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

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11 **Abstract**

12 To recycle papermaking sludge, a novel lignin-based flocculant with high cationic
13 degree and molecular weight was introduced. The product, lignin-diallyl dimethyl
14 ammonium chloride-acrylamide (LDA) was combined with polyferric chloride (PFC)
15 to treat simulated humic acid (HA) solution. To identify its flocculation mechanisms,
16 coagulation efficiencies and floc properties under different dosing method and pH
17 conditions were studied. Results showed that LDA was superior to polyacrylamide,
18 poly diallyldimethylammonium chloride as well as lignin-acrylamide in the aspect of
19 DOC and turbidity removal efficiencies, which demonstrated its significant
20 flocculating efficiency. Compared with single PFC, the addition of LDA enhanced
21 coagulation performance and floc properties including floc size, growth rate and
22 recovery ability during the investigative pH range. Dosing sequence also showed an

1 effect on coagulation mechanism and performance. When PFC was dosed firstly,
2 negatively charged Fe(III) hydrolysates-colloids were neutralized and bridged by
3 LDA. On the contrary, colloids-LDA complexes with slightly negative charge were
4 destabilized by the entrapment and sweeping effect of Fe(III) hydrolysates. As a result,
5 coagulation efficiencies were in the order: PFC dosed firstly (PFC+LDA) > LDA
6 dosed firstly (LDA+PFC) > PFC. PFC+LDA achieved the maximum floc size and
7 growth rate, while flocs with the most open structure was formed by LDA+PFC.
8 Moreover, the effect of solution pH on coagulation behavior was noteworthy due to
9 the variance of hydrolyzed Fe species. PFC was more sensitive to pH in the aspect of
10 coagulation efficiencies and flocs structure. The variations caused by different pH
11 lowered after the addition of LDA. Regardless of the coagulant types, the optimal
12 coagulation performance and floc characteristics were achieved under acidic
13 conditions, especially at pH 6. Overall, LDA could introduce strong charge
14 neutralization and adsorption bridging effect during relatively wider pH range and
15 offer a positive effect on coagulation behavior and flocs properties.

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

18 **1. Introduction**

19 The presence of natural organic matter (NOM) in aquatic environment has
20 attracted more and more attention owing to its environmental impact and potential
21 harm to human health. Many researchers reported that NOM was the carrier of heavy
22 metals and hazardous chemicals¹. Furthermore, NOM could react with free chlorine

1 to form a series of genotoxic and carcinogenic disinfection by-products during
2 chlorination². Coagulation/flocculation processes have been preferentially applied to
3 dissolved and suspended organic matter removal due to low cost, high performance
4 and easy operation³. Coagulation efficiency and effluent quality are highly dependent
5 on coagulants; previous researches have showed that synthetic polymers in
6 combination with metal coagulants could achieve better coagulation behaviors⁴. In
7 order to satisfy the increasing demand of environmental friendliness and NOM
8 removal efficiency, it is crucial to develop modified natural polymeric flocculants,
9 especially making use of industrial and agricultural by-products⁵.

10 Pulp and papermaking sludge is a largely generated waste product in water
11 treatment processes of papermaking industry, for instance, about 8 and 30 million tons
12 per year in United States and China separately^{6,7}. Traditional disposal methods such
13 as landfill, combustion and bio-compost are restricted to the ingredients of sludge and
14 more likely to cause secondary pollution⁸. Owing to special organic composition (e.g.,
15 lignin, hemicellulose and cellulose), it is used as raw materials to produce chemical
16 products such as polyelectrolyte, adsorbent, dispersant and scale inhibitor^{7,9,10}. Rong
17 et al. reported a neutral lignin-acrylamide flocculant (LAM) and demonstrated that it
18 could enhance coagulation performance in combination with aluminum coagulants⁶.
19 However, it was difficult for LAM to remove NOM with low zeta potential as well as
20 small molecular weight. Generally, a flocculant with higher cationic and molecular
21 weight could achieve better removal of negative micro particles¹¹. So far, there have
22 been few reports about preparation and application of cationic flocculant using lignin

1 as well as papermaking sludge.

