



Treatment of wastewater from dye manufacturing industry by coagulation*

YUAN Yu-li, WEN Yue-zhong^{†‡}, LI Xiao-ying, LUO Si-zhen

(Institute of Environmental Science, Zhejiang University, Hangzhou 310029, China)

[†]E-mail: wenyuezhong@zju.edu.cn

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Abstract: Chemical coagulation was used to remove the compounds present in wastewater from dye manufacturing industry. The character of wastewater was determined. Most compounds found in the wastewater are phenol derivatives, aniline derivatives, organic acid and benzene derivatives, output from dye manufacturing. Various polyferric chloride coagulants were investigated. Results showed that high extent of Fe(III) hydrolysis was not always suited for chemical oxygen demand (COD) removal in our wastewater, that electrostatic interaction between flocs and organic contaminants played an important role in removal of organic contaminants, that copolymers of Al(III), Si(IV) and Fe(III) were helpful for high flocculating effect, that COD removal efficiency of poly-silicate-aluminium-ferric chloride (PSAFC) and polyferric chloride (PFC) coagulant increased with increasing dose of coagulants, and that the performance of PSAFC and PFC coagulants was superior to PAC coagulant. This difference in efficiency may also be attributed to the copolymers of Si(IV), Al(III) and Fe(III). However, compared with PFC, PSAFC can easily reach high COD removal efficiency below coagulant dose 0.3 g/L. Thus, from the economic point of view, PSAFC is more suitable for treatment of wastewater effluent from dye manufacturing.

Key words: Dye manufacturing industry, Coagulation, Treatment, Wastewater

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INTRODUCTION

Wastewater derived from the production of dyes is highly variable in composition, and contains a large number of different compounds such as raw materials (anilines), intermediate products, and even the dye itself (Sarasa *et al.*, 1998). As with many other industrial sectors, growing concern about environmental issues has prompted the dye manufacture industry and textile industry to investigate more appropriate and environmentally friendly treatment technologies to meet the discharge restraints that are becoming stricter every day. Dyes production, textile preparation, dyeing and finishing plants are currently

being forced to treat their effluents at least partially prior to discharge to publicly owned treatment works because of the high organic load, strong and resistant colour as well as high dissolved solids content of the discharged wastewater (Arslan, 2001).

Conventional treatments of wastewater containing organic compounds include biological oxidation, chemical coagulation, advanced oxidation and adsorption. Biological methods are generally cheap and simple to apply and are currently used to remove organics and color from dyeing and textile wastewater. However, this dyeing wastewater cannot be readily degraded by conventional biological processes, e.g., the activated sludge process, because the structures of most commercial dye compounds are generally very complex and many dyes are non-biodegradable due to their chemical nature, molecular size; thus, this results in sludge bulking. Although dyestuffs and color materials in wastewater

[‡] Corresponding author

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can be effectively destroyed by wet oxidation, advanced chemical oxidation such as H_2O_2/UV , O_3 , and adsorption using activated carbon, the costs of these methods are relatively high (Kim *et al.*, 2004; Liu and Jiang, 2005; Wen *et al.*, 2005). Presently, wastewater from dye manufacturing industry is usually treated by combination process of biological treatment and coagulation treatment, before being fed to the biological treatment units, coagulation can reduce the wastewater loading and thus reduce the treatment cost.

Inorganic polymer flocculants (IPFs) are a new kind of water and wastewater treatment reagents, which have been developed worldwide since the 1960s (Tang, 1990). Because of their superior efficiency and relatively lower cost compared with traditional coagulants such as aluminum or iron salts, IPFs are becoming the main water and wastewater treatment reagents, with production and applications on a large scale in Japan, Russia, West Europe and China presently. The USA has also paid much attention to it in recent years (Wang and Tang, 2001).

In this study, chemical coagulation was used to remove the compounds present in wastewater from dye manufacturing industry. Various polyferric chloride coagulants were investigated, and the COD removal effectiveness of wastewater was compared in order to choose optimal coagulant.

MATERIALS AND METHODS

Materials

Aluminium chloride crystal and ferric chloride were supplied by Eoulpment Chemical Regent Company. PAC was of industrial grade. NaOH and H_2SO_4 were of reagent grade. Polyferric chlorides (PFCs) were prepared according the Wang's method (Wang *et al.*, 2003). Poly-silicate-aluminium-ferric chloride (PSAFC), poly-aluminium-ferric chloride (PAFC) and poly-silicate-ferric chloride (PSFC) were prepared in the base of PFC preparation by adding aluminium chloride or silicate.

