

# Coagulation efficiency and floc structural characteristics of ferrum-polymer dual-coagulant for treatment of synthetic dyes wastewater

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## Abstract

In this study, the cationic lignin-based flocculant was prepared and used with polyferric chloride (PFC) to treat disperse and reactive dyes wastewater. The effects of dosage, initial pH, hardness and ionic strength on the interactions and floc properties were studied. Results showed that hydroxyl and quaternary ammonium groups of LBF could combine with -NH- and sulfo groups of dyes. Large flocs with extended structure were formed due to the absorption bridging and charge neutralization effect of LBF. Solution pH had a significant effect on floc size and compactness by the variance of Fe(III) hydrolysates and charge of LBF. Moderate hardness and ionic strength both could improve floc properties but the mechanisms were different:  $\text{Ca}^{2+}$  ions could combine with hydroxyl and sulfo groups to produce chelates and decrease the electric repulsion simultaneously,  $\text{Na}^+$  ions only compressed the electric double layer. Excess hardness and ionic strength showed a slight influence because of the limited binding sites and strong electric repulsion, respectively.

## Keywords

Lignin-based polymer; Dual-coagulant; Floc properties; Flocculation mechanism; Decoloration

## INTRODUCTION

In Textile and dyeing industries, a large amount of water is consumed and much larger quantities of wastewater are discharged subsequently due to its special manufacturing operations (Torrades & García-Montaño 2014). Dyes wastewater accounts for 40 percent of the yield of the whole industries (Zhu *et al.* 2011). Generally, wastewater containing anionic dyes poses a direct threat to environment and health. Some investigators reported that dyes had bioaccumulation and biological toxicity including carcinogenicity, teratogenicity and mutagenicity (eg., tumors, cancers and allergies) (Saratale *et al.* 2010; Zhang *et al.* 2011). Besides, parts of dyes would damage and inhibit the growth of bacteria, protozoan, plants and aquatic organisms (Khalid & Mahmood 2015). Due to the variable yield and the wide diversity of dyes properties, it is necessary to develop a commonly used technology to treat these wastewaters (Ge *et al.* 2012). High consumption of oxidant, secondary pollution and residual dye molecules through decomposition limit the application of advanced oxidation (Fang *et al.* 2010). Traditional biological methods are unlikely to achieve good performance because of unstable pH and the low ratio of biological oxygen demand to chemical oxygen demand (COD) (Torrades & García-Montaño 2014). Adsorption processes need a long time and have a restricted adsorption capacity. Other methods, such as membrane distillation, ion exchange and membrane electrowinning, always need high constructive, operational and maintainable expenditure (Ciminelli *et al.* 2006).

Coagulation/flocculation processes is one of the most widely used water treatment technology for the removal of organic matter with relatively low cost. And it has been demonstrated to be widely used as the pretreatment process. Coagulated effluent quality is highly dependent on coagulants (Liang *et al.* 2014). Traditional coagulants including aluminum and ferric-based salts have some drawbacks: to achieve identical efficiency, high dosages are used and large volume of sludge is

produced accordingly. Ferric-based salts hardly have toxicity and are conducive to the growth of activated sludge and biological films in the coagulation and bio-treatment combined processes (Edzwald 1993). Previous researches showed that metal coagulants in combination with polymers were one of the most efficient and widely used coagulation methods (Ou *et al.* 2014). Thus the development of novel flocculants has attracted more attention. To promote environmental sustainability, researchers have made efforts to synthesize efficient polymers utilizing industrial and agricultural wastes as raw materials. For instance, there are more than 10,000 papermaking enterprises in China and thus papermaking black liquor or sludge is discharged in a large amount (Wang *et al.* 2009). Among them, the abundant biomass (mainly lignin) cannot be reclaimed efficiently at the current stage. Lignin monomer composes of aromatic rings with methoxyl and hydroxyl groups, which providing the possibilities of producing value-added chemicals (Azadfar *et al.* 2015). Rong *et al.* reported it was possible to develop a neutral flocculant (LA) by recycling lignin containing in papermaking sludge (Rong *et al.* 2014). Based on previous literatures, the application of cationic papermaking sludge-based flocculant and the researches of floc structural characteristics using dual-coagulant (ferrum combined with papermaking sludge-based polymer) in dyes wastewater are still limited. In addition, coagulation performance not only depends on the characteristics of coagulants but also the water quality parameters (Daviau *et al.* 2000). Previous studies have widely investigated the influence of initial pH, but the effects of hardness and ionic strength on the removal of dyes by dual-coagulation have not been systemically studied.