2 Floc characteristic (e.g., floc size, growth rate, recoverability and compactness)
3 had an effect on coagulation behavior and the cost of water treatment. As a result, it
4 was always used to evaluate the efficiency of chemicals. In general, the larger flocs,
5 the quicker sedimentation velocity¹². Faster growth rate requires a relatively small
6 tanker in actual water treatment. Flocs recovery factors stand for the ability to regrow.
7 Fractal dimension (D_f), a quantitative index to describe flocs structure, is
8 co-determined by flocs mass and size. Flocs with lower D_f have a looser or branchy
9 structure, while higher D_f value stands for a more compact structure.¹³. Therefore, it
10 is considered to be significant to investigate the influence of coagulant species and
11 hydraulic conditions on floc formation processes. Previous studies demonstrated that
12 floc properties were related with coagulation mechanisms^{14, 15}. However, literatures
13 about floc characteristics in cationic lignin-based polymer coagulated effluent and
14 their relationship with hydraulic conditions were still limited.

15 In this study, lignin-based flocculant LDA was synthesized through grafting diallyl
16 dimethyl ammonium chloride (DADMAC) and acrylamide (AM) onto lignin
17 containing in papermaking sludge in the presence of $K_2S_2O_8$ and edetate disodium. To
18 demonstrate its flocculating efficiency, comparison of coagulation performance
19 between LDA and other flocculants including polyacrylamide (PAM), poly
20 dimethyldiallylammonium chloride (PDADMAC) and lignin-acrylamide (LAM) was
21 studied. The effect of dosing method including polyferric chloride (PFC), PFC+LDA
22 (PFC was dosed firstly) and LDA+PFC (LDA was dosed firstly) and solution pH on

1 coagulation performance and floc proprieties in kaolin-humic acid (HA) water
2 treatment were comparatively studied. Coagulation models of LDA combined with
3 polyferric chloride (PFC) under different conditions were described to further
4 understand the mechanisms.

5 **2. Materials and methods**

6 **2.1. Preparation of coagulants and test water**

7 LDA was made from dried papermaking sludge, which was acquired from an
8 alkaline paper mill of Shandong Province, China. The synthetic route was grafting
9 acrylamide (AM) and dimethyl diallyl ammonium chloride (DADMAC) onto alkali
10 lignin containing in dried sludge. The detailed steps (Fig. 1) were as follows: firstly,
11 sludge powder in aqueous alkali was centrifuged to obtain lignin supernatant and then
12 transferred into a three-neck round bottom flask; secondly, $K_2S_2O_8$ and edetate
13 disodium were successively added with N_2 inlet⁶. Then certain amounts of AM and
14 DADMAC were dripped into the reactor at 70 °C; thirdly, the product was extracted
15 with acetone, soxhlet extracted with acetone-ethanol and then washed with ethanol
16 after 3 h reaction; finally, the product was vacuum dried at 50-60 °C. The
17 physicochemical properties of LDA were listed as follows: molecular weight =
18 800-1100 KDa, cationic degree = 28.9±1.4 %, Viscosity (60 rpm at 25 °C) =
19 1.110±0.045 mPa•s. In addition, zeta potential of LDA under different pH condition
20 was shown in Fig. S2.

21 PAM with molecular weight of 3000 KDa was purchased from Sinopharm
22 Chemical Reagent Co., Ltd. Beijing. The cationic polymer PDADMAC was obtained

1 from Bin Zhou Chemical Co., Shandong, China ¹⁶. LAM was prepared based on Rong
2 et al ¹⁷. These solutions were all prepared with a concentration of 1.0 g/L and stored at
3 4 °C before usage.

4 PFC stock solution with B value ($[\text{OH}^-]/[\text{Al}^{3+}]$ mole ratio) of 0.5, was prepared
5 based on Wei et al ¹⁶. Humic acid (Aladdin Industrial Corporation, Shanghai, China)
6 and kaolin stock solution was used to synthesize HA-kaolin samples ¹⁸. The
7 physicochemical characteristics of raw water were as follows: pH = 8.20 ± 0.05 , DOC
8 = 4.450 ± 0.320 mg/L, turbidity = 15.0 ± 0.5 NTU.

9 **2.2. Jar tests**

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

18 Zeta potential of coagulated water sample was measured by Zetasizer 3000HSA
19 (Malvern Instruments, UK) immediately after rapid stirring without dilution ¹⁹.
20 Turbidity collected water was measured directly via Portable turbidimeter 2100P,
21 Hach, US. Filtered water (by 0.45 μm fiber membrane) was used to test DOC (with
22 TOC analyzer, Shimadzu, Japan).