The wastewater treated in this study came from a sewage factory located in Zhejiang, China, where wastewater of dyes and intermediary products industry was treated. The pH of sample was about 8~9, which was not adjusted during tests in favor of biological treatment in the next step.

Procedures

A six-beaker jar test apparatus was used in this study. Each beaker contained 1000 ml of the wastewater. After adding the coagulant, a period of 3 min was allowed for the mixing of the coagulant, and the sample at 80~85 r/min, followed by a period of 10 min of slow agitation at 30~35 r/min. The solution was then allowed to settle and the time of settlement was recorded, the supernatant was taken for analysis.

Analytical methods

The U.S.E.P.A. Method 625 was followed to concentrate the samples for characterization of raw and final treated water (Sarasa *et al.*, 1998). Starting with the amount of 500 ml of sample, a liquid-liquid extraction with CH_2Cl_2 is performed and two extracts are obtained: one containing basic+neutral compounds and the other containing acid compounds. The base+neutral extracts are dried with anhydrous Na_2SO_4 . The acid extract is derived with 4 ml of BF_3 /methanol. The concentration factor obtained for both extracts (base+neutrals and acids) is approximately 50. These extracts are later subjected to GC/MS analysis. The recovery value of the total extraction is between 80%~100% for aniline and nitrobenzene derivatives, the principal compounds present in the wastewater. Subsequently, the sample was analyzed using a HP6890/5973 GC-MS with HP-5MS capillary column of 30 m length. The intermediates were determined by matching with the standard samples, considering both elution time and mass spectrum. COD analysis was performed according to Standard Methods (APHA, 1980).

RESULTS AND DISCUSSION

Characteristic analysis of wastewater

The raw wastewater was subjected to GC-MS analysis. Table 1 provides a list of the majority compounds characterized in raw wastewater. The compounds are classified in groups according to their principal functional group. The relative contents of identified compounds were calculated on the basis of their relative peak area.

The majority of compounds found in the wastewater are phenol derivatives, aniline derivatives, organic acid and benzene derivatives, resulting from

Table 1 Majority compounds identified in raw and treated water (sample COD: 1342.91 mg/L)

Compound	Relative content (%)
Phenol	1.67
<i>p</i> -Nitrophenol	4.40
Biphenyl-4,4'-diol	1.10
2,4-Dinitro-phenol	1.13
Phenol derivatives	3.96
Aniline	0.97
Benzene-1,3-diamine	1.35
3,4-Dichloro-phenylamine	1.39
3-(phenylamino)-propanenitrile	6.18
<i>N</i> -Propyl-benzenamine	1.91
<i>p</i> -Nitroaniline	1.98
<i>p</i> -Pentylaniline	1.98
2,6-Dichloro-benzene-1,4-diamine	0.43
Benzoic acid	1.41
Benzyl alcohol	8.19
Naphthalene	3.71
Quinoline	1.40
2-Methyl naphthalene	3.97
Biphenyl	3.56

dye manufacturing, *p*-chloronitrobenzene, nitrobenzene and aniline are used in this industry as raw materials and *N,N*-dimethylaniline, *N,N*-diethylaniline, *p*-nitroaniline and dinitro-benzene are intermediary products. Some of the identified compounds are chlorinated derivatives, resulting from the chlorination treatment carried out by the factory (Sarasa et al., 1998). The presence of compounds belonging to List I of EEC and U.S.E.P.A. Priority Pollutant List, such as *p*-nitroaniline, *p*-nitrophenol is noteworthy.

The performance of COD removal by chemical coagulation depends upon the solubility of the organic contaminants. The organic contaminants with low solubility, such as disperse dyes, have been generally reported to be removed well by coagulation and/or flotation methods. The organic contaminants with low solubility can be easily adsorbed and flocculated by coagulants (Al-Degs et al., 2000). However, the soluble organic contaminants cannot be well removed efficiently by coagulation. As organic acids and benzyl alcohol have $-\text{COO}^-$, $-\text{OH}$ groups, these contaminants have high solubility and are not prone to be adsorbed.

