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Coagulation behavior and floc structure characteristic of cationic lignin-based polymer-polyferric chloride dual-coagulants under different coagulation conditions

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Abstract

To recycle papermaking sludge, a novel lignin-based flocculant with high cationic degree and molecular weight was introduced. The product, lignin-diallyl dimethyl ammonium chloride-acrylamide (LDA) was combined with polyferric chloride (PFC) to treat simulated humic acid (HA) solution. To identify its flocculation mechanisms, coagulation efficiencies and floc properties under different dosing method and pH conditions were studied. Results showed that LDA was superior to polyacrylamide, poly diallyldimethylammonium chloride as well as lignin-acrylamide in the aspect of DOC and turbidity removal efficiencies, which demonstrated its significant flocculating efficiency. Compared with single PFC, the addition of LDA enhanced coagulation performance and floc properties including floc size, growth rate and recovery ability during the investigative pH range. Dosing sequence also showed an
effect on coagulation mechanism and performance. When PFC was dosed firstly, negatively charged Fe(III) hydrolysates-colloids were neutralized and bridged by LDA. On the contrary, colloids-LDA complexes with slightly negative charge were destabilized by the entrapment and sweeping effect of Fe(III) hydrolysates. As a result, coagulation efficiencies were in the order: PFC dosed firstly (PFC+LDA) > LDA dosed firstly (LDA+PFC) > PFC. PFC+LDA achieved the maximum floc size and growth rate, while flocs with the most open structure was formed by LDA+PFC. Moreover, the effect of solution pH on coagulation behavior was noteworthy due to the variance of hydrolyzed Fe species. PFC was more sensitive to pH in the aspect of coagulation efficiencies and flocs structure. The variations caused by different pH lowered after the addition of LDA. Regardless of the coagulant types, the optimal coagulation performance and floc characteristics were achieved under acidic conditions, especially at pH 6. Overall, LDA could introduce strong charge neutralization and adsorption bridging effect during relatively wider pH range and offer a positive effect on coagulation behavior and flocs properties.

**Keywords:** Lignin-based polymer; Polyferric chloride; Coagulation model; Flocculation mechanism; Solution pH

1. Introduction

The presence of natural organic matter (NOM) in aquatic environment has attracted more and more attention owing to its environmental impact and potential harm to human health. Many researchers reported that NOM was the carrier of heavy metals and hazardous chemicals \(^1\). Furthermore, NOM could react with free chlorine
to form a series of genotoxic and carcinogenic disinfection by-products during chlorination. Coagulation/flocculation processes have been preferentially applied to dissolved and suspended organic matter removal due to low cost, high performance and easy operation. Coagulation efficiency and effluent quality are highly dependent on coagulants; previous researches have showed that synthetic polymers in combination with metal coagulants could achieve better coagulation behaviors. In order to satisfy the increasing demand of environmental friendliness and NOM removal efficiency, it is crucial to develop modified natural polymeric flocculants, especially making use of industrial and agricultural by-products.

Pulp and papermaking sludge is a largely generated waste product in water treatment processes of papermaking industry, for instance, about 8 and 30 million tons per year in United States and China separately. Traditional disposal methods such as landfill, combustion and bio-compost are restricted to the ingredients of sludge and more likely to cause secondary pollution. Owing to special organic composition (e.g., lignin, hemicellulose and cellulose), it is used as raw materials to produce chemical products such as polyelectrolyte, adsorbent, dispersant and scale inhibitor. Rong et al. reported a neutral lignin-acrylamide flocculant (LAM) and demonstrated that it could enhance coagulation performance in combination with aluminum coagulants. However, it was difficult for LAM to remove NOM with low zeta potential as well as small molecular weight. Generally, a flocculant with higher cationic and molecular weight could achieve better removal of negative micro particles. So far, there have been few reports about preparation and application of cationic flocculant using lignin.
as well as papermaking sludge.

Floc characteristic (e.g., floc size, growth rate, recoverability and compactness) had an effect on coagulation behavior and the cost of water treatment. As a result, it was always used to evaluate the efficiency of chemicals. In general, the larger flocs, the quicker sedimentation velocity \(^{12}\). Faster growth rate requires a relatively small tanker in actual water treatment. Flocs recovery factors stand for the ability to regrow. Fractal dimension \((D_f)\), a quantitative index to describe flocs structure, is co-determined by flocs mass and size. Flocs with lower \(D_f\) have a looser or branchy structure, while higher \(D_f\) value stands for a more compact structure. \(^{13}\). Therefore, it is considered to be significant to investigate the influence of coagulant species and hydraulic conditions on floc formation processes. Previous studies demonstrated that floc properties were related with coagulation mechanisms\(^{14,15}\). However, literatures about floc characteristics in cationic lignin-based polymer coagulated effluent and their relationship with hydraulic conditions were still limited.