1 2.3. Floc characteristics

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

$$8 \quad \text{Growth rate} = \frac{\Delta \text{size}}{\Delta \text{time}} \quad (1)$$

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

$$10 \quad R_f = \frac{d(3) - d(2)}{d(1) - d(2)} \times 100 \quad (2)$$

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

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

$$16 \quad I \propto Q^{-D_f} \quad (3)$$

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

18 3. Results and discussion

19 3.1 Comparison of coagulation performance between LDA and other flocculants

20 Comparison of coagulation performance between LDA and other flocculants was
21 performed at the same flocculant dosage (1.0 mg/L) and the results were shown in
22 Table 1. In PFC coagulation, the addition of polymer all could improve removal

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

17 **3.2 Influence of pH on coagulation performance**

18 Preliminary tests were performed to ascertain the optimum PFC and LDA dosage
19 for HA and turbidity removal at the pH of raw water. According to previous studies,
20 PFC dosage of 14 mg/L and LDA dosage of 1.0 mg/L were chosen to accomplish
21 following experiments. In order to identify the influence of solution pH, coagulation

1 performance of PFC+LDA and LDA+PFC dual-coagulants were contrastively
2 evaluated in terms of turbidity and DOC removal ratios (Fig. 2).

3 DOC and turbidity removal appeared a different trend: when $\text{pH} \geq 7$, DOC
4 removal efficiency decreased with pH, while turbidity removal efficiency maintained
5 stable in investigated range. Under acidic condition, DOC removal ratios at pH 4 and
6 5 were similar and less than that of pH 6. Nevertheless, turbidity removal showed a
7 significant enhancement as pH rose from 4 to 6. This phenomenon demonstrated the
8 difference of dominant coagulation mechanisms between DOC and turbidity removal.
9 As shown in Fig. 2c, zeta potential was negative when $\text{pH} > 6$ and then increased and
10 transformed into positive with the decrease of pH, which was related with the
11 variance of Fe(III) hydrolysates under different pH conditions. Under alkaline
12 condition, major Fe(III) species of PFC transformed into $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_4^-$ with
13 the action of hydroxyl ions²⁰. As a result, zeta potential of PFC coagulated flocs was
14 less than -10.0 mV (Fig. 2c), which resulting in stronger repulsion forces between
15 flocs. It was believed that adsorption of HA or particle onto Fe hydroxides through
16 surface complexation or ligand exchange was the dominating mechanism under this
17 condition²¹. When pH was lower than 6, PFC hydrolyzed to positively charged
18 complexes, such as Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$ and $\text{Fe}_2(\text{OH})_2^{4+}$ ²⁰. Accordingly, absolute
19 value of zeta potential became lower under this condition and it achieved isoelectric
20 point at pH 6. Thus charge neutralization effect played a role in floc formation. In
21 conclusion, neutralization of negative charge showed a higher efficiency in humic

1 substances removal¹⁹, while the mechanism dominating kaolin particles removal was
2 more related with sweeping effect²².

3 In the case of LDA addition, DOC removal showed the same variation tendency
4 with that of PFC, but removal ratios improved obviously. In detail, PFC+LDA and
5 LDA+PFC enhanced the DOC removal efficiencies by approx. 5.0% compared with
6 PFC under alkaline condition. For turbidity removal, PFC lowered the removal ratio
7 by 33.6% and 14.4% compared with PFC+LDA and LDA+PFC at pH 4, respectively.
8 There existed differences of floc aggregation between PFC coagulation and
9 dual-coagulations (Fig. 3). When PFC was dosed firstly, NOM carboxyl groups-Fe
10 hydrolysates complexes with negative charge on the surface were formed rapidly.
11 Once positively charged LDA was dosed, it would attach to Fe-NOM via neutralizing
12 residual negative charge. Besides, the long chain of polymeric LDA could absorb
13 micro flocs and bridge them^{15, 23}. Hence, charge neutralization and adsorption
14 bridging of LDA played a significant role during PFC+LDA coagulation. In contrast,
15 when LDA was dosed prior to PFC, it attracted colloids to form slightly negative
16 LDA-NOM complexes and bridged them together. Thereafter, the whole organic
17 complexes were coagulated by Fe(III) precipitates. In other words, entrapment and
18 sweeping of PFC played the leading role in the aggregation of flocs²⁴.

