

## Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species

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### Abstract

Removal of three direct dyes (Direct Black 19, Direct Red 28, and Direct Blue 86) by coagulation with three different Al based coagulants was investigated. The main purpose of this paper is to examine the coagulation features of polymeric aluminum coagulants in treatment of dye-polluted waters and the emphasis was placed on the roles of preformed Al species, particularly Al<sub>13</sub>. The performance of Al<sub>13</sub> in coagulation of dyes was observed through jar tests by comparing traditional Al salt, polyaluminum chloride (PACl), and purified Al<sub>13</sub>. The results showed that under most cases Al<sub>13</sub> had significantly higher efficiency in removal of direct dyes than traditional Al salt and commercial PACl with the exception of Direct Red 28 removal under high pH range. The coagulation of direct dyes could be greatly affected by pH. Reducing pH was favorable for preformed Al species in a broad pH range. For traditional Al coagulant, efficient dye removal only occurred in a relatively narrow pH range of near 6.0. The outstanding coagulation behavior of Al<sub>13</sub> could be ascribed to its high charge neutralization ability, relative stability and potential self-assembly tendency.

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**Keywords:** Direct dye; Coagulation; Al speciation; Polyaluminum chloride; Al<sub>13</sub>

### 1. Introduction

The release of dye compounds from industries of textile dyeing, printing, as well as food and papermaking can cause severe water pollution problems. It has been estimated that more than 700,000 tonnes of dyestuff are produced annually, and about 10–15% of these dyes are left in effluents during dyeing processes [1,2]. The presence of dyes in water is aesthetically undesirable, even very low concentration of dyes is highly visible. On the other hand, dye polluted natural waters can result in serious disturbance to aquatic biosphere due to the reduction of sunlight penetration and depletion of dissolved oxygen. Additionally, the majority of synthetic dyes are highly water-soluble azo dyes, which are toxic to some aquatic organisms and may pose serious health threat to human beings. It has been found that some azo dyes are able to produce carcinogenic aromatic amines

in the process of reductive degradation [3,4]. In the recent years, regulations on dye pollutants are becoming more and more stringent world widely. Thus, dyes in wastewater have to be removed completely before discharged into receiving waters.

However, since synthetic dye compounds usually have very complex structure and are intentionally designed to be recalcitrant with poor biodegradability, they are difficult to decolorize by conventional aerobic biological treatments, such as activated sludge process. The widely used methods for dyeing wastewater treatment involve many physical–chemical techniques, such as coagulation, adsorption, membrane filtration, and advanced oxidation, etc. [5–8]. Each treatment method has its advantages and disadvantages. Generally, advanced oxidation processes are effective for removal of most dyes, but a common problem with such operations is their relatively high cost in large-scale utilization [1,9]. In addition, chemical oxidation usually attacks only the chromophore groups of dyes instead of mineralizing organic dyes completely. Moreover, the possible occurrence of some more toxic intermediate products could be of concern. Adsorption techniques have much potential in the treatment of

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dye-containing waters if high performance and cheap adsorbents are available [10]. Membrane filtration has some special features unrivalled by other methods, but the high capital cost and clogging problems associated with this method may limit its application.

Coagulation/flocculation is one of the most popular unit operations in water and wastewater treatment trains. Dye removal by coagulation is not based on the partial decomposition of dye compounds, thus no potentially harmful and toxic intermediates are produced. Furthermore, this process can be used in large-scale operation with relatively high operability and cost effectiveness [2,11,12]. A limitation of this technique is that some high-soluble, low molecular and cationic dyes might not be effectively removed. The disposal of sludge produced by coagulation could be another restriction associated with this technique.

Although the application of coagulation in water and wastewater treatment has a long history, the mechanisms involved in this process are still not fully understood. Coagulation is a very complicated process involving a series of physical–chemical interactions. The type of coagulant applied can play important roles in the removal of target pollutants. Aluminum and ferric-based salts, such as alum, aluminum chloride, ferric chloride, ferric sulfate, are commonly used traditional coagulants. After dosing, aluminum and ferric ions will experience continuous self-hydrolysis and evolve into hydroxide solids finally. The *in situ* formed hydrolysis products and hydroxide solids can neutralize, and/or adsorb particulate and dissolved matters to achieve removal of pollutants. The hydrolyzing process of aluminum and ferric salts are subject to water quality conditions. Alkalinity, pH, temperature and co-existing ions can significantly affect the treatment effectiveness of such traditional coagulants. During the last decades, inorganic polymer flocculants (IPFs) are receiving more and more attention as a new generation of flocculants. Polyaluminum chloride (PACl) is one of the most important IPFs and being more and more widely used in the world. PACl contains polymeric Al species formed by partially neutralization. The preformed Al species in PACl are relatively stable after dosing, and thus their effectiveness can be less influenced by the specific water quality conditions [13–17].  $Al_{13}$  ( $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ ) is considered as the most important species in PACl and has long been research interest.

The removal of reactive and disperse dyes by regular coagulation and electro-coagulation has been studied by some researchers [9,18–22]. The coagulants used in most of the studies are traditional aluminum, ferric-based salts or synthesized organic coagulants. Although PACl has ever been applied in color removal [9,22], the comparative study on coagulation of dye by PACl and traditional Al salts has not been extensively and systematically carried out to date. Furthermore, the potential roles of  $Al_{13}$  in dye removal need to be elucidated.

