Enhanced removal for humic-acid (HA) and coagulation process using carbon nanotubes (CNTs)/polyaluminium chloride (PACl) composites coagulants

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HIGHLIGHTS

- Removal efficiency for DOC decreased with increasing the concentration of DOC.
- Concentration of CNTs had no significant effects on the strength factors for flocs.
- Electrostatic patch effects may be important in the coagulation process.

GRAPHICAL ABSTRACT

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ABSTRACT

Humic acid could react with chlorine during drinking water treatment process, and how to remove HA molecules more efficiently from source water is important for the safety of drinking water. In order to improve the coagulation performances, some new coagulants were prepared by adding different amounts of carbon nanotubes to the polyaluminium chloride. In the coagulation process, the removal process for HA molecules may be caused by two mechanisms, one is the adsorption of CNTs, and the other is the coagulation process. When the concentration of DOC was increased to 4.0 mg/L under pH 5.0 (Al 0.1 mmol/L), the recovery factors decreased with increasing the concentration of CNTs. When the coagulant dosage was increased to 1.0 mmol/L (pH 5.0), there were no flocs formed in the coagulation process under three DOC concentrations due to larger positive charges. The coagulation performances under different solution pH conditions were also investigated. When the concentration of DOC was increased to 4.0 mg/L or 8.0 mg/L (pH 7.5), there would be large flocs formed at the beginning of slow mixing period, and the floc size decreased with increasing the coagulation period.

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1. Introduction

Humic acids (HA) are widely existed in natural environment, such as in groundwater, surface water, drinking water, and soil

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Fig. 1. Zeta potential for CNTs under different pH conditions.

[1–5]. There are many functional groups in HA molecules, and the functional groups endow the molecules some abilities to function-alize as an electron-transfer mediator during organic contaminants degradation processes [5–7]. HA molecules could also cause some adverse environmental consequences due to the characteristics of HA molecules. For example, HA molecules could bring undesirable color, odor and taste to drinking water [8,9]. HA molecules are not only a major source of foulant during ultrafiltration process, but also can compete for adsorption sites with target contaminants during activated carbon adsorption to decrease the pollutant removal efficiency [10–13]. They can also react with chlorine during drinking water treatment processes to produce potentially carcinogenic such as trihalomethanes and haloacetic acids [14–17]. Activated carbon adsorption, coagulation, electro-coagulation, and biosorption have been widely used for the removal of HA [18–21]. However, most of these methods suffered from high cost and/or the removal efficiency was small. In view of decreasing cost, the coagulation process using coagulants which had larger removal efficiency would be a very widely used method for the removal of HA molecules. There are many materials which could be used for the adsorption of HA [22–25]. Carbon nanotubes (CNTs) are relatively new adsorbents that have been proven to possess great potential in removing many kinds of pollutants such as organic matter from aqueous solutions [26–28]. Although CNTs have acceptable potential for organic matter adsorption from aqueous solutions but the removal efficiency remained limited at lower concentration of CNTs [29,30].

The flocs formed in the coagulation process could be broken due to larger stirring rate in the coagulation process, and after the breakage, the broken flocs would be reformed due to the stirring rate was decreased [31–33]. There are many factors which could affect the breakage and regrowth process [34,35]. Some previous researches have showed that the flocs could not regrow to former size before breakage, and the floc size after breakage decreased with increasing the breakage rate. Some nano materials were used to improve the coagulation performances, but the improvement was achieved only through the simply mixed [36–38]. In these new coagulants, the effects of nano materials on coagulants were only adsorption, and the effects on Al transformation were not investigated well. In order to better understand the effects of nano materials on coagulants, different amounts of CNTs were added to the solution in the formation process of Al based coagulants.

The objectives of this study were: (1) to investigate the effects of different coagulation conditions on the removal efficiency for HA molecules; (2) to investigate the effects of different concentration of CNTs in coagulation process; (3) to investigate the floc size and fractal dimension in the coagulation process using different coagulants.

Fig. 2. SEM images for CNTs used in this study before and after modification.

2. Materials and methods

2.1. Carbon nanotubes used in this study

The carbon nanotubes used in this study were purchased from Beijing DK Nano Technology Co., Ltd. Before the experiments, the samples were cleaned with 0.1 mmol/L HCl and dried at 40 °C for 24 h. The carbon nanotubes were observed directly using a scanning electron microscope (SEM) (Leo, 1530, Germany). Raman spectra of carbon nanotubes were obtained using a Renishaw RM 1000 microscopic confocal Raman spectroscopy equipped with a laser excitation of 633 nm (He–Ne laser). Zeta potential of carbon nanotubes suspensions was determined using a Malvern Zetasizer 2000 instrument. Fourier transform infrared (FTIR) spectroscopy (8700, Nicolet, America) was employed to analyze surface functional groups. The characteristics of carbon nanotubes used in this study were summarized in from Fig. 1 to Fig. 3.