Application of PFC

Polyferric chlorides (PFCs) were prepared at various extents of Fe(III) hydrolysis. *B* was used as a formation function to characterize the extent of Fe(III) hydrolysis and polymerization (Cheng, 2001). It is defined as:

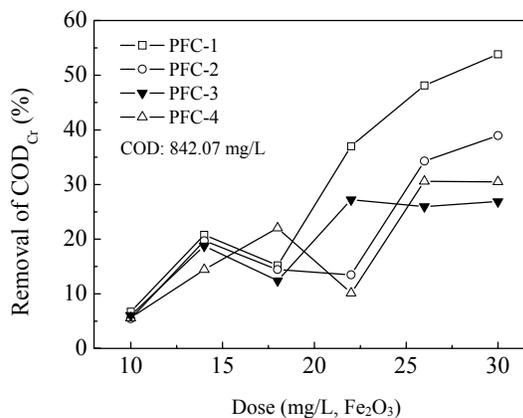
$$B = [\text{OH}^-]/[\text{Fe}],$$

where *B* is the number of OH^- ions that each iron ion bonds in the hydrolysis process.

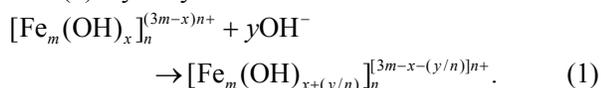
From Table 2, it can be seen that the extent of Fe(III) hydrolysis can be ranked: PFC-1 < PFC-2 < PFC-3 < PFC-4. Fig.1 also showed effects of hydrolysis of PFC on COD removal. At low dose of PFC (<200 mg/L), the COD removal efficiencies of four PFC coagulants were not different. However, COD removals of wastewater were ranked as PFC-1 > PFC-2 > PFC-3 ≈ PFC-4 at dose over 20 mg/L. These results showed that high extent of Fe(III) hydrolysis was not always suited for COD removal in our wastewater. From the dynamic point of view, the hydrolysis of Fe^{3+} and the complex-formation of polyferric chloride with organic contaminants could be explained as follows (Cheng and Chi, 2002):

Table 2 Characteristics of PFC coagulants

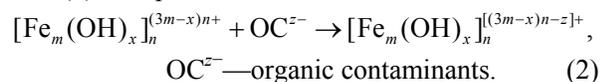
Items	PFC-1	PFC-2	PFC-3	PFC-4
Fe_2O_3 (%)	7	6.8	6.8	6.9
OH/Fe	0.146	0.254	0.283	0.297
pH	2	2	2	2
Colour	Henna	Henna	Henna	Henna
Stability	Good	Good	Good	Good

**Fig.1 Effects of hydrolysis of PFC on COD removal**

(1) Hydrolysis:



(2) Complex-formation:



The above equations show that when the concentration of the hydroxide ion is decreased but with constant PFC concentration, the reaction rate of Eq.(1) will decline. Since the negative charge on the organic contaminants preferably conjugates the PFC, the complexes formed will precipitate out of the solution through charge neutralization [Eq.(2)]. Hence, it can be concluded that the removal rate of organic contaminants is higher at acidic solution. Also, at low pH there is enough positive charge on PFC to neutralize the negative charge on organic contaminants. Therefore, the organic contaminants could precipitate through charge neutralization. Conversely, the hydrolysis of PFC increases as the solution pH increases. Thus, the positive charges on PFC decrease with increase of concentration of the hydroxide ion. Since the negative charge on the organic contaminants preferably conjugates the PFC, the complexes formed will precipitate out of the solution through charge neutralization. Hence, at low extent of Fe(III) hydrolysis, there is enough positive charge on PFC to neutralize the negative charge on organic contaminants. While the hydrolysis of PFC increases, the PFC could still react with organic contaminants, but its ability to neutralize the negative charge on organic contaminants decreased.

Application of PAFC

It was reported that copolymers of Al(III) and Fe(III) were helpful for high flocculating effect (Huang *et al.*, 2004; Jiang and Graham, 1998). The actual coagulant species present in the process are formed during and after these chemicals are mixed the water to be treated, and Al/Fe(III) ions are not primarily involved in the coagulation process. When added to water, Al/Fe(III) ions hydrolyse to form soluble monomeric and polymeric species and solid precipitates. Thus, poly-aluminium-ferric chloride (PAFC) was prepared in the base of PFC. The COD removal efficiency of PAFC was compared with PFC

as shown in Fig.2. It can be seen that when coagulant dose was below 0.2 g/L, the COD removal efficiencies of PFC and PAFC were lower than PAC, but increased with the increase of dose of PFC and PAFC. However, under the conditions studied, the performance of PAFC coagulant was consistently superior to PFC coagulant. This is attributed to the copolymers of Al(III) and Fe(III).