In this study, a cationic lignin-based flocculant (LBF) was prepared by grafting polyacrylamide and dimethyl diallyl ammonium chloride (DADMAC) onto lignin existing in papermaking sludge. And it was used with polyferric chloride (PFC) to treatment disperse and reactive dyes wastewater. Floc properties were characterized by flocculation index and time-weighted ratio variance. The effects of coagulant dosages, dyes types, solution pH, hardness and ionic strength on floc structural characteristics and coagulation efficiency were studied in detail. Coagulation mechanisms and interactions under different conditions were also discussed.

## **MATERIALS AND METHODS**

### **Chemicals**

In this study, coagulant dosages were calculated by ferric content (mg Fe/L). PFC solution was prepared by adding Na<sub>2</sub>CO<sub>3</sub> solution (18.9264 g/L) drop by drop into FeCl<sub>3</sub>·6H<sub>2</sub>O (10.0 g Fe/L) solution under the magnetic stirring. A certain amount of Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O with a P/Fe ratio of 0.08 was added into the liquor as a stabilizer till no bubble existing and the mixture was stirred another 3.0 h before usage (Li *et al.* 2015). LBF was prepared from dried papermaking sludge (obtained from an alkaline papermaking mill in the Linyi City, Shandong Province, China) by extracting lignin, addition reaction, separation and purification successively .

### **Coagulation tests**

Simulative dyes wastewater with a concentration of 100 mg/L was prepared by dissolving disperse yellow RGFL (D-Y) and reactive blue KN-R (R-B) directly into tap water. The physicochemical properties of raw water were listed in Table 1. Before coagulation, water samples were adjusted to the predetermined pH by 0.1 mol/L HCl and NaOH solutions. The total hardness of raw water was adjusted to given levels by CaCl<sub>2</sub> and the dosages were calculated as the concentration of CaCO<sub>3</sub>. Sodium chloride was used to regulate the ionic strength of the test water. Water samples were mixed uniformly before treatment. Coagulation tests were performed in 1.5 L beakers by a program-controlled jar tester (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). Based on optimization experiments, the whole coagulation processes consisted of three steps and detailed parameters were listed as follows: (I) rapid mixing: adding predetermined

amounts of PFC and LBF at an interval of 30 s into water samples. This dual-coagulation was denoted by PFC+LBF. And then the system was stirred at 200 r/min for another 1 min. (II) slow mixing: reducing the stirring speed to 35 r/min and maintaining 12.5 min. (III) precipitation: letting it stand for 15 min.

### Floc dynamics

The dynamic processes of floc aggregation for treatment of synthetic dyes wastewater were online monitored through an optical unit of photometric dispersion analyzer (PDA 2000, Brother Co. Ltd., UK). The suspension maintained flowing at a rate of 2.0 L/h through inflow/outflow tube by a peristaltic pump. The output data of PDA 2000 was the average ratio of the root mean square (RMS value) to transmitted light intensity (DC value) and recorded per second. Based on Gregory and Carlson (McCurdy *et al.* 2004), ratio of DC to RMS (denoted as *Ratio*) is significant positive correlation linear with floc size under the given conditions.

## RESULTS AND DISCUSSION

### Dosage optimization

Coagulation performance in the treatment of D-Y under different conditions was characterized by color removal efficiency. The results are shown in Fig. 1a.