The results (Fig. 1) showed that the iso-electric point of samples was at pH 5.5. When the carbon nanotubes were composited with Al based coagulants, they could decrease the charge neutralization ability due to adsorption of Al based coagulants on the surface of CNTs when the solution pH was at neutral condition. Although the charge neutralization abilities would be decreased, the removal efficiency for HA may be increased due to the adsorption in existence of CNTs. The results of SEM image (Fig. 2A) indicated that the diameters of the MWCNTs were 13 nm, and the MWCNTs had lengths of 10–20 μm. After modification by Al, there were many aluminum crystal on the surface of MWCNTs (Fig. 2B). These results indicated that the Al species were loaded on the surfaces of CNTs, and the effects of these aluminum crystals on the coagulation process would be researched later. As shown in FTIR spectra (Fig. 3A), all spectra had a broad band at approximately 3450 cm⁻¹, which was generally attributed to the stretching vibration of the

Fig. 3. FTIR and Raman spectrum for CNTs ((A) FTIR; (B) Raman).

O–H groups. The adsorption at 1641 cm^{-1} in the CNTs indicated the existence of an aromatic C=C structures. Peaks observed at 1722 cm^{-1} were attributed to the –CO stretch and C=O stretch of COOH, respectively. These peaks moved to larger position indicated that the connection between Al and –COOH on the surface of CNTs. Raman spectroscopy revealed complementary information on the evolution of CNTs after modification. Fig. 3B illustrated the Raman spectra of the as-received CNTs as well as the post mixed CNTs. As clearly from Fig. 3B, there were two peaks at 1320 cm^{-1} (D band) and the other at 1580 cm^{-1} (G band). By comparison of the ID/IG ratios of the spectra, it could be seen that this ratio varied. The as-received CNTs had the lowest ID/IG. The ID/IG ratios increased. The ID/IG ratio represents the defect density in graphitic structures. In addition, the G-band shift of the low energy and high energy ball-milled CNTs to a large wavenumber could be observed. In this study, it is suggested that the shift of G band contributed to the residual strain in the CNTs, which was the result from the mechanical alloying. When a strain is applied to them, the interaromatic distances of the CNTs change, hence the vibrational frequencies of some of normal modes change, resulting in a Raman peaks shift. The larger the strain that the CNT experiences, the larger the Raman peak shifts.

Table 1
Al species distribution of PACI samples.

Coagulants	Al _a (%)	Al _b (%)	Al _c (%)
PACI(0)	15.28	22.68	62.04
PACI(1)	11.36	17.218	71.422
PACI(2)	4.85	15.906	79.244
PACI(3)	0.9386	14.864	84.197
PACI(4)	0.8493	12.948	86.2027
PACI(5)	0.6484	10.924	88.4276

2.2. Preparation of coagulants

Some amounts of Na_2CO_3 was added to AlCl_3 solution (1.0 mmol/L), and the solution reacted for 16 h at 80°C . The prepared PACI was described as PACI(0). In order to investigate the effects of CNTs on the coagulants, 0.25 g, 0.50 g, 1.0 g, 1.5 g, 2.0 g of CNTs were added to 60 mL AlCl_3 solution, and the formation processes were the same as preparation of PACI(0). The coagulants were analyzed for Al species by Ferron method [31], and the results are summarized in Table 1. Former studies had indicated that the Ferron method enabled one to partition soluble aluminum species into such categories

Fig. 4. Effects of different amounts of CNTs on the removal efficiency of DOC under different DOC concentrations ((A) pH 5.0; (B) pH 7.5; (C) pH 9.0).

as monomeric, fast-reacting polymeric, or slow-reacting colloidal species denoted simply as Al_a , Al_b , and Al_c , respectively [39]. The results in Table 1 indicated that the existence of carbon nanotubes had significant effects on the Al species distribution in the coagulants. The ratio of Al_c increased with increasing the concentration of carbon nanotubes, while the ratio of Al_a and Al_b decreased. When the amount of carbon nanotubes increased to 2.0 g, the ratio of Al_a could decreased to 0.6484%, and the concentration of residual Al could also decreased due to the lowest concentration of Al_a [40].

2.3. HA stock solution and water samples

The stock solution of HA was prepared by dissolving 0.5 g of HA in 0.01 mol/L NaOH under continuous stirring for 24 h. After that, the solution was filtered through 0.45 μ m membrane and stored in refrigerator for later use. The water samples used in this study were diluted from HA stock solution, and the water samples were added 5.0 mmol/L $NaNO_3$ and 4.0 mmol/L $NaHCO_3$ to provide ionic strength and alkalinity. In order to investigate the effects of the concentration of DOC on the coagulation process, the water samples were prepared under three DOC concentrations (2.0 mg/L, 4.0 mg/L, 8.0 mg/L). Solution pH values had significant effects on the coagulation process, so the solution pH was adjusted to 5.0, 7.0 and 9.0 by 0.1 mol/L HCl (0.1 mol/L) and NaOH (0.1 mol/L).

2.4. Jar test and characteristics of flocs

Coagulation experiments were conducted in 500 mL glass beakers using conventional Jar-test apparatus. A four-stage mixing process was conducted in this study, including rapid mixing (1.5 min for 200 rpm) after addition of coagulants and slow mixing (10.0 min for 40 rpm) was followed. After the growth of flocs,

the flocs were exposed to 200 rpm for 5.0 min, and after which the mixing speed was reduced to 40 rpm for 10.0 min. In the Sections of 3.1 and 3.2, the suspension after slow mixing period were settled for 30 min, and the residual DOC of supernatant below 2.0 cm from surface was measured. The characteristics of flocs formed in this study were measured as described in former studies [36–38].