In this study, lignin-based flocculant LDA was synthetized through grafting diallyl dimethyl ammonium chloride (DADMAC) and acrylamide (AM) onto lignin containing in papermaking sludge in the presence of \(K_2S_2O_8\) and edetate disodium. To demonstrate its flocculating efficiency, comparison of coagulation performance between LDA and other flocculants including polyacrylamide (PAM), polydimethyldiallylammonium chloride (PDADMAC) and lignin-acrylamide (LAM) was studied. The effect of dosing method including polyferric chloride (PFC), PFC+LDA (PFC was dosed firstly) and LDA+PFC (LDA was dosed firstly) and solution pH on
coagulation performance and floc proprieties in kaolin-humic acid (HA) water treatment were comparatively studied. Coagulation models of LDA combined with polyferric chloride (PFC) under different conditions were described to further understand the mechanisms.

2. Materials and methods

2.1. Preparation of coagulants and test water

LDA was made from dried papermaking sludge, which was acquired from an alkaline paper mill of Shandong Province, China. The synthetic route was grafting acrylamide (AM) and dimethyl diallyl ammonium chloride (DADMAC) onto alkali lignin containing in dried sludge. The detailed steps (Fig. 1) were as follows: firstly, sludge power in aqueous alkali was centrifuged to obtain lignin supernatant and then transferred into a three-neck round bottom flask; secondly, K$_2$S$_2$O$_8$ and edetate disodium were successively added with N$_2$ inlet. Then certain amounts of AM and DADMAC were dripped into the reactor at 70 °C; thirdly, the product was extracted with acetone, soxhlet extracted with acetone-ethanol and then washed with ethanol after 3 h reaction; finally, the product was vacuum dried at 50-60 °C. The physicochemical properties of LDA were listed as follows: molecular weight = 800-1100 KDa, cationic degree = 28.9±1.4 %, Viscosity (60 rpm at 25 °C) = 1.110±0.045 mPa•s. In addition, zeta potential of LDA under different pH condition was shown in Fig. S2.

PAM with molecular weight of 3000 KDa was purchased from Sinopharm Chemical Reagent Co., Ltd. Beijing. The cationic polymer PDADMAC was obtained
from Bin Zhou Chemical Co., Shandong, China. LAM was prepared based on Rong et al. These solutions were all prepared with a concentration of 1.0 g/L and stored at 4 °C before usage.

PFC stock solution with B value ([OH\(^-\)]/[Al\(^{3+}\)] mole ratio) of 0.5, was prepared based on Wei et al. Humic acid (Aladdin Industrial Corporation, Shanghai, China) and kaolin stock solution was used to synthesize HA-kaolin samples. The physicochemical characteristics of raw water were as follows: pH = 8.20 ± 0.05, DOC = 4.450 ± 0.320 mg/L, turbidity = 15.0 ± 0.5 NTU.

2.2. Jar tests

To determine the effect of pH on coagulation performance, predetermined pH value (from 4 to 9) of samples was adjusted by 1.0 mol/L HCl and NaOH solutions. Standard jar tests were conducted on a program-controlled jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China) at 25 ± 2.0 °C. Operation procedure was follows: i) under the phase of rapid stirring (G = 102.5 s\(^{-1}\)), predetermined amount of PFC and flocculant were dosed with different dosing sequence; ii) after 1.0 min, mixing speed was reduced to 11.8 s\(^{-1}\) with a duration of 15 min; iii) water samples were collected after quiescent settling for 20 min.

Zeta potential of coagulated water sample was measured by Zetasizer 3000HSa (Malvern Instruments, UK) immediately after rapid stirring without dilution. Turbidity collected water was measured directly via Portable turbidimeter 2100P, Hach, US. Filtered water (by 0.45µm fiber membrane) was used to test DOC (with TOC analyzer, Shimadzu, Japan).
2.3. Floc characteristics

Dynamic floc size was online monitored by Malvern Mastersizer 2000 (Malvern, UK). Coagulation experiments were conducted on the jar tester mentioned above and running procedure was similar. Median equivalent diameter (d_{50}) was used to stand for floc size. In order to study coagulation mechanisms determining floc regrowth, breakage region and re-steady region were introduced after steady-state region. Floc growth rate, the slope of rapid growth region, was calculated as follows:

\[
\text{Growth rate} = \frac{\Delta \text{size}}{\Delta \text{time}} \tag{1}
\]

Floccs recover ability was expressed by recovery factor (R_f), as follows:

\[
R_f = \frac{d(3) - d(2)}{d(1) - d(2)} \times 100 \tag{2}
\]

where \(d(1), d(2)\) and \(d(3)\) are the average floc size in steady region, breakage period and re-growth region, respectively.