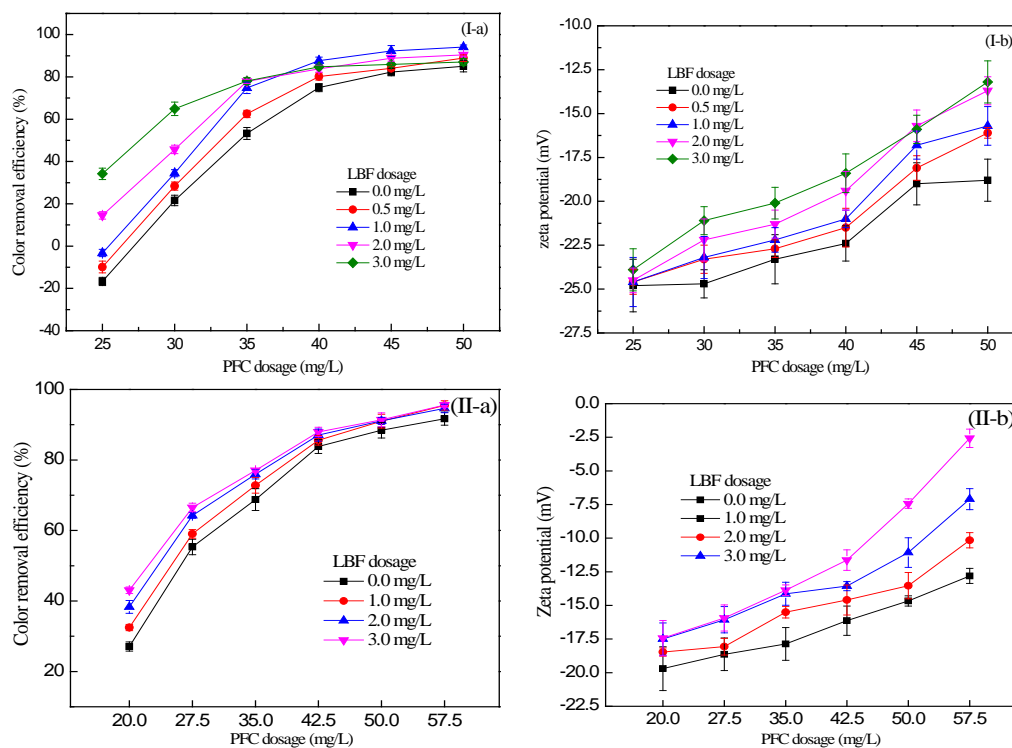


Figure 1 Coagulation efficiencies of coagulant dosages in the treatment of D.Y. (I) and R. B. (II) wastewater: (a) color removal efficiency; (b) zeta potential.

It was obviously that color removal ratio rose with the increase of coagulants dosage and then maintained steady when PFC were dosed over 40 mg/L. When the dosage of coagulants was lower, a part of D-Y substances were coagulated by Fe species. Formed flocs were micro and suspended in the water sample. These flocs enhanced the absorbance value of treated water greatly and hence color removal efficiency was minus at the dosage of 25 mg/L. PFC combined with LBF (1 mg/L) enhanced approx. 10% D-Y removal compared with single PFC, which demonstrated flocculating effect of LBF. The addition of LBF could also enhance color removal efficiencies in the treatment

of R-B, which was shown in Fig. 1b. During the PFC dosage range of 20.0-42.5 mg/L, PFC combined with 3.0 mg/L LBF increased R-B removal ratio by 5-16 % compared with single PFC. When PFC was dosed more than 50 mg/L, the effect of LBF dosage on coagulation efficiency was unapparent, while color removal efficiencies all reached more than 90 % under these conditions and PFC+LBF dual-coagulant further rose color removal efficiency by 3%. According to the above result, the optimal PFC and LBF dosages for the subsequent experiments were chosen as 40 mg/L and 1.0 mg/L in the treatment of D-Y wastewater, respectively. And 42.5 mg/L of PFC and 1.0 mg/L LBF were used to treat R-B water samples.

### Coagulant dosage

To analyze the effect of coagulant dosage on floc properties, floc dynamics were monitored by a photometric dispersion analyzer. As illustrated in Fig. 2,  $FI_0$  of flocs increased with PFC dosage and then showed a drop when the dosage reached 45 mg/L in the coagulation of D-Y. When PFC was 25 mg/L,  $FI_0$  was lower than 0.20 and most flocs were difficult to precipitate. When LBF was added alone,  $FI_0$  rose to 0.94 and more D-Y was removed by natural sedimentation. In the range of 30-50 mg/L,  $FI_0$  increased by 0.23-0.58 when LBF was dosed on the basis of equal PFC, which demonstrated the efficiency of LBF as a coagulation aid. For R-B,  $FI_0$  showed the same tendency with that of D-Y.  $FI_0$  peaked at PFC dosages of 35 and 42.5 mg/L for PFC and PFC+LBF coagulated flocs, respectively. The maximum  $FI_0$  values in PFC and PFC+LBF systems were 0.73 and 0.83 separately. Overall, TWV showed a decreasing trend as PFC dosage increased both in the treatment of D-Y and R-B wastewater, which indicated the formation of more compact flocs at higher PFC dosage. The TWV of flocs formed by PFC+LBF was larger compared with PFC, which demonstrated that flocs coagulated by PFC+LBF had a looser structure and wider size distribution.