In this work, the coagulation behaviors of direct dye removal by different Al based coagulants were investigated in detail using jar tests. Emphasis was placed on the distinct roles of  $Al_{13}$  species in coagulation of direct dyes. Three commonly used direct dyes were chosen as model dye pollutants.  $AlCl_3$

and commercially available PACl were applied as typical traditional coagulant and inorganic polymer flocculant. Since PACl contains multiple Al species including both  $Al_{13}$  and colloidal species, it is difficult to distinguish the roles of  $Al_{13}$  from other species. In this study, laboratory purified  $Al_{13}$  as a novel material was utilized to identify the exclusive functions of  $Al_{13}$ . The effect of pH on coagulation was examined to give better insights into the possible mechanisms involved in direct dye removal by different Al species.

## 2. Experimental

### 2.1. Dye compounds and test waters

Three direct dyes—Direct Black 19, Direct Red 28, and Direct Blue 86 (Tianjin Chemical Material Co., China) were used to simulate dye-polluted waters. These dyes were selected because they are currently among the widely used commercial dyes, especially in some Asian countries. In addition, the chemical structures of these dyes are different so that the treatability of dyes with different molecular characteristics could be compared. The molecular structures of these dye compounds are presented in Fig. 1. Stock dye solutions of  $1000\text{ mg l}^{-1}$  were prepared and then diluted using tap water to obtain final concentration of  $50\text{ mg l}^{-1}$ . The pH of the simulated test water was controlled within  $7.80 \pm 0.05$ ; the alkalinity was  $155\text{ mg l}^{-1}$  as  $CaCO_3$ . The wavelengths of maximum absorbance ( $\lambda_{\text{max}}$ ) of these dyes with the background of tap water were determined according to scanning patterns performed on an UV–vis 8500 Spectrophotometer (Shanghai, China). The  $\lambda_{\text{max}}$  values of Direct Black 19, Direct Red 28 and Direct Blue 86 in the visible light range are shown in Table 1.

### 2.2. Coagulants and speciation characterization

Analytical grade of  $AlCl_3 \cdot 6H_2O$  was used as traditional Al salt. Solid PACl product was obtained from Wanshui® Water Purifying Chemicals Co. (Beijing, China). Purified  $Al_{13}$  material was prepared in laboratory following the method described in [23]. The coagulants were dissolved in deionized water, and the total Al concentrations were measured using ICP-OES (1100-1155V, Jarrell-Ash, USA). The species distribution of these coagulants was characterized by both ferron assay [24] and  $^{27}Al$  NMR (Avance 500, Bruker, USA). Ferron assay can differentiate Al species into three categories:  $Al_a$ , the monomeric species;  $Al_b$ , the polymeric species;  $Al_c$ , the colloidal species.  $^{27}Al$  NMR technique can identify both monomeric and  $Al_{13}$  species. The  $^{27}Al$  NMR patterns of the three coagulants are demonstrated in Fig. 2. The signal at 0 ppm corresponds to monomeric species

Table 1  
The relationship between dye concentration ( $C$ ,  $\text{mg l}^{-1}$ ) and absorbance ( $A$ )

Dye name	$\lambda_{\text{max}}$ (nm)	Equation	$R^2$
Direct Black 19	630	$C = 144.9A - 0.1$	0.999
Direct Red 28	490	$C = 117.6A - 0.4$	0.999
Direct Blue 86	610	$C = 147.0A + 0.0$	0.998

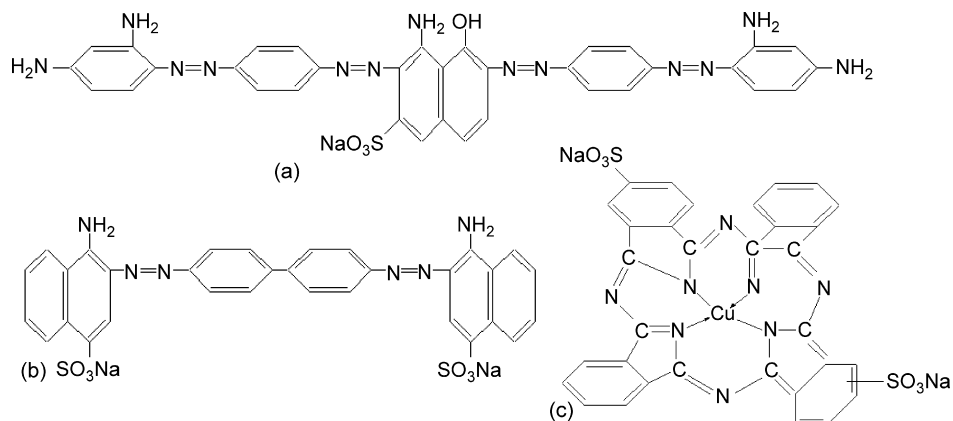


Fig. 1. Chemical structures of dye compounds (a) Direct Black 19, (b) Direct Red 28 and (c) Direct Blue 86.

and the signal at 62.5 ppm corresponds to  $Al_{13}$  species (only the central Al atom in  $Al_{13}$  structure could produce resonance signal), the signal at 80 ppm is ascribed to the inner standard of  $NaAl(OD)_4$ . Other Al species, such as colloidal species could

not be observed by  $^{27}Al$  NMR. Obviously, no  $Al_{13}$  was detected from  $AlCl_3$  solution, and both  $Al_{13}$  and monomeric Al species existed in PACl. As to the purified  $Al_{13}$ , the signal of monomeric species was almost negligible.