19 Dose sequence showed an obvious effect on coagulation performance and the
20 efficiency was in the order of PFC+LDA > LDA+PFC > PFC. From Fig. 2, zeta
21 potential of PFC+LDA was slightly larger than that of LDA+PFC. Similar conclusion
22 that dosing sequence of dual-coagulant had a particular influence on zeta potential

1 along with coagulation performance was also found by Bo et al²⁵. The positive charge
2 in the surface of LDA was offered by cationic quaternary ammonium groups existing
3 in LDA, which interacted electrostatically with negatively charged NOM or micro
4 flocs through charge neutralization effect. When PFC was added preferentially,
5 plentiful hydroxyl molecules would be occupied by ferric ions and pH of water
6 samples was lowered (Fig. S2)²⁶. Previous studies demonstrated that zeta potential of
7 LDA showed an increase with the decline of pH (Fig. S3). As a result, flocs formed in
8 PFC+LDA coagulation showed a larger zeta potential value. On the contrary, in the
9 case of LDA being dosed prior to PFC, positive charge of LDA was neutralized partly
10 by ion exchange between the loaded Cl⁻ and hydroxyl ions, which resulted in
11 combining with less negatively charged NOM and particles. This may be the reason
12 why LDA+PFC showed relatively weak coagulation efficiency than PFC+LDA.

13 **3.3 Floc characteristics**

14 **3.3.1 Floc size and growth rate**

15 Floc growth, breakage and regrowth under different coagulation conditions were
16 monitored. And variation of floc size and growth rate as a function of PFC dosage
17 was listed in Fig. 4a. Both floc size and growth rate increased with PFC dosage rising
18 in three coagulations and these values were in the flowing order: PFC+LDA >
19 LDA+PFC > PFC. This result was consistent with the order of zeta potential. At lower
20 PFC dosages, stronger repulsion forces between Fe species and impurities impeded
21 the further formation of flocs. As PFC dosage increased, abundant Fe hydrolysates
22 united with NOM and particles to formed larger flocs. For PFC+LDA and LDA+PFC,

1 the systems were exposed to weaker repulsion forces which could be explained by the
2 lower absolute value of zeta potential ²⁷. LDA with long-chain structure could also
3 attached to HA or HA-Fe hydroxides flocs ¹⁵. Thus, adsorption bridging of LDA also
4 offered a positive effect on floc growth. Additionally, flocs formed through bridging
5 effect were much larger than those formed by charge neutralization ¹⁴. As a
6 consequence, floc size increased by 40-140 μm for PFC+LDA and 30-100 μm for
7 LDA+PFC than those in PFC coagulation processes.

8 Growth rate was determined by interaction of coagulants and charged colloids.
9 When PFC or LDA was added to water samples, negative charge on the surface of
10 colloids and NOM was neutralized and this physical process was accomplished
11 quickly. Subsequently, collision and aggregation of destabilized micro flocs
12 proceeded slowly ^{13,28,29}. Growth period would be finished till achieving the balance
13 between the formation and breakage of flocs ³⁰. As presented in Fig. 4a, faster
14 aggregation was performed by dual-coagulants, especially PFC+LDA, which
15 indicated that charge neutralization and adsorption bridging of LDA played a positive
16 role in promoting floc growth. At PFC dosage of 14 mg/L, d_{50} and floc growth rate
17 showed upward trends with the growth of LDA dosage (Fig. 4b). When dosing LDA
18 of 1.5 mg/L, d_{50} and grow rate were 108-130 μm and 30-66 larger than those of flocs
19 formed by PFC.

20 As shown in Fig. 5, pH also had a significant influence on floc formation. The
21 trends of floc size and growth rate with the variance of pH were similar in the three
22 coagulations. And PFC+LDA achieved the maximum floc size and growth rate during

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

16 **3.3.2 Floc structure**

17 Figure 6 showed fractal dimension of flocs under different PFC and LDA dosages.
18 Overall, D_f maintained steady during the growth period and then rose rapidly when
19 introducing the rapid stirring. During re-growth region, D_f dropped little compared
20 with breakage region. Dosage also showed a noteworthy influence on D_f value: D_f
21 rose with the increase of PFC and LDA dosage. More inner bonds took shape with the
22 increasing coagulant concentrations due to the more sweeping and adsorption