3. Results and discussion

3.1. Dosage optimum

In this study, the concentration by DOC was adjusted to 4.0 mg/L, and the coagulant dosage was ranged from 0.02 to 0.4 mmol/L calculated as Al. After the coagulation process, the residual DOC was analyzed. The coagulant used in this study was PACl(0).

The results indicated that the residual concentration of DOC decreased with increasing the coagulant dosage, and the removal efficiency reached the highest point when the coagulant dosage was 0.10 mmol/L. When the coagulant dosage was larger than 0.10 mmol/L, the residual concentration of DOC increased due to charge reversal, so the coagulant dosage used in this study for these coagulants was 0.10 mmol/L calculated as Al.

3.2. The removal efficiency for DOC under different conditions

The concentration of DOC was adjusted to 2.0 mg/L, 4.0 mg/L and 8.0 mg/L. In order to better understand the effects of solution pH value on the removal efficiency for DOC, the solution pH values were adjusted to 5.0, 7.5 and 9.0. Coagulant dosage was 0.10 mmol/L calculated as Al, and after the coagulation process, the residual DOC concentration was analyzed. The results are summarized in Fig. 4.

Fig. 5. Effects of different amounts of CNTs on the coagulation process (pH 5.0, coagulant dosage = 0.1 mmol/L calculated as Al, (A) DOC = 2.0 mg/L; (B) DOC = 4.0 mg/L; (C) DOC = 8.0 mg/L).

The results in Fig. 4 showed that the removal efficiency for DOC decreased when the concentration of DOC was increased from 2.0 to 4.0 mg/L at all three pH values. But when the concentration of DOC was increased to 8.0 mg/L, the removal efficiency increased. These results may be caused by the different collision efficiencies for HA molecules. The HA molecules in solution may form complex with coagulants, and the coagulation performances may be affected. But when the amount of HA molecules was large enough (8.0 mg/L), the collision efficiency between HA molecules and coagulants increased, so the removal efficiency was also increased. The results (Fig. 4A) indicated that when the concentration of DOC was fixed at one concentration (2.0 mg/L), the removal efficiency for DOC increased from 24.04 to 76.04% with increasing the concentration of CNTs. When the solution pH was adjusted to 7.5 and the concentration of DOC was 2.0 mg/L, the removal efficiency increased from 41.84 to 80.56% with increasing the amount of CNTs. But when the amount of CNTs was larger enough (using PACI(4) and PACI(5) as coagulants), the removal efficiency was almost the

same (Fig. 4B). In the adsorption experiments for HA, researchers have showed that the removal efficiency increased with increasing the concentration of CNTs. So in the coagulation process, the removal process for HA may be caused by two mechanisms, one is the adsorption of CNTs, and the other is the coagulation process. When the amount of CNTs was large enough, the CNTs particles which had negative charges would react with Al species, so the coagulation performances may be decreased due to the decreasing of charge neutralization abilities. The removal efficiency for DOC when the solution pH value was adjusted to 7.5 at three concentration of DOC conditions was 56.93%, 18.58% and 34.55% using PACI(1) as coagulant. The removal efficiency decreased to 39.04%, 14.52% and 20.91% in acidic range. And when the solution pH value was increased to 9.0, the removal efficiency decreased to 47.54%, 14.01% and 21.51%. When the solution pH value was adjusted in acidic range (pH 5.0), the Al loaded on the surfaces of CNTs would be dissolved into Al^{3+} , and these Al^{3+} ions would form a complex with HA molecules. These complexes would produce repulsive

Fig. 6. Effects of different amounts of CNTs on the coagulation process (pH 7.5, coagulant dosage = 0.1 mmol/L calculated as Al, (A) DOC = 2.0 mg/L; (B) DOC = 4.0 mg/L; (C) DOC = 8.0 mg/L).

interaction with carbon nanotubes, so the removal efficiency for DOC decreased. When the solution pH was in alkaline range (pH 9.0), the functional groups of Al-OH would disappear. The negatively charged surfaces would reject the HA molecules in the solution. At the same time, large amount of OH^- would compete with HA for the adsorption sites. So in acidic or alkaline conditions, the removal efficiency for DOC decreased due to the charges on the surfaces of CNTs.

3.3. Characteristics of flocs formed under different conditions

The flocs formed under different coagulation conditions were exposed to larger breakage rate (200 rpm for 5.0 min). After the breakage, the stirring rate was decreased to 40 rpm for 10 min for re-growth. The concentration of DOC was adjusted to 2.0 mg/L, 4.0 mg/L and 8.0 mg/L. In order to better understand the effects of solution pH on the characteristics of flocs, the solution pH was adjusted to 5.0, 7.5 and 9.0. Two coagulant dosages were used

(0.1 mmol/L and 1.0 mmol/L calculated as Al), and the floc size in