A current study found that the  $Al_b$  species determined by ferron assay was equivalent to the  $Al_{13}$  species on the condition that the B value (OH/Al molar ratio) was in the range of 1.5–2.5 [25]. In this work, the B values of the PACl and  $Al_{13}$  were 2.37 and 2.46, respectively, thus the  $Al_b$  component determined by ferron assay in both PACl and purified  $Al_{13}$  could be regarded as  $Al_{13}$  species. The speciation characteristics of three coagulants are listed in Table 2. As evidenced by  $^{27}Al$  NMR patterns, the predominant species of  $AlCl_3$  was Al monomers ( $Al_a$ ), accounted for 94.2%; while, the  $Al_b$  component ( $Al_{13}$ ) of purified  $Al_{13}$  was as high as 95.8%; PACl was consisted of mixed species with more than 50% of  $Al_c$ .

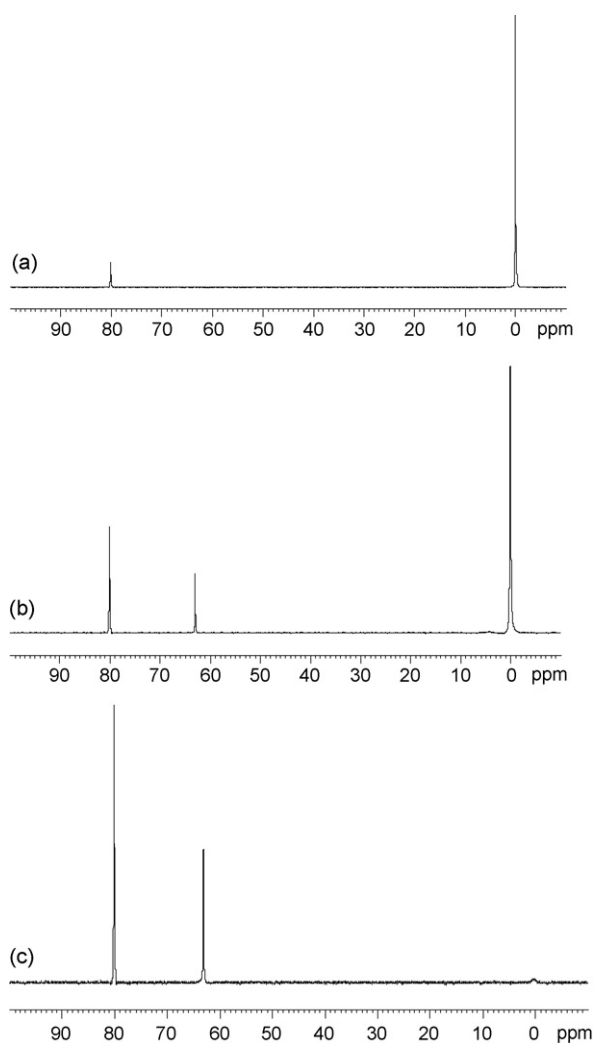


Fig. 2.  $^{27}Al$  NMR patterns of coagulant solutions (a)  $AlCl_3$ , (b) PACl and (c)  $Al_{13}$ .

### 2.3. Jar tests

Jar tests were conducted on a program-controlled JTY-4 Jar Tester (Beijing, China). Dye containing test water of 500 ml was transferred into a 800-ml beaker; under rapid stirring of 200 rpm, predetermined amount of coagulant was added, after 2 min, the stirring was changed to 40 rpm with a duration of 15 min; then samples were collected and filtered using 0.45  $\mu m$  membrane filter for residual dye measurement. Turbidity was also measured (2100N Turbidimeter, Hach, USA) for some tests after 20 min of quiescent settling, samples for turbidity measurement were taken from 2 cm below the surface. The pH of test water was adjusted by adding 0.5 mol l<sup>-1</sup> HCl and 0.1 mol l<sup>-1</sup> NaOH solutions. The measurement of

Table 2  
Al species distribution of three different coagulants

	Concentration (mol l <sup>-1</sup> Al)	pH	$Al_a$ (%)	$Al_b$ (%)	$Al_c$ (%)
$AlCl_3$	0.20	2.62	94.2	5.8	0.0
PACl	0.20	3.65	17.6	29.9	52.5
$Al_{13}$	0.11	4.15	2.0	95.8	2.2

pH was carried out using a MP220 pH meter (Mettler-Toledo, Switzerland).

#### 2.4. Measurement of residual dye concentration after coagulation

The linear relationships between dye concentration and absorbance at wavelength of  $\lambda_{\max}$  were obtained for each dye at pH of 7.80 (Table 1). For residual dye concentration measurement, the pH of filtered samples was adjusted to 7.80 first, and then the absorbance was read at wavelength of  $\lambda_{\max}$ . The residual dye concentration after coagulation was calculated based on the equations in Table 1. The removal was recorded as the ratio of residual dye concentration and initial test water concentration.

