenon at the pH beyond their optimum values [11,12].

3.3. Effect of terephthalic acid concentration

A series of experiments were conducted to investigate the dependence of removal of terephthalic acid on concentration of terephthalic acid at pH 11. The concentrations of terephthalic acid varied from 300 to 1000 mg/l, while keeping a dosage of ferric chloride of 0.7 g/l constant. Fig. 4 showed the effect of concentration of terephthalic acid on removal of terephthalic acid at pH 11. As can be observed, the increase of terephthalic acid concentration led to the increase of ferric chloride dosage in order to get the same removal of terephthalic acid. There was approximately a negative linear relationship between terephthalic acid concentration and removal of terephthalic acid. When keeping dosage of ferric chloride constant, the relative adsorptive surface of ferric hydroxide precipitates decreased with increase of concentration of terephthalic acid. Thus, the adsorptive coagulation and electrostatic interaction decreased, which led to decrease of removal of terephthalic acid.

3.4. Interactions of FeCl_3 and terephthalic acid

In order to further reveal nature of coagulant effects on removal of terephthalic acid, we have investigated IR spectroscopy of terephthalic acid and coagulant flocs by using Fourier transform infrared (FTIR) spectroscopy. Fig. 5 shows the spectrum of the mixtures of terephthalic acid and flocs.

As can be seen from Fig. 5, the characteristic spectrum corresponding to the terephthalic acid cover in $500\text{--}4000\text{ cm}^{-1}$. However, the quality fraction of terephthalic acid in floc complex was less than 25% (w/w), the most of the characteristic spectrum corresponding to terephthalic acid are masked by the enormous inorganic flocs. Thus, the carbonyl stretching band of the carbonyl group of terephthalic acid, centered at 1687 cm^{-1} , has been analyzed for the complexes. Fig. 5 shows that there is different between $\text{Mg}(\text{OH})_2$ floc and $\text{Al}(\text{OH})_3$ floc and $\text{Fe}(\text{OH})_3$ floc at 1687 cm^{-1} , and the characteristic absorptions of carbonyl

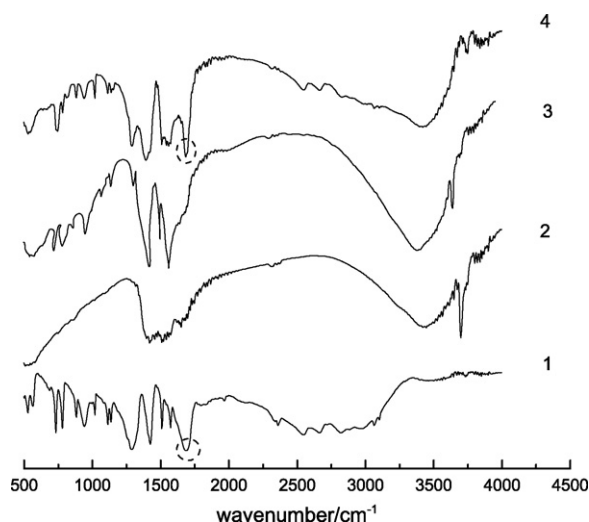


Fig. 5. FTIR spectra of terephthalic acid and floc: (1) terephthalic acid; (2) MgCl_2 floc; (3) AlCl_3 floc; (4) FeCl_3 floc.

groups of terephthalic acid are present in $\text{Fe}(\text{OH})_3$ floc, but are not present in $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ flocs. This indicated the formation of $\text{Fe}(\text{OH})_3$ floc and terephthalic acid anion complexes by electrostatic interaction.

At the pH values above 8, the terephthalic acid particles were more negatively charged. Ferric species in the pH range 8–11 are almost completely insoluble; the hydrolysis of ferric chloride generates ferric hydroxide particles, which are more positively charged. These particles agglomerate form macroscopic flocs and apparently readily adsorbed terephthalate anions. However, the concentration of $\text{Fe}(\text{OH})_4^-$ increased with increase of pH values from 12 to 13, thus, the amount of flocs with positive charges decrease. So the removals of terephthalic acid decrease dramatically. This is consistent with the assumption of adsorption of the dissociated form of terephthalic acid to micelle-bound Fe^{3+} . This result showed that electrostatic interaction between flocs and terephthalic acid played an important role in removal of terephthalic acid and the adsorptive coagulation will eventually lead to disruption of the flocs. However, small flocs could lead to a difficult sedimentation of solid particle. So, big adsorptive surface of flocs could be easy to form big sediments, which is easy to separate from water.

Our results showed that terephthalate anions strongly binds to positive flocs of ferric chloride and forms insoluble complexes, probably through a mechanism involving electrostatic attraction. The electrostatic attraction may be particularly useful means of purifying wastewater. In a future research, we intend to take further insight into interaction. Also, a similar test will be carried out on an industrial dye waste for recovery of terephthalic acid and recycling of water.

4. Conclusion

Terephthalic acid is efficiently removed using ferric chloride in high pH solutions. About 90% removal of terephthalic acid

is achieved at pH between 8 and 11. Especially, the removal reached 94.3% at pH 11. However, as the pH increased from pH 12 and 13, the low removal of terephthalic acid were found. The increasing ferric chloride dosage had a dramatic positive impact on the achieved removal of terephthalic acid. However, further increase in the ferric chloride dosage did not produce better removal rate. The increase of terephthalic acid concentration also led to the increase of ferric chloride dosage in order to get the same removal of terephthalic acid. There was approximately a negative linear relationship between terephthalic acid concentration and removal of terephthalic acid. Compared with other coagulants, it can be seen that ferric chloride is more effective in a high pH solution and the amount of ferric chloride required is also less as compared with aluminum chloride. Our results clearly showed that terephthalate anions strongly binds to positive $\text{Fe}(\text{OH})_3$ flocs and forms insoluble complexes, probably through a mechanism involving electrostatic attraction. The electrostatic attraction may be particularly useful means of purifying wastewater.

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