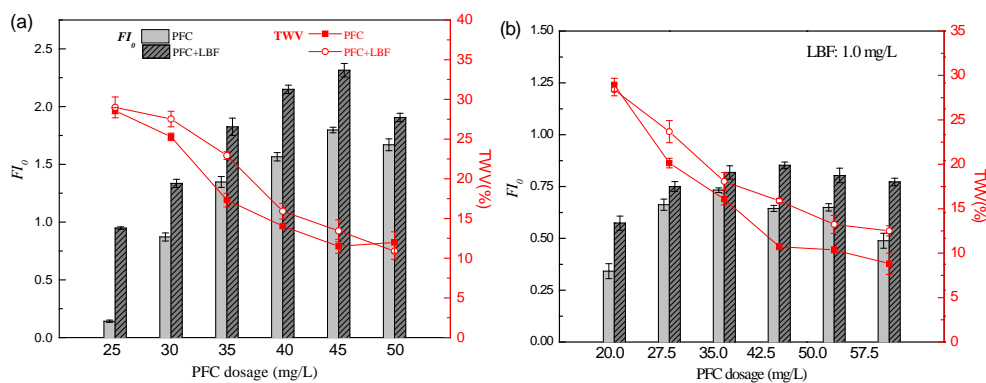


Figure 2 Variance of  $F_0$  and TWV under different PFC dosage conditions in the treatment of D-Y (a) and R-B (b)

At lower PFC dosages, the comparatively strong repulsion forces between the dyes and the ferric species impede floc formation. Also, limited Fe hydrolysates are hard to react with sufficient dyes to produce complexes. When more PFC is dosed, more dyes are coagulated to form the larger flocs with compact structure. With the further increase of PFC dosage,  $FI_0$  showed a drop due to the decrease of internal repulsion forces between flocs. Wei et al. has demonstrated that floc structural characteristics depend on coagulation mechanisms, which are related to the chemical structures of the dyes and hydrolysates of the coagulant as well as the characteristics of the flocculant. As shown in Table 1, the D-Y monomer has abundant hydrophobic groups, such as amidogen, ether, phenyl and amide groups, which tend to be absorbed and swept by ferric hydrolysates (Kim *et al.* 2004). Whereas R-B has negatively charged  $-SO_3^-$  groups as well as high solubility. Ferric ions and hydrolysates can unite with sulfo groups to produce stable chelates. With the action of hydroxyl ions, the chelates are prone to transform into precipitates by the charge neutralization and bridging effect of polymeric ferric hydrolysates. Consequently, entrapment and charge neutralization are the

dominant mechanisms in the coagulation of D-Y and R-B, respectively. Ray and Hoog reported that flocs formed in bridging and sweeping flocculation are much larger than those formed by charge neutralization (Ray & Hogg 1987). Li et al. also have showed that compactness of flocs formed by different mechanisms are in the order of sweeping > charge neutralization > bridging (Li *et al.* 2006). Therefore, flocs in D-Y coagulation have a relatively larger  $FI_0$  and TWV compared with R-B. In the case of PFC+LBF, LBF can neutralize negatively charged dyes and relieve inter repulsion between the destabilized flocs. Hydroxyl groups existing in LBF could combine with -NH- of dyes through the effect of hydrogen bonds (Yang *et al.* 2012). Additionally, unsaturated functional groups in LBF could enhance the adsorption effect.

Then the LBF chains acted as bridges between flocs. Steric crowding of Fe(III) hydrolysates and the repulsive forces between micro flocs promoted the chains of LBF to be extended, leading to the formation of large but open-structure flocs. The diagram of mechanism is shown in Fig. 3. Thus the charge neutralization and absorption bridging effect of LBF promotes the formation of flocs with a relatively larger size and looser structure.