1 bridging effect. Meanwhile, the increase of zeta potential resulted in the relatively
2 weak repulsion forces between flocs. D_f value under different coagulation processes
3 was in the order of PFC > PFC+LDA > LDA+PFC, which was inconsistent with the
4 result acquired by Wei et al. that PFC and PDADMAC dual-coagulants gave more
5 compact flocs than PFC¹⁶. This might be because major difference between LDA and
6 conventional polymeric flocculants in chemical structure. LDA had a chainlike form,
7 which contributed to the formation of flocs with poriferous and open structure²³. In
8 general, flocs with highly branched and loosely bound structures usually have lower
9 D_f ²⁵. In addition, adsorption bridging was demonstrated as the least effective
10 mechanism on improving fractal dimension under the same condition^{15,31}. Rong et al.
11⁶ also reported that aluminum salts combining with lignin-AM showed a decline in D_f
12 comparing with single aluminum coagulants, which might be caused by bridging
13 effect of lignin-AM. In PFC coagulation, flocs were denser due to entrapment and
14 sweeping, which was proved as the most effective mechanism on the formation of
15 flocs with higher D_f ^{32,33}. When PFC dosage was identical, more LDA could rapidly
16 saturate the surface of formed flocs and reduce electrostatic repulsion. As a result,
17 more compact flocs came into being along with the enhancement of LDA dosage.

18 Variation of floc D_f under different initial pH conditions was listed in Fig. 7. The
19 trend of D_f vs. time was similar with that described in Fig. 6. Under acidic condition,
20 D_f raised significantly with the increase of pH and achieved maximum at pH 6 in
21 dual-coagulants system, which was caused by the inner repulsion force between flocs.
22 D_f at pH 5 was the largest in PFC coagulation, which existed for two main reasons: on

1 one hand, Jarvis et al.³⁴ proved that relatively small flocs had more compact structure;
2 on the other hand, it might be caused by the different ferric hydrolytic species as well
3 as coagulation mechanisms. Compared with other mechanisms, flocs formed by
4 charge neutralization effect would be less compact³³. When pH was 5, Fe(III)
5 combined with hydroxyl ions and produced hydrolysates like $\text{Fe}(\text{OH})^{2+}$ or $\text{Fe}(\text{OH})_2^+$,
6 which could provide sweeping effect³⁵. However, at pH 4, ferric ions could hardly
7 hydrolyze and charge neutralization was the dominant mechanism. Therefore, D_f at
8 pH 5 was larger than pH 4 and 6. Besides, because of more entrapment and sweeping
9 effect, D_f maintained growth with the increase of pH when $\text{pH} \geq 7$.

10 3.3.3 Floc recoverability

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

13 Floc regrowth capacity of three coagulation systems all showed a successional
14 decline with PFC dosage increasing. Previous researches showed that flocs formed by
15 charge neutralization had total recoverability after breakage, while sweeping flocs
16 were irreversible¹⁵. As more PFC was dosed, massive sweeping flocs were formed
17 due to sufficient hydrolysates. Thereby, R_f dropped accordingly. The order of R_f was
18 as follows: PFC+LDA > LDA+PFC > PFC, which indicated that charge neutralization
19 effect played a more important role in the enhancement of R_f for PFC+LDA flocs.
20 LDA, as a cationic polymer, could bond with floc fragments and aggregate them
21 together though electrostatic attraction and Van der Waals force^{15, 27}. Increasing of
22 LDA dosage also influenced floc recoverability and resulted in the rise of R_f , which

1 could be explained by smaller absolute value of zeta potential. LDA increased R_f by
2 0.39-7.55 in comparison with single PFC.

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

14 **4. Conclusions**

15 The main conclusions were listed as follows:

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

20 (2) Addition of LDA would introduce charge neutralization and adsorption
21 bridging effect. PFC+LDA increased the DOC and turbidity removal ratios up to 5.6%
22 and 33.6% compared with PFC, respectively. Floc size enhanced by 40-140 μm for

1 PFC+LDA than those in PFC system and growth rate also rose accordingly. More
2 reversible flocs were formed by the charge neutralization effect of LDA. Adsorption
3 bridging effect of LDA contributed to the formation of flocs with open structure.