### 3. Results and discussion

#### 3.1. General coagulation behaviors of direct dyes

Removal of Direct Black 19 by coagulation was firstly carried out under pH of 7.80, which was the average pH value of tap water. The variations of dye removal with dosage are shown in Fig. 3 (the dosage was measured as “ $\text{mol l}^{-1} \text{Al}$ ” in this paper). With the increase of coagulant dosage, the removal increased and the curves associated with different coagulants exhibited similar changing trends: slow increase at low dosages, then followed by a rapid increase with dosage; finally the increase became slow again and the curves approached plateau. The removal could be reached near 100% at high dosage zone for all three coagulants. Before reaching plateau, the coagulation efficiency was:  $\text{Al}_{13} > \text{PACl} > \text{AlCl}_3$ . It should be pointed out that no re-stabilization phenomenon (removal reduction with increase of dosage) was observed even the dosage increased to  $40 \times 10^{-5} \text{ mol l}^{-1}$  (data are not included). The turbidity evolution with dosage is illustrated in Fig. 4. It was found that with the increase of dosage, the turbidity increased first and then decreased. Moreover, it was noticed that during the turbidity increasing phase, no observable flocs were formed. When the dosage was greater than a certain value (dosage corresponding

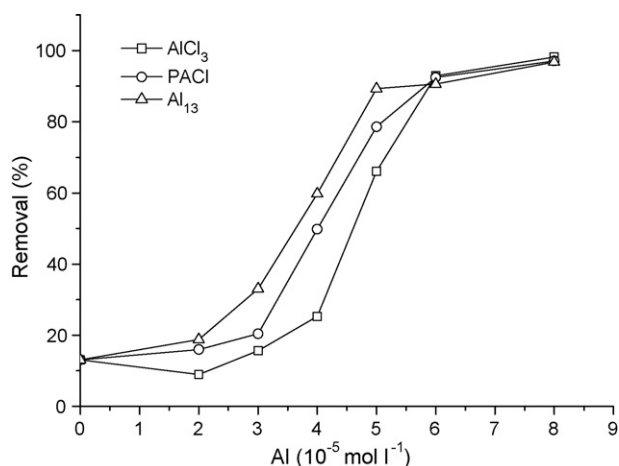


Fig. 3. Coagulation of Direct Black 19 under pH of 7.80.

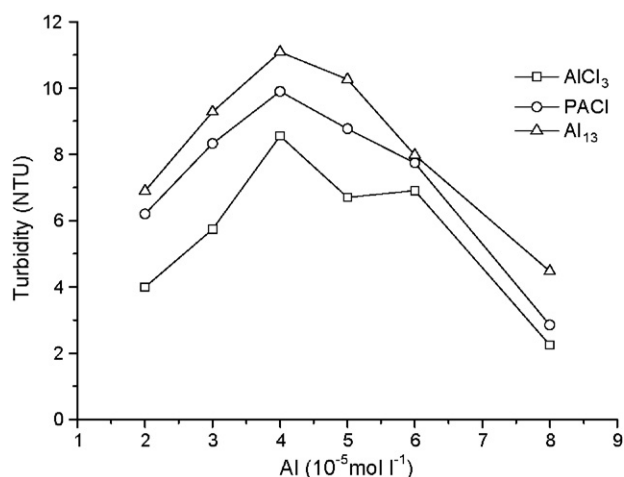


Fig. 4. Turbidity changes with dosage for coagulation of Direct Black 19.

to the maximum turbidity in Fig. 4), turbidity began to decrease and fine particulate matters could be seen with the increase of dosage. When the dosage was high enough, large flocs appeared. Fig. 4 also shows that during the turbidity increasing phase, coagulants related to higher dye removal also caused higher turbidity ( $\text{Al}_{13} > \text{PACl} > \text{AlCl}_3$ ); in the turbidity decreasing phase, the dye removal efficiencies were all much high, but the settling velocity of flocs formed by  $\text{AlCl}_3$  was more rapid.

The coagulation of Direct Red 28 and Direct Blue 86 was examined under the same condition as that of Direct Black 19. Like the coagulation of Direct Black 19, it was also found that with the increase of dosage, turbidity increased first and then decreased with the appearance of appreciable particulates. However, the dye removal kept increase within the whole dosage range (Fig. 5). The dye removal performance of three coagulants exhibited different characteristics depending on the type of dyes and dosage levels. In the coagulation of Direct Red 28,  $\text{Al}_{13}$  was

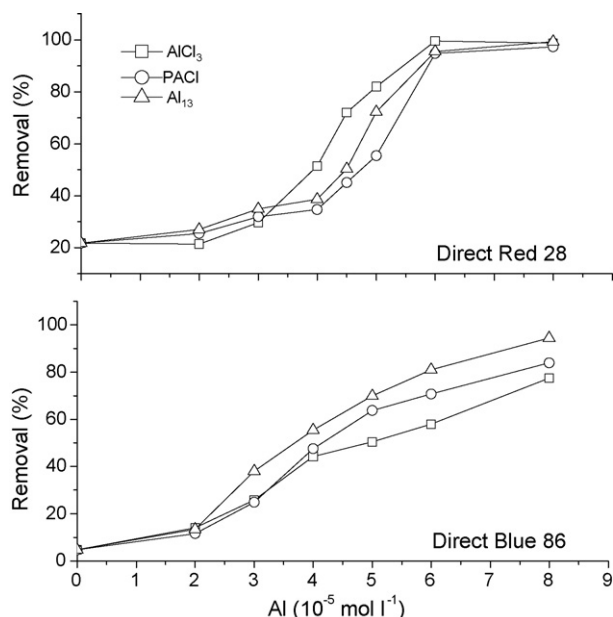


Fig. 5. Coagulation of Direct Red 28 and Direct Blue 86 under pH of 7.80.