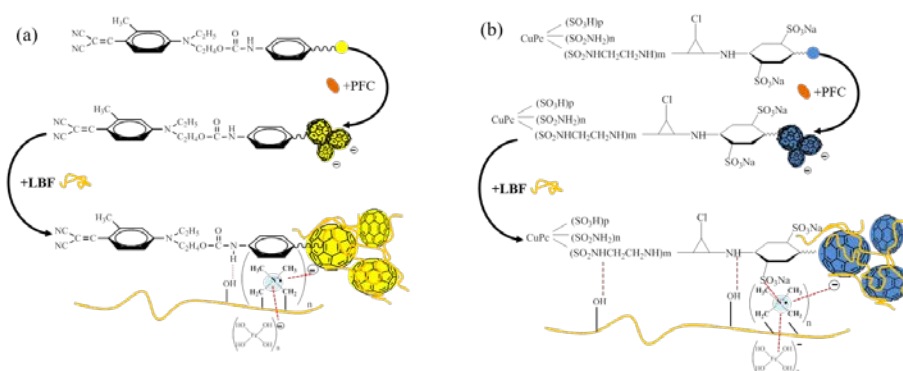


Figure 3 The mechanism schematics of PFC+LBF dual-coagulant in the treatment of (a) D-Y and (b) R-B

### Solution pH

Effect of solution pH on floc dynamics was also monitored and these results are shown in Fig. 4. In the treatment of D-Y, the maximum  $FI_0$  was achieved at pH 6.0 and it decreased significantly under alkaline conditions, especially at pH 10, where  $FI_0$  was less than 0.70 and zeta potential was about -28.7 mV (Fig. S2). When dosing PFC+LBF,  $FI_0$  peaked at 6.5 but showed a little change in the range of 5-9. Although  $FI_0$  decreased to 0.99 at pH 10, flocs which coagulated by PFC+LBF could be removed by natural settling processes. Thus after the addition of LBF, color removal ratios increased from 13.3% to 55.1% at PFC dosage of 40 mg/L. TWV values in PFC+LBF systems were all above those of PFC. But the differences were slight under acidic conditions but were great when pH was larger than 7. In the treatment of R-B, the values of  $FI_0$  were approximate under acidic conditions and then decreased with the further increase of pH. Overall, the values of TWV under acidic conditions were larger than those under alkaline conditions. PFC+LBF dual-coagulant could also enhance the  $FI_0$  and TWV significantly compared with equal PFC during the investigative pH range.

As shown in Fig. 3, the variance trends of  $FI_0$  and TWV versus initial pH were similar with those of PFC, which demonstrated that Fe(III) hydrolysates played a foremost role in dual-coagulation in terms of pH variation. Based on the previous studies, the transformation of Fe(III) hydrolysates is significantly affected by pH. When pH is less than 7, the action of hydroxyl ions is limited and Fe(III) hydrolysates are more likely to be positively charged complexes, such as  $FeOH^{2+}$ ,  $Fe(OH)_2^+$ ,  $Fe_2(OH)_2^{4+}$  and  $Fe_3(OH)_4^{5+}$  (Gabelich *et al.* 2002). For R-B, those cationic Fe(III) hydrolysates

could react with the sulfo and sulfonyl groups ( $-\text{SO}_3^-$  and  $\text{R-SO}_2^-$ ) by electrostatic interaction (Wei *et al.* 2009) and then sulfo/sulfonyl groups-Fe(III) hydroxide complexes were produced. Thus reactive blue molecule would be transformed into colloid flocs and then be removed. For D-Y, there not existed obvious electrostatic interaction in the absence of sulfo groups. But negative charge existing in the disperse yellow molecule could be neutralized, where charge neutralization was the leading mechanism (Palomino *et al.* 2011). Under alkaline conditions, PFC would hydrolyze to  $\text{Fe}(\text{OH})_3$  even  $\text{Fe}(\text{OH})_4^-$  or  $\text{Fe}_2(\text{OH})_8^{2-}$  when  $\text{pH} \geq 10$  (Gabelich *et al.* 2002). As drawn from Fig. S2, there was a negative correlation between  $\text{FI}_0$  and absolute value of zeta potential. Notably, the huge electrostatic repulsion between micro flocs hindered the growth of  $\text{FI}_0$  under alkaline conditions. More compact flocs were formed under alkaline conditions due to the sweeping effect in both reactive and disperse dyes water treatment, which was similar with Section 3.2.1.