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

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

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1 **Table captions**

2 Table1 Comparison of coagulation performance between LDA and other flocculants

3 (at flocculant dosage of 1.0 mg/L)

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

5 Table 3 Variation of floc R_f under different initial pH conditions.

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1 Table1 Comparison of coagulation performance between LDA and other flocculants
 2 (at flocculant dosage of 1.0 mg/L)

| Dual-coagulants | PFC dosage (mg/L) | DOC removal ratio (%) | Turbidity removal ratio (%) | Zeta potential (mV) |
|-----------------|----------------------|--------------------------|-----------------------------------|------------------------|
| PFC+LDA | | 38.0±0.9 | 53.3±2.9 | -13.5±1.6 |
| PFC+PAM | | 33.1±1.1 | 49.8±1.9 | -14.4±1.7 |
| PFC+PDADMAC | 8 | 28.9±1.3 | 41.0±1.8 | -13.9±1.9 |
| PFC+LAM | | 26.7±0.8 | 39.8±2.1 | -14.3±1.4 |
| PFC | | 23.0±1.3 | 36.6±3.5 | -15.1±1.1 |
| PFC+LDA | | 49.3±0.4 | 89.6±1.3 | -4.5±1.6 |
| PFC+PAM | | 46.8±0.5 | 87.9±1.1 | -9.5±1.1 |
| PFC+PDADMAC | 14 | 46.2±0.9 | 87.7±0.3 | -6.7±0.8 |
| PFC+LAM | | 45.2±0.5 | 88.1±1.5 | -10.0±0.9 |
| PFC | | 42.9±0.7 | 87.6±1.9 | -13.1±0.5 |

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

| coagulants | PFC dosage (mg/L) | | | | | |
|------------|-------------------|-------|-------|-------|-------|-------|
| | 8 | 10 | 12 | 14 | 16 | 18 |
| PFC | 42.60 | 32.12 | 25.04 | 24.86 | 21.06 | 20.32 |
| PFC + LDA | 35.10 | 34.28 | 32.32 | 31.85 | 29.43 | 24.49 |
| LDA + PFC | 41.27 | 34.00 | 30.21 | 25.48 | 22.55 | 20.92 |
| | LDA dosage (mg/L) | | | | | |
| | 0.0 | 0.5 | 1.0 | 1.5 | - | - |
| PFC + LDA | 24.86 | 30.26 | 31.85 | 32.41 | - | - |
| LDA + PFC | 24.86 | 25.25 | 25.48 | 26.85 | - | - |

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1 Table 3 Variation of floc R_f under different initial pH conditions.

| pH | 4 | 5 | 6 | 7 | 8 | 9 |
|-----------|-------|-------|-------|-------|-------|-------|
| PFC | 27.86 | 27.50 | 29.70 | 26.35 | 25.34 | 23.77 |
| PFC + LDA | 32.13 | 33.72 | 35.30 | 32.95 | 32.12 | 31.19 |
| LDA + PFC | 31.35 | 32.31 | 33.76 | 28.06 | 26.14 | 24.98 |