slightly superior to the other two coagulants when the dosage was low. With the increase of dosage,  $\text{AlCl}_3$  became the most efficient one. At the high dosage zone, the differences among three coagulants tended to diminish. While in the case of Direct Blue 86,  $\text{Al}_{13}$  achieved the highest removal within the whole dosage range, and  $\text{AlCl}_3$  was the poorest coagulant. It can also be observed that higher dosages were required for removal of Direct Blue 86 than for removal of other two dyes. At the dosage of  $6 \times 10^{-5} \text{ mol l}^{-1}$ , the removal of Direct Red 28 had reached more than 90% for all coagulants, but the removal of Direct Blue 86 was only about 60, 70 and 80% for  $\text{AlCl}_3$ , PACl and  $\text{Al}_{13}$ , respectively. It indicates that Direct Blue 86 was more difficult to be removed than the other two dyes. This phenomenon implies that the treatability of different dyes by coagulation might be associated with the properties of dyes themselves, such as molecular size and chemical structure. According to Fig. 1, the molecular sizes of both Direct Black 19 and Direct Red 28 are larger than Direct Blue 86 in at least one dimension (the longest dimension of Direct Black 19 molecule had been estimated to be 3 nm [10]). It is well recognized that organic matters with longer molecular chain and larger molecular weight are more favorable for removal by coagulation.

Fig. 6 demonstrates the pH changes after coagulation of Direct Blue 86: pH decreased with the increase of coagulant dosage. Once  $\text{AlCl}_3$  was dosed, the pH was depressed obviously. However, when the PACl and  $\text{Al}_{13}$  were dosed, only slight pH decrease could be observed. It can be explained by the differences of hydrolyzing potentials between monomeric and preformed polymeric Al species.  $\text{AlCl}_3$ , mainly consisted of monomeric Al species, has much stronger hydrolyzing tendency than preformed polymeric coagulants once added into test

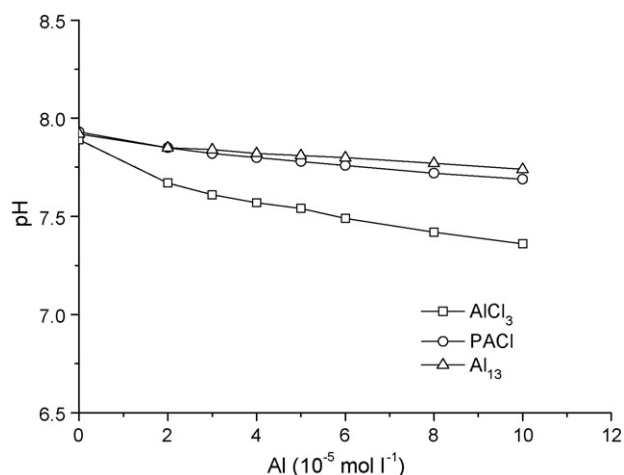


Fig. 6. Changes of pH with dosage in coagulation of Direct Blue 86.

water, particularly when the pH and alkalinity of test water are at high levels.

Similar pH changing phenomena were also observed in the coagulation of other two dyes. It should be noted that the pH values after coagulation were all higher than 7.0 within the dosage range. In order to get more insight into the roles of preformed Al species in removal of dyes, the effect of pH on coagulation performance was further investigated.

### 3.2. Effect of pH on coagulation of direct dyes

The removal of each dye under different pH by  $\text{AlCl}_3$ , PACl and  $\text{Al}_{13}$  is presented in Fig. 7. The experiments were con-