As shown in Fig. S3, solution pH also had an effect on the charge of LBF. With the decrease of pH, the zeta potential of LBF showed a rising trend due to the improvement of protonation (Hunter 2013). Under acidic conditions, average zeta potential was +35 mV. And it dropped to +28 mV in the pH range of 8-9 and even +20 mV when pH rose to 10. So with the decrease of pH, relatively stronger charge neutralization was provided by LBF. But zeta potential was above isoelectric point in the range of 5-6, leading to the stronger electric repulsive. That is, charge neutralization of LBF did not provide positive effect on further growth of floc size. But the absorption bridging effect of LBF promoted the increase of  $\text{FI}_0$  in acid regions. Under alkaline conditions, LBF could react with  $-\text{NH}_x$  and neutralize negative charges to lower the solubility of dyes-Fe(III) hydroxide complexes (Kim *et al.* 2004; Wei *et al.* 2009). Finally, the complexes were destabilized by the bridging effect of LBF. Therefore, flocs coagulated by the bridging effect showed a looser structure as well as a larger TWV value.

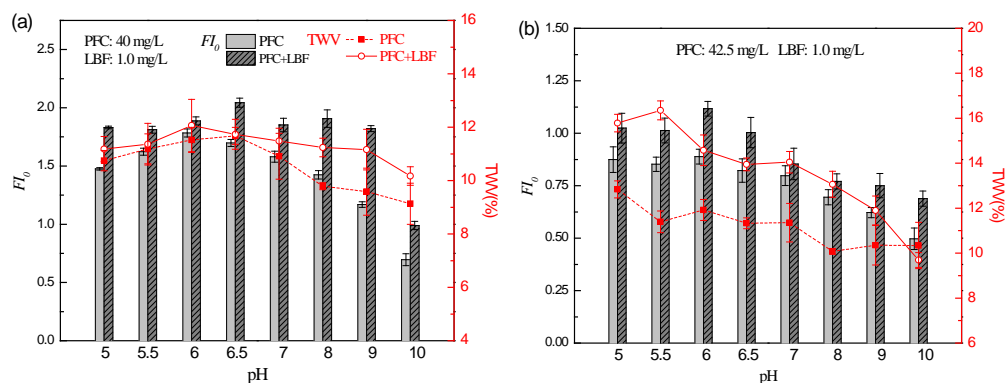


Figure 4 Effect of initial pH on  $\text{FI}_0$  and TWV in the treatment of (a) D-Y and (b) R-B

### Total hardness

Based on the level of total hardness, water can be classified from very soft water ( $< 89 \text{ mg/L}$  as  $\text{CaCO}_3$ ) to very hard water ( $> 535 \text{ mg/L}$  as  $\text{CaCO}_3$ ). Excessive hardness would lower the quality of textile and reduce the flux in the transportation (Wang *et al.* 2010). So total hardness of water used in the dyeing industries must be less than 325-400 mg/L, especially no more than 17.5 mg/L as  $\text{CaCO}_3$  in the given processes. In this study, six different hardness values of raw dyes water were determined as follows: 10 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L, 300 mg/L as  $\text{CaCO}_3$ . And the effects of total hardness under different conditions are presented in Fig. 5. In the treatment of D-Y,  $\text{FI}_0$  increased with hardness but growth rate slowed down till 150 mg/L. And more compact flocs were formed under larger hardness conditions. Further increase of hardness ( $> 150 \text{ mg/L}$ ) showed a slight effect on  $\text{FI}_0$  and TWV. The addition of Ca(II) could also increase the size of flocs in the coagulation of R-B. But the influence on the TWV was not significant: TWV of flocs in the

presence of Ca(II) was a little lower compared with those in absence of Ca(II). When LBF was dosed, the variance trend of  $FI_0$  versus total hardness was similar with that of single PFC. TWV showed an obvious decline in the range of 0-150 mg/L and then maintained steady in the PFC+LBF systems.