As a quantitative index to describe floc structure, fractal dimension of independently scattering aggregates was related with scattered light intensity \(I\) and scattering vector \(Q\), which is presented as follows:

\[
I \propto Q^{-D_f} \tag{3}
\]

Hence, \(-D_f\) can be expressed as the slope of a plot of log \(I\) as a function of log \(Q\).

3. Results and discussion

3.1 Comparison of coagulation performance between LDA and other flocculants

Comparison of coagulation performance between LDA and other flocculants was performed at the same flocculant dosage (1.0 mg/L) and the results were shown in Table 1. In PFC coagulation, the addition of polymer all could improve removal
efficiencies. At PFC dosage of 8 mg/L, PFC+LDA enhanced coagulation efficiencies significantly and the order was as follows: PFC+LDA > PFC+PAM > PFC+PDADMAC > PFC+LAM. Specifically, PFC+LDA enhanced the DOC and turbidity removal ratios by 11.3% and 13.5% compared with PFC+LAM. Zeta potential of flocs formed by PFC+LDA was slightly larger than those of other coagulants. This was related with the positive charge existing in the surface of flocculants. As illustrated in Table 1, relatively stronger repulsive forces between flocs (which could be drawn from zeta potential) hindered floc aggregation and thus coagulation efficiencies increased. When PFC dosage was 14 mg/L, the HA removal ratio in PFC+LDA system was 2.5-4.1% larger than those in other dual-coagulations. But the effect on improving turbidity removal efficiency was not remarkable. Under this condition, zeta potential of PFC+LDA flocs was far above those coagulated by other dual-coagulants. Overall, LDA was superior to PAM, PDADMAC as well as LAM in the aspect of DOC and turbidity removal efficiencies, which demonstrated its flocculation efficiency. The reason why LDA promoted the coagulation performance was listed in the following section.

3.2 Influence of pH on coagulation performance

Preliminary tests were performed to ascertain the optimum PFC and LDA dosage for HA and turbidity removal at the pH of raw water. According to previous studies, PFC dosage of 14 mg/L and LDA dosage of 1.0 mg/L were chosen to accomplish following experiments. In order to identify the influence of solution pH, coagulation
performance of PFC+LDA and LDA+PFC dual-coagulants were contrastively
evaluated in terms of turbidity and DOC removal ratios (Fig. 2).

DOC and turbidity removal appeared a different trend: when pH ≥ 7, DOC
removal efficiency decreased with pH, while turbidity removal efficiency maintained
stable in investigated range. Under acidic condition, DOC removal ratios at pH 4 and
5 were similar and less than that of pH 6. Nevertheless, turbidity removal showed a
significant enhancement as pH rose from 4 to 6. This phenomenon demonstrated the
difference of dominant coagulation mechanisms between DOC and turbidity removal.

As shown in Fig. 2c, zeta potential was negative when pH > 6 and then increased and
transformed into positive with the decrease of pH, which was related with the
variance of Fe(III) hydrolysates under different pH conditions. Under alkaline
condition, major Fe(III) species of PFC transformed into Fe(OH)$_3$ and Fe(OH)$_4^-$ with
the action of hydroxyl ions $^{20}$. As a result, zeta potential of PFC coagulated flocs was
less than -10.0 mV (Fig. 2c), which resulting in stronger repulsion forces between
flocs. It was believed that adsorption of HA or particle onto Fe hydroxides through
surface complexation or ligand exchange was the dominating mechanism under this
condition $^{21}$. When pH was lower than 6, PFC hydrolyzed to positively charged
complexes, such as Fe$^{3+}$, FeOH$^{2+}$, Fe(OH)$_2^+$ and Fe$_2$(OH)$_3^{4+}$ $^{20}$. Accordingly, absolute
value of zeta potential became lower under this condition and it achieved isoelectric
point at pH 6. Thus charge neutralization effect played a role in floc formation. In
conclusion, neutralization of negative charge showed a higher efficiency in humic
substances removal\textsuperscript{19}, while the mechanism dominating kaolin particles removal was
more related with sweeping effect\textsuperscript{22}.