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1 **Figure captions**

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

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

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

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

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

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

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

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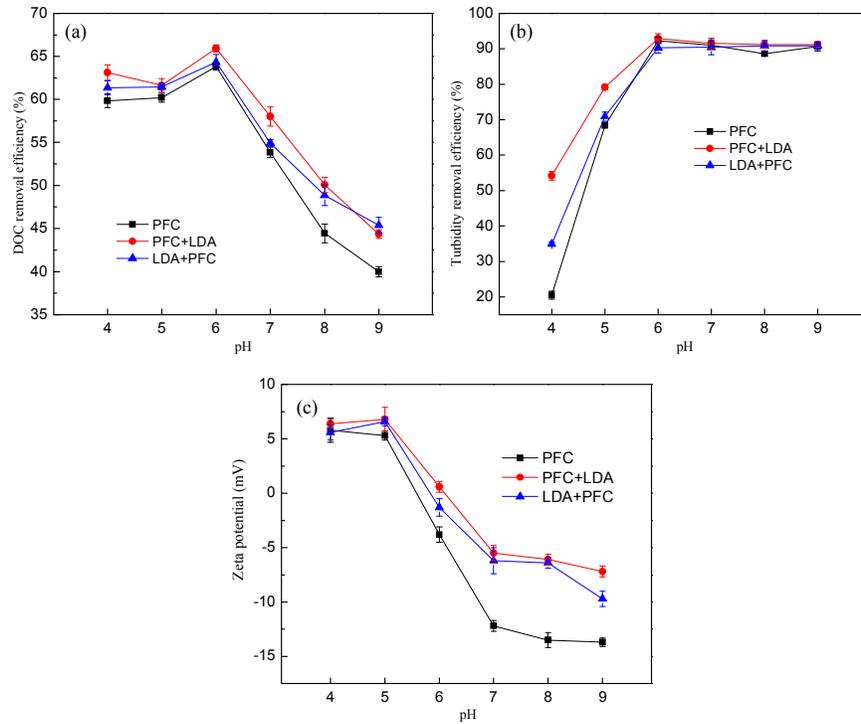
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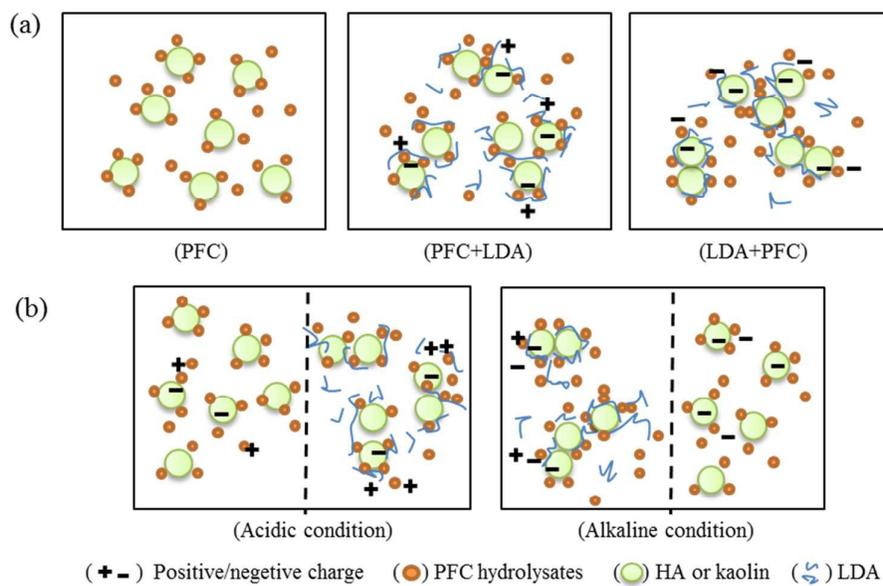
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3 Fig. 2 Effect of initial pH on DOC removal ratio (a), turbidity removal ratio (b) and

4 zeta potential (c) at PFC dosage of 14 mg/L and LDA dosage of 1.0 mg/L.

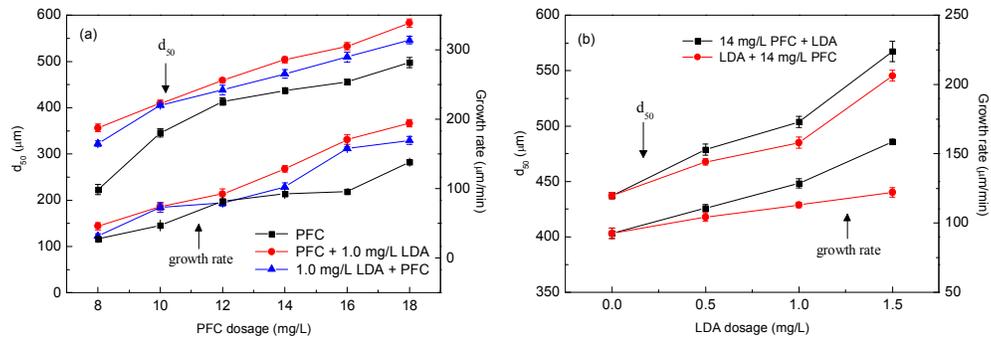
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2 Fig. 3 Coagulation models of PFC coagulation and dual-coagulations under different
 3 conditions of dosing sequence (a) and solution pH (b).