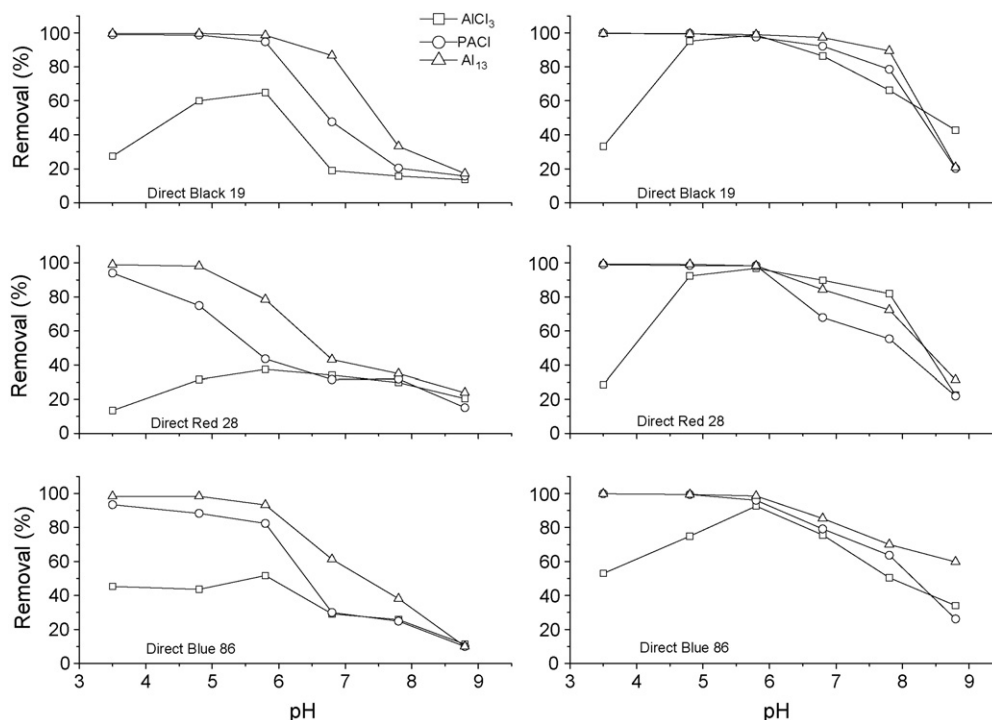


Fig. 7. Effect of pH on the removal of direct dyes by  $\text{AlCl}_3$ , PACl and  $\text{Al}_{13}$  (left column: Al dosage of  $3.0 \times 10^{-5} \text{ mol l}^{-1}$ ; right column: Al dosage of  $5.0 \times 10^{-5} \text{ mol l}^{-1}$ ).



ducted under two dosage levels of low and medium:  $3.0$  and  $5.0 \times 10^{-5} \text{ mol l}^{-1}$ , respectively. An obvious feature can be seen from the plots of Fig. 7 that the coagulation efficiencies of both PACl and  $\text{Al}_{13}$  tended to increase with the decrease of pH and approached almost complete dye removal when the pH was sufficiently low (less than 6.0). At the same time, appreciable and even large flocs were developed rapidly under depressed pH levels. However, the removal curves associated with different conditions were more or less different depending on the type of dyes, type of coagulants and level of dosages. Generally,  $\text{Al}_{13}$  could achieve better removal than PACl within the whole experimental pH range regardless of the type of dyes, and the superiority of  $\text{Al}_{13}$  was more obvious under the lower dosage of  $3 \times 10^{-5} \text{ mol l}^{-1}$ .

While in the case of  $\text{AlCl}_3$ , its coagulation efficiency increased first and then tended to decrease rapidly with the decrease of pH. The optimal pH range for  $\text{AlCl}_3$  varied with the type of dyes and level of dosages. Nevertheless, it can be deduced based on the overall results that the maximum removal occurred at pH around 6.0 for  $\text{AlCl}_3$ , which was in agreement with the results reported by Lee et al. [3]. It can also be seen that under higher dosage, the coagulation zone of  $\text{AlCl}_3$  was broader than that under lower dosage. In addition, the coagulation zones corresponding to Direct Black 19 and Direct Red 28 were larger than that corresponding to Direct Blue 86.

Another feature shown in Fig. 7 is that even at the optimal pH for  $\text{AlCl}_3$ , the coagulation efficiencies of both PACl and  $\text{Al}_{13}$  were higher than that of  $\text{AlCl}_3$  under most cases, particularly under the lower dosage of  $3 \times 10^{-5} \text{ mol l}^{-1}$ .

In order to better understand the coagulation behaviors of three coagulants, the dye removal changes with the increase of dosage were investigated at both pH of 5.8 and 3.5 (Fig. 8). It

is obvious that  $\text{Al}_{13}$  was the most efficient coagulant at both pH levels. PACl exhibited significantly higher removals than  $\text{AlCl}_3$  although the pH of 5.8 was within the coagulation zone favorable for  $\text{AlCl}_3$ . It can be seen that the coagulation features of  $\text{AlCl}_3$  were markedly different under pH of 5.8 and 3.5. If the dosage was high enough, the dye removal by  $\text{AlCl}_3$  was able to reach near 100% at pH 5.8. But under pH of 3.5, the coagulation efficiency of  $\text{AlCl}_3$  was dramatically deteriorated, and the dye removal could not achieve even 60% for all three dyes within the dosage range. Furthermore, in the coagulation of Direct Blue 86, the removal curve approached a plateau value of only 50% removal. Meanwhile, no observable flocs developed for all the jar tests associated with  $\text{AlCl}_3$  at pH of 3.5. It has been reported that the Al species was dominated by  $\text{Al}_a$  after dosing at pH of less than 4.0 when traditional Al salt was applied [21,24], thus it could be inferred that monomeric Al species was not effective for direct dye removal.

With the aid of dye removal measurement, careful observation of the floc developing process indicated that once appreciable flocs were formed, the dye removal could be reached relatively high levels of not less than 80%. The 80% removal seemed to be a critical point for removing direct dyes by coagulation. In order to more clearly elucidate the effect of pH on the performance of different coagulants, the dosages required to achieve 80% dye removal for different coagulants were obtained by interpolating the corresponding curves of dosage versus removal under different pH conditions (Fig. 9). The dosages to achieve 80% removal decreased greatly with the reduction of pH for both PACl and  $\text{Al}_{13}$ , and the associated dosages of  $\text{Al}_{13}$  were all lower than those of PACl. From pH 7.80 to 3.50, the dosages corresponding to 80% removal decreased more than 70% averagely for both PACl and  $\text{Al}_{13}$  despite the type of dyes.