In the case of LDA addition, DOC removal showed the same variation tendency
with that of PFC, but removal ratios improved obviously. In detail, PFC+LDA and
LDA+PFC enhanced the DOC removal efficiencies by approx. 5.0% compared with
PFC under alkaline condition. For turbidity removal, PFC lowered the removal ratio
by 33.6% and 14.4% compared with PFC+LDA and LDA+PFC at pH 4, respectively.
There existed differences of floc aggregation between PFC coagulation and
dual-coagulations (Fig. 3). When PFC was dosed firstly, NOM carboxyl groups-Fe
hydrolysates complexes with negative charge on the surface were formed rapidly.
Once positively charged LDA was dosed, it would attach to Fe-NOM via neutralizing
residual negative charge. Besides, the long chain of polymeric LDA could absorb
micro flocs and bridge them\textsuperscript{15, 23}. Hence, charge neutralization and adsorption
bridging of LDA played a significant role during PFC+LDA coagulation. In contrast,
when LDA was dosed prior to PFC, it attracted colloids to form slightly negative
LDA-NOM complexes and bridged them together. Thereafter, the whole organic
complexes were coagulated by Fe(III) precipitates. In other words, entrapment and
sweeping of PFC played the leading role in the aggregation of flocs\textsuperscript{24}.

Dose sequence showed an obvious effect on coagulation performance and the
efficiency was in the order of PFC+LDA > LDA+PFC > PFC. From Fig. 2, zeta
potential of PFC+LDA was slightly larger than that of LDA+PFC. Similar conclusion
that dosing sequence of dual-coagulant had a particular influence on zeta potential
along with coagulation performance was also found by Bo et al.\textsuperscript{25} The positive charge in the surface of LDA was offered by cationic quaternary ammonium groups existing in LDA, which interacted electrostatically with negatively charged NOM or microflocs through charge neutralization effect. When PFC was added preferentially, plentiful hydroxyl molecules would be occupied by ferric ions and pH of water samples was lowered (Fig. S2).\textsuperscript{26} Previous studies demonstrated that zeta potential of LDA showed an increase with the decline of pH (Fig. S3). As a result, flocs formed in PFC+LDA coagulation showed a larger zeta potential value. On the contrary, in the case of LDA being dosed prior to PFC, positive charge of LDA was neutralized partly by ion exchange between the loaded Cl$^{-}$ and hydroxyl ions, which resulted in combining with less negatively charged NOM and particles. This may be the reason why LDA+PFC showed relatively weak coagulation efficiency than PFC+LDA.

3.3 Floc characteristics

3.3.1 Floc size and growth rate

Floc growth, breakage and regrowth under different coagulation conditions were monitored. And variation of floc size and growth rate as a function of PFC dosage was listed in Fig. 4a. Both floc size and growth rate increased with PFC dosage rising in three coagulations and these values were in the flowing order: PFC+LDA > LDA+PFC > PFC. This result was consistent with the order of zeta potential. At lower PFC dosages, stronger repulsion forces between Fe species and impurities impeded the further formation of flocs. As PFC dosage increased, abundant Fe hydrolysates united with NOM and particles to formed larger flocs. For PFC+LDA and LDA+PFC,
the systems were exposed to weaker repulsion forces which could be explained by the lower absolute value of zeta potential. LDA with long-chain structure could also attached to HA or HA-Fe hydroxides flocs. Thus, adsorption bridging of LDA also offered a positive effect on floc growth. Additionally, flocs formed through bridging effect were much larger than those formed by charge neutralization. As a consequence, floc size increased by 40-140 µm for PFC+LDA and 30-100 µm for LDA+PFC than those in PFC coagulation processes.

Growth rate was determined by interaction of coagulants and charged colloids. When PFC or LDA was added to water samples, negative charge on the surface of colloids and NOM was neutralized and this physical process was accomplished quickly. Subsequently, collision and aggregation of destabilized micro flocs proceeded slowly. Growth period would be finished till achieving the balance between the formation and breakage of flocs. As presented in Fig. 4a, faster aggregation was performed by dual-coagulants, especially PFC+LDA, which indicated that charge neutralization and adsorption bridging of LDA played a positive role in promoting floc growth. At PFC dosage of 14 mg/L, \(d_{50}\) and floc growth rate showed upward trends with the growth of LDA dosage (Fig. 4b). When dosing LDA of 1.5 mg/L, \(d_{50}\) and grow rate were 108-130 µm and 30-66 larger than those of flocs formed by PFC.