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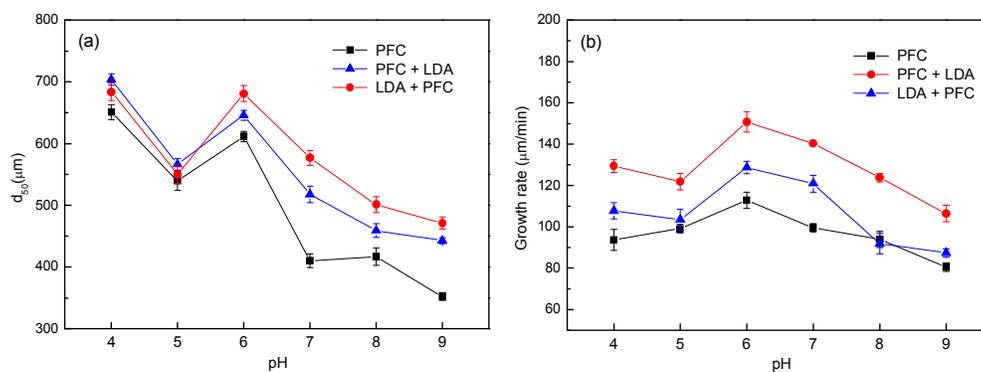


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2 Fig. 4 Floc size and growth rate under different coagulant dosages conditions: (a) PFC

3 dosage; (b) LDA dosage.

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2 Fig. 5 Floc size and growth rate under different initial pH conditions: (a) Floc size; (b)

3 Growth rate at PFC dosage of 14 mg/L and LDA dosage of 1.0 mg/L.

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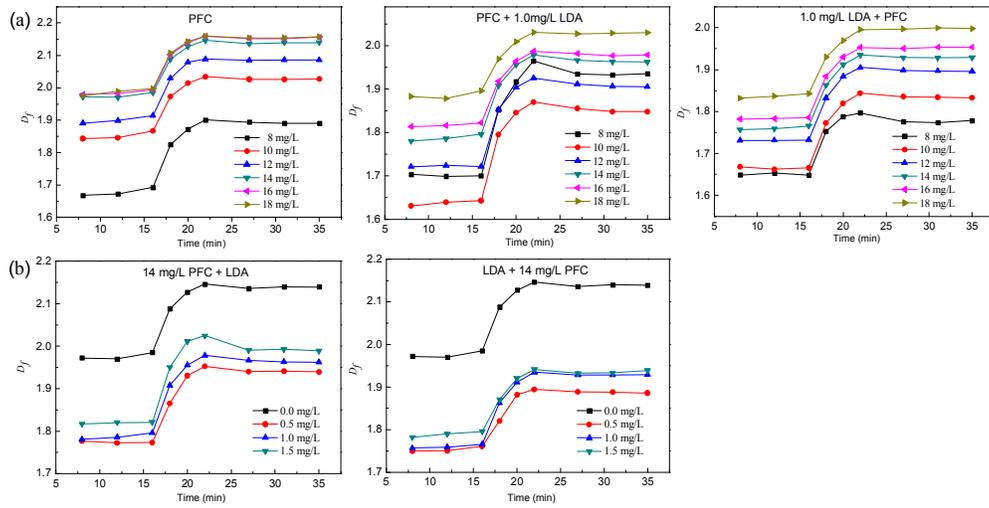
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2 Fig. 6 Effect of coagulant dosages on the variation of floc fractal dimension during

3 coagulation processes: (a) PFC dosage; (b) LDA dosage.

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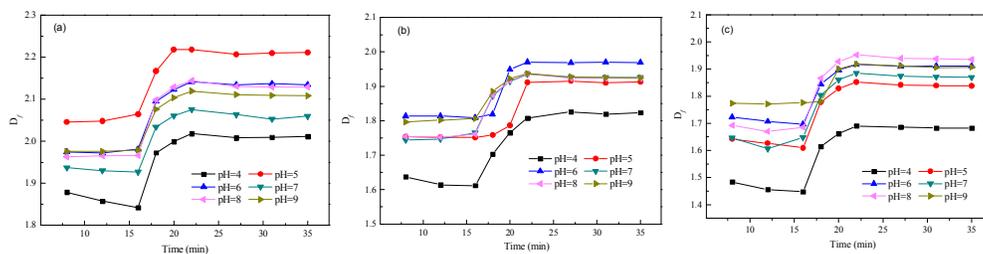
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2 Fig. 7 Variation of floc fractal dimension under different initial pH conditions: (a)

3 PFC; (b) PFC+LDA; (c) LDA+PFC.

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