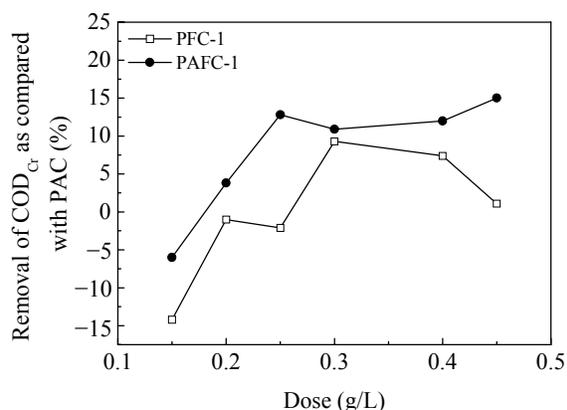


Fig.2 Comparison of COD removal between PFC and PAFC

Application of PSFC

The silica species are preferred because of their strong coordinate and aggregating effects and for their different aqueous behaviours. They can be used as modifiers to tailor-make polyferric silicate. Thus, poly-silicate-ferric chloride (PSFC) was prepared in the base of PFC (Wang and Tang, 2001).

The COD removal efficiencies of PSFC were compared with PAC as shown in Fig.3 showing that

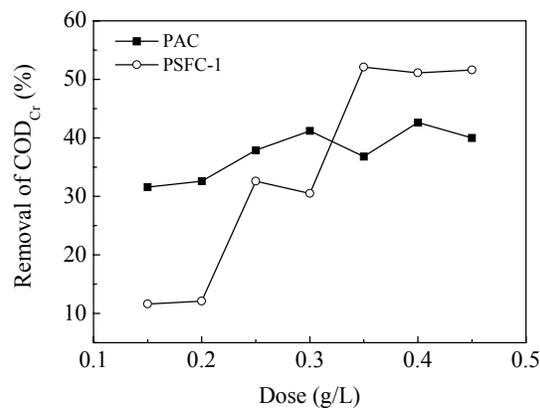


Fig.3 Comparison of COD removal between PSFC and PAC

when coagulant dose was below 0.3 g/L, the COD removal efficiencies of PSFC were lower than PAC, but increased with increasing PSFC dose. At PSFC doses above 0.3 g/L, the performance of PSFC coagulant was superior to PAC coagulant. This may be also attributed to the copolymers of Si(IV) and Fe(III).

Application of PSAFC

In view of the synergic effects of Si(IV), Al(III) and Fe(III), poly-silicate-aluminium-ferric chloride (PSAFC) was prepared in the base of PFC. The COD removal efficiencies of PSAFC were compared with PAC and PFC in Fig.4 showing that when coagulant dose was below 0.2 g/L, the COD removal efficiencies of PSAFC and PAC coagulants had no difference, but PFC coagulant had lower COD removal efficiency than PSAFC and PAC. However with increasing coagulant dose, the performances of PSFC and PFC coagulants were superior to PAC coagulant. This result may also be attributed to the copolymers of Si(IV), Al(III) and Fe(III). However, compared with PFC, PSAFC can easily reach high COD removal efficiency below coagulant dose of 0.3 g/L. Thus, from the economic point of view, PSAFC was more suitable for treatment of our wastewater.

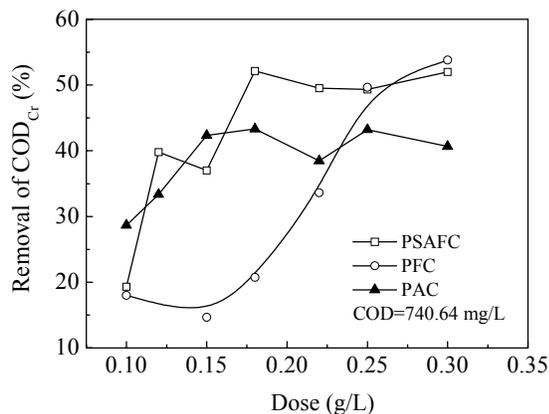


Fig.4 Comparison of various coagulants applied

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