As shown in Fig. 5, pH also had a significant influence on floc formation. The trends of floc size and growth rate with the variance of pH were similar in the three coagulations. And PFC+LDA achieved the maximum floc size and growth rate during
the investigative pH range, while those in PFC coagulation were minimal. Floc sizes under alkaline conditions as well as at pH 5 were small due to stronger repulsion forces, which could be drawn from larger absolute value of zeta potential (Fig. 2). Meanwhile, floc aggregation was finished within the similar time, so floc growth rate greatly depended on floc size. That is, the larger floc size, the quicker floc growth rate. Floc sizes at pH 4 and 6 were similar and much larger than those under other pH conditions, whereas mechanisms were quite different. At pH 6, repulsion forces between micro flocs were significantly weakened and also further aggregation. At the lower pH, especially under acidic or strong acidic conditions, HA was less hydrophilic and then easier to destabilize and precipitate. These phenomena indicated that water-solubility of HA and charge neutralization played the foremost role in floc size. In general, growth rate was more sensitive to charge neutralization effect. Though the same floc sizes were achieved at pH 4 and 6, stronger repulsion forces would impede floc growth. As a result, growth rate at pH 4 was smaller than that of pH 6.

3.3.2 Floc structure

Figure 6 showed fractal dimension of flocs under different PFC and LDA dosages. Overall, $D_f$ maintained steady during the growth period and then rose rapidly when introducing the rapid stirring. During re-growth region, $D_f$ dropped little compared with breakage region. Dosage also showed a noteworthy influence on $D_f$ value: $D_f$ rose with the increase of PFC and LDA dosage. More inner bonds took shape with the increasing coagulant concentrations due to the more sweeping and adsorption
bridging effect. Meanwhile, the increase of zeta potential resulted in the relatively weak repulsion forces between flocs. $D_f$ value under different coagulation processes was in the order of PFC > PFC+LDA >LDA+PFC, which was inconsistent with the result acquired by Wei et al. that PFC and PDADMAC dual-coagulants gave more compact flocs than PFC. This might be because major difference between LDA and conventional polymeric flocculants in chemical structure. LDA had a chainlike form, which contributed to the formation of flocs with poriferous and open structure. In general, flocs with highly branched and loosely bound structures usually have lower $D_f$. In addition, adsorption bridging was demonstrated as the least effective mechanism on improving fractal dimension under the same condition. Rong et al. also reported that aluminum salts combining with lignin-AM showed a decline in $D_f$ comparing with single aluminum coagulants, which might be caused by bridging effect of lignin-AM. In PFC coagulation, flocs were denser due to entrapment and sweeping, which was proved as the most effective mechanism on the formation of flocs with higher $D_f$. When PFC dosage was identical, more LDA could rapidly saturate the surface of formed flocs and reduce electrostatic repulsion. As a result, more compact flocs came into being along with the enhancement of LDA dosage.

Variation of floc $D_f$ under different initial pH conditions was listed in Fig. 7. The trend of $D_f$ vs. time was similar with that described in Fig. 6. Under acidic condition, $D_f$ raised significantly with the increase of pH and achieved maximum at pH 6 in dual-coagulants system, which was caused by the inner repulsion force between flocs. $D_f$ at pH 5 was the largest in PFC coagulation, which existed for two main reasons: on
one hand, Jarvis et al. \(^{34}\) proved that relatively small flocs had more compact structure; on the other hand, it might be caused by the different ferric hydrolytic species as well as coagulation mechanisms. Compared with other mechanisms, flocs formed by charge neutralization effect would be less compact \(^{33}\). When pH was 5, Fe(III) combined with hydroxyl ions and produced hydrolysates like Fe(OH)\(^{2+}\) or Fe(OH)\(^{2+}\), which could provide sweeping effect \(^{35}\). However, at pH 4, ferric ions could hardly hydrolyze and charge neutralization was the dominant mechanism. Therefore, D\(_f\) at pH 5 was larger than pH 4 and 6. Besides, because of more entrapment and sweeping effect, D\(_f\) maintained growth with the increase of pH when pH \(\geq\) 7.

### 3.3.3 Floc recoverability

Floc recover capacity under different dosage and pH conditions was calculated by Eq. (2), the results were separately illustrated in Table 2 and Table 3.