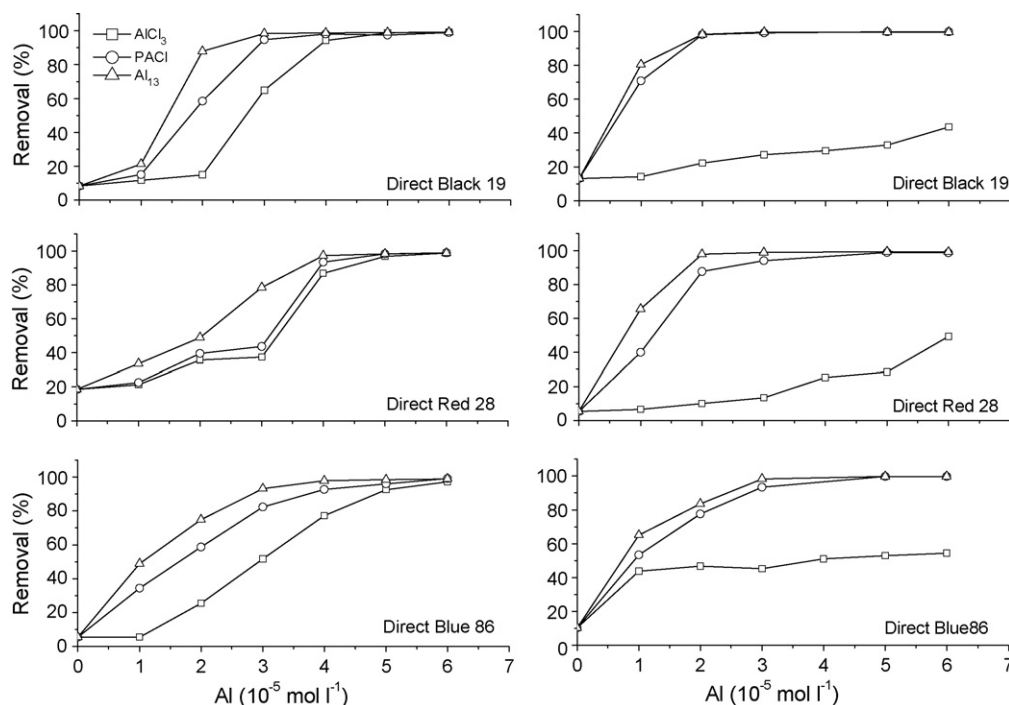


Fig. 8. Coagulation of direct dyes by  $\text{AlCl}_3$ , PACl and  $\text{Al}_{13}$  at pH of 5.8 and 3.5 (left column: pH 5.8; right column: pH 3.5).

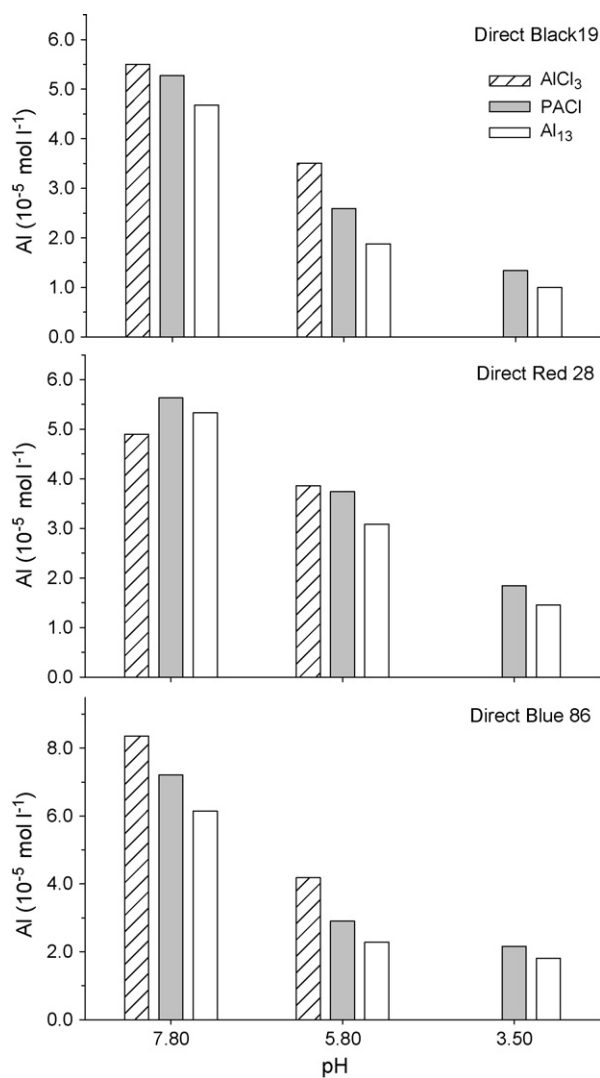


Fig. 9. Comparison of dosages required for achieving 80% dye removal at different pH conditions.

The required dosages of  $\text{AlCl}_3$  for 80% removal were lower at pH 5.8 than those at pH 7.80, but 80% removal was not able to be reached at pH 3.5.