When D-Y was treated, pH of effluent coagulated by PFC in the presence and absence of Ca(II) was  $6.06 \pm 0.03$  and  $6.01 \pm 0.08$ , respectively. For R-B, those values were  $5.51 \pm 0.02$  and  $5.46 \pm 0.06$ . And the effect of hardness level on pH of effluent was negligible. So the hydrolysis of Ca(II) in the coagulation was limited at the pH of raw water. Tipping (Tipping 1994) has reported that  $Ca^{2+}$  can react with carboxyl, hydroxyl, phenolate and sulfo groups to produce chelate. So when  $Ca^{2+}$  ions were dosed, it first combined with the unsatisfied bonds of organic matter and neutralized the negative charge of dyes (Zhao *et al.* 2014). Then these Ca-dye chelates with weaker repulsive force would be absorbed and swept easily by colloidal  $Fe(OH)_3$  with large surface area after the addition of PFC. Larger flocs with dense structure were formed under higher hardness conditions. When Ca(II) was overdosed, binding sites in the dye molecule for  $Ca^{2+}$  ions were saturated and zeta potential of micro flocs change less (Zhao *et al.* 2014). So floc properties were independent of hardness level till 150 mg/L.

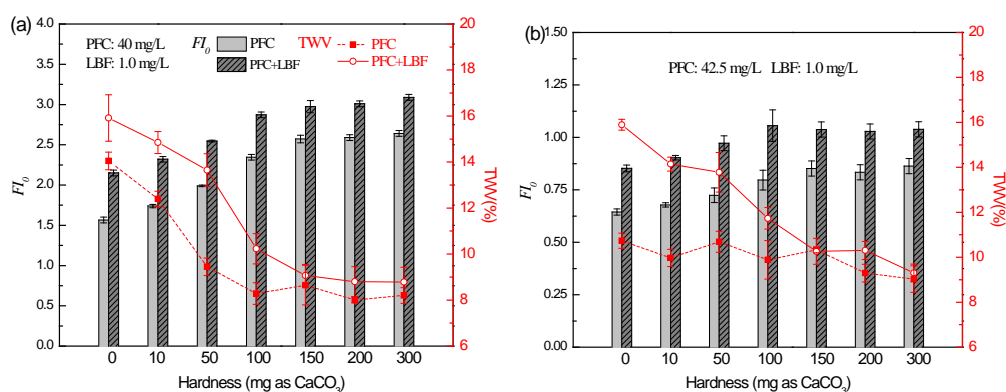


Figure 5 Variance of  $FI_0$  and TWV in the treatment of (a) D-Y and (b) R-B under different hardness condition

In the case of dosing LBF, pH of effluent in the treatment of D-Y and R-B wastewater was  $6.11 \pm 0.05$  and  $5.51 \pm 0.04$  in the absence of  $Ca^{2+}$  ions, respectively. These two values changed to  $6.06 \pm 0.11$  and  $5.49 \pm 0.07$  when  $CaCl_2$  was dosed. Addition of LBF could not facilitate the hydrolysis of Ca(II). But LBF chains could combine with not only Fe(III) hydrolysates-dyes but also  $Ca^{2+}$  ions to form the larger flocs. In the hardness range of 10-100 mg/L, TWV of flocs coagulated by PFC+LBF was larger than that of PFC, especially for R-B. That is to say, bridging effect of LBF offered a significant role in the formation of flocs. Thus flocs with open structure were formed under these conditions. Due to the decrease of absolute value of zeta potential as well as electrostatic repulsion, TWV presented a decline trend with the total hardness (Fig. S4). With the further increase of hardness, the combination of LBF chains and  $Ca^{2+}$ -Fe(III) hydrolysates-dyes trended toward constant due to the limited binding sites (Adachi *et al.* 2002). So the TWV changed a little in the range of 150-300 mg/L.

### Ionic strength

The content of dyeing wastewater is complex. Except  $Ca^{2+}$ ,  $Mg^{2+}$  and a handful of heavy metals, there exists abundant metal ions (i.e.  $Na^+$ ), which are not restrained by the water quality standards. In this study, the influence of ionic strength on the floc properties coagulated by ferric-polymer dual-coagulants was determined and the results are presented in Fig. 6. When PFC was used to treat

D-Y,  $FI_0$  showed an increase in the ionic strength range of 0-0.10 mol/L and maintained approx. 2.25 as the ionic strength further rose. TWV decreased continuously during the investigative range. In the case of dosing LBF, the variance trends of  $FI_0$  and TWV were similar with those of single PFC. For R-B, the effect of ionic strength on floc properties in PFC coagulation was slight:  $FI_0$  increased a little but TWV decrease slightly with ionic strength. An obvious drop of TWV was observed in the range of 0-0.07 mol/L in the PFC+LBF system.