Floc regrowth capacity of three coagulation systems all showed a successional decline with PFC dosage increasing. Previous researches showed that flocs formed by charge neutralization had total recoverability after breakage, while sweeping flocs were irreversible \(^{15}\). As more PFC was dosed, massive sweeping flocs were formed due to sufficient hydrolysates. Thereby, R\(_f\) dropped accordingly. The order of R\(_f\) was as follows: PFC+LDA > LDA+PFC > PFC, which indicated that charge neutralization effect played a more important role in the enhancement of R\(_f\) for PFC+LDA flocs.

LDA, as a cationic polymer, could bond with floc fragments and aggregate them together though electrostatic attraction and Van der Waals force \(^{15, 27}\). Increasing of LDA dosage also influenced floc recoverability and resulted in the rise of R\(_f\), which
could be explained by smaller absolute value of zeta potential. LDA increased $R_f$ by 0.39-7.55 in comparison with single PFC.

As shown in Table 3, flocs formed at pH 6 had better re-growth capability than other conditions, especially alkaline condition. The reason was that more irreversible sweeping flocs were formed with the increasing of pH under alkaline condition. In the case of PFC+LDA, the variance range was much narrow than PFC, which demonstrated the difference of coagulation models listed in Section 3.1. Under acidic condition, $D_f$ at pH 4 and 5 was similar and smaller than that at pH 6 for all three coagulation conditions. The reason was that charge neutralization was the foremost mechanism under this condition. Weaker electrostatic repulsion between floc fragments was good for floc reaggregation. Meanwhile, solution pH did not change before or after breakage and thus water-solubility of HA had no effect on floc recovery ability.

4. Conclusions

The main conclusions were listed as follows:

1. Cationic LDA polymer was synthesized using lignin as the starting material existing in papermaking sludge. Its flocculating efficiencies in the aspect of DOC and turbidity removal were superior to PAM, PDADMAC and LAM at the polymer dosage of 1.0 mg/L.

2. Addition of LDA would introduce charge neutralization and adsorption bridging effect. PFC+LDA increased the DOC and turbidity removal ratios up to 5.6% and 33.6% compared with PFC, respectively. Floc size enhanced by 40-140 µm for
PFC+LDA than those in PFC system and growth rate also rose accordingly. More reversible flocs were formed by the charge neutralization effect of LDA. Adsorption bridging effect of LDA contributed to the formation of flocs with open structure.

(3) Dosing sequence had an influence on coagulation behavior due to the difference of coagulation mechanisms. PFC+LDA achieved optimum coagulation efficiency and floc size where charge neutralization of LDA was the foremost mechanism. In the case of LDA+PFC, sweeping of PFC played a role in the formation of aggregation and thus $D_f$-value of flocs was minimum.

(4) Solution pH had a significant effect on coagulation efficiencies and flocs structure. Better coagulation performance and floc characteristics were achieved under faintly acidic condition, especially at pH 6. After addition of LDA, coagulation behavior increased and removal variations caused by the change of pH decreased, which ensured the potential application of LDA in treating a wide pH range of water.

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**References**


1. 2004, 73, 251-259.


Table captions

Table 1 Comparison of coagulation performance between LDA and other flocculants (at flocculant dosage of 1.0 mg/L)

Table 2 Comparison of floc $R_f$ under different coagulant dosage conditions.

Table 3 Variation of floc $R_f$ under different initial pH conditions.
Table 1 Comparison of coagulation performance between LDA and other flocculants (at flocculant dosage of 1.0 mg/L)

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Table 2 Comparison of floc $R_f$ under different coagulant dosage conditions.

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Figure captions

Fig. 1 Synthesis route of LDA using lignin monomer as starting structure.

Fig. 2 Effect of initial pH on DOC removal ratio (a), turbidity removal ratio (b) and zeta potential (c) at PFC dosage of 14 mg/L and LDA dosage of 1.0 mg/L.

Fig. 3 Coagulation models of PFC coagulation and dual-coagulations under different conditions of dosing sequence (a) and solution pH (b).

Fig. 4 Floc size and growth rate under different coagulant dosages conditions: (a) PFC dosage; (b) LDA dosage.

Fig. 5 Floc size and growth rate under different initial pH conditions: (a) Floc size; (b) Growth rate at PFC dosage of 14 mg/L and LDA dosage of 1.0 mg/L.

Fig. 6 Effect of coagulant dosages on the variation of floc fractal dimension during coagulation processes: (a) PFC dosage; (b) LDA dosage.

Fig. 7 Variation of floc fractal dimension under different initial pH conditions: (a) PFC; (b) PFC+LDA; (c) LDA+PFC.
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