As mentioned above, the type of dyes could affect the coagulation performance of different coagulants. To achieve 80% removal, Direct Blue 86 required higher dosage of PACl and  $\text{Al}_{13}$  than the other two dyes at pH of 7.80 and 3.50. However, at pH of 5.80, highest dosages of PACl and  $\text{Al}_{13}$  were needed for removal of Direct Red 28. When  $\text{AlCl}_3$  was applied, the highest dosage was with Direct Blue 86 at both pH of 7.80 and 5.80; while Direct Black 19 exhibited the poorest removal at pH of 3.50 (Fig. 8). Therefore, in order to achieve high treatment efficiency, the coagulation pH must be optimized based on the function of coagulants and the property of specific dyes at different pH conditions.

### 3.3. Further discussion

Many studies have confirmed that traditional coagulants and inorganic polymeric coagulants have much different coagulation

behaviors and mechanisms [18–21,26]. Charge neutralization is considered to be a prerequisite condition for most coagulation processes to occur. In the case of traditional Al salts, charge neutralization is induced by the Al hydrolysis products formed *in situ* after dosing. The *in situ* formed Al hydrolysis products could aggregate, rearrange and further hydrolyze to amorphous hydroxide precipitate. Such freshly formed amorphous solids can further neutralize, adsorb colloidal matters and function as bridges among fine particles. At high dosages, the coagulation caused by amorphous hydroxide can be a dominant mechanism, which is the so-called “sweep flocculation”. Previous work had demonstrated that  $\text{Al}_n$  species could disappear rapidly and evolve into polymeric species in 2 min after dosing, and then further change to hydroxide precipitate gradually. However, preformed Al species, such as  $\text{Al}_{13}$  and colloidal species could possess relatively high stability after dosing in a broad pH range [24]. Therefore, it is difficult for them to form Al hydroxide by way of *in situ* hydrolysis. Due to the high positive charge (+7),  $\text{Al}_{13}$  has strong charge neutralization ability for negatively charged colloids or large molecules. In addition,  $\text{Al}_{13}$ , with nanometer size, has tendency of self-assembly to form large aggregates, which makes it effective to function as bridges among particles. Thus,  $\text{Al}_{13}$  is considered to be the most efficient species for coagulation/flocculation by some researchers. As to the colloidal Al species ( $\text{Al}_c$  component), its charge neutralization ability is much less than that of  $\text{Al}_{13}$ , although its stability is relatively high too. It has been observed that under some circumstances, the coagulation efficiency of colloidal Al species could be higher than that of  $\text{Al}_{13}$  species due to the larger size of such species. “Electrostatic patch coagulation” has been put forward to interpret the coagulation mechanism of colloidal Al species [19].

All the direct dyes used in this study contain sulfonic functional groups, which are negatively charged when dissolved in water. The electrostatic repulsion between negative charges on different molecules enhances the solubility of dyes. In order to coagulate these dyes, the negative charges of dye molecules need to be sufficiently neutralized. It could be one of the reasons that  $\text{Al}_{13}$ , with high charge neutralization ability, is superior to the other coagulants in general. In the coagulation of Direct Red 28 under pH of tap water (Fig. 5), the higher removal by  $\text{AlCl}_3$  might be due to the “sweep flocculation” mechanism, which is inclined to occur at high dosage and high pH conditions.

On the other hand, with the decrease of pH, dye protonation processes could lead to reduction of charge density and induce self-aggregation of dye molecules. Therefore, less coagulant would be required to destabilize them. As noted in Fig. 7, the coagulation of the dyes became much more easier with the decrease of pH (with the exception of pH less than 6.0 in the case of  $\text{AlCl}_3$ ). When  $\text{AlCl}_3$  was used as coagulant, the changing trend of dye removal with pH implied that the intermediate Al hydrolysis products (such as six-member ring Al species) could play an important role in dye coagulation process. When the pH was high (greater than 7.0), the Al hydrolysis could continue very rapidly and amorphous hydroxide would form in a short time. Thus, amorphous hydroxide was deemed to be the major product inducing the coagulation/flocculation. Due to the

weaker charge neutralization ability, amorphous hydroxide was not effective in dye removal, particularly when the dosage was low. When the pH was in the low range (less than 5.0), the Al hydrolysis could be significantly inhibited, and the monomeric and/or oligomeric Al species would exist for a long duration, and these species was not as effective as polymeric Al species in terms of both charge neutralization and particle bridging functions.

#### 4. Conclusion

Al based coagulants could be used to treat waters polluted by some direct dyes. The coagulation performances of traditional Al salt, PACl and purified Al<sub>13</sub> were significantly different due to their different speciation characteristics. Preformed Al species, particularly Al<sub>13</sub>, could play important roles in the coagulation of direct dyes.

Adjustment of pH was necessary for improving dye removal efficiency and saving coagulant usage. For PACl and purified Al<sub>13</sub>, the decrease of pH was always beneficial for enhancing dye removal. With respect to traditional Al salt, an optimal pH of around 6.0 should be used.

Generally, purified Al<sub>13</sub> had the highest dye removal efficiency. The importance of Al<sub>13</sub> in coagulation of direct dyes could be attributed to its high charge neutralization ability, relative anti-hydrolysis stability and its nanometer-sized structure with self-assembly tendency.

#### Acknowledgement

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