$Na^+$  ions cannot hydrolyze in the aqueous environment or combine with organic matter to produce chelate. But the introduction of ionic strength ( $Na^+$  ions) could offer positive charge and then compress electric double layer. Once Fe(III) hydrolysates-dyes complexes were formed,  $Na^+$  ions were permeated through the surface of these complexes and neutralize their negative charges (Palomino *et al.* 2012). Therefore larger flocs with the compact structure were formed at the high ionic strength due to the relatively weak electric repulsion. Considering that not all the  $Na^+$  ions could combine with these complexes efficiently, zeta potential was not the single parameter to determine the effect of  $Na^+$  ions (Fig. S5) (Hunter 2013). Zhao *et al.* (Zhao *et al.* 2014) has reported that the increase of ionic strength could accelerate sweeping coagulation because of the compressed electric double layer. As discussed in Section 3.2.1, the foremost mechanism of the removal of D-Y was sweeping effect, but charge neutralization was more efficient to remove R-B. Therefore, the effect of ionic strength on floc properties was more significant in the treatment of disperse yellow. When PFC and LBF were used to treat reactive blue, the variance trend of TWV was consistent with that of zeta potential in the range of 0-0.10 mol/L. When the ionic strength was too large, excessive  $Na^+$  ions would not be neutralized by Fe(III) hydrolysates-dyes complexes and remain in the surface of micro flocs. These  $Na^+$  ions hindered LBF chains to infiltrate into different flocs and promoted the chains to be extended (Mabire *et al.* 1984). Thus more loose flocs were formed under these conditions, which was consistent with the results of Zhao *et al.* (Zhao *et al.* 2014).

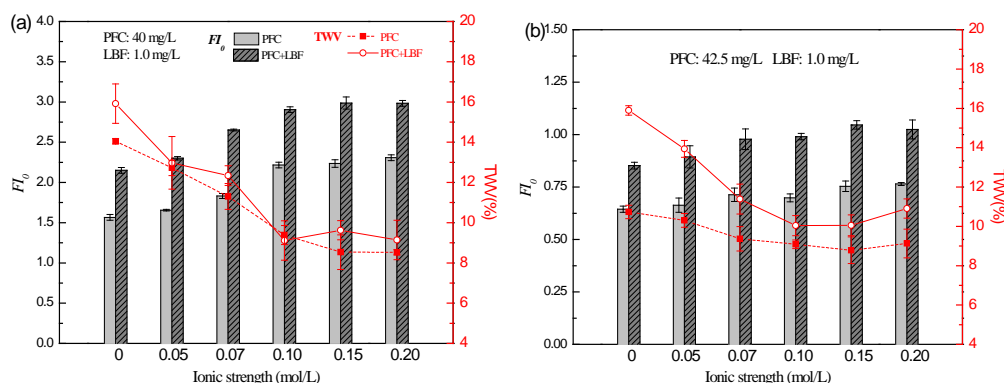


Fig. 6 Schematic of  $FI_0$  and TWV of flocs coagulated by PFC+LBF in the treatment of (a) D-Y and (b) R-B under different ionic strength conditions

## CONCLUSIONS

- i) Due to the difference of molecular structure, the foremost mechanisms to remove D-Y and R-B were sweeping and charge neutralization, respectively. LBF could combine with -NH- and sulfo groups, and introduce strong absorption bridging and charge neutralization effect. Thus addition of LBF could increase the removal ratios of D-Y and R-B. And larger flocs with the extended structure were formed.
- ii) In acidic regions, charge neutralization of Fe(III) hydrolysates and bridging effect of LBF promoted the formation of flocs with large size. Under alkaline conditions, flocs with compact structure were formed because of the sweeping of  $Fe(OH)_3/Fe(OH)_4^-$  and charge neutralization of LBF.



- iii) Both for D-Y and R-B, floc size and compactness increased with the total hardness due to the decrease of electric repulsion and the chelation of  $\text{Ca}^{2+}$  combined with hydroxyl and sulfo groups. In the dual-coagulation, TWV changed slightly in the range of 150-300 mg/L as  $\text{CaCO}_3$  due to the limited binding sites.
- iv) The effect of ionic strength on floc properties in the treatment of D-Y was more significant compared with R-B. Moderate ionic strength could improve floc properties by the compressed electric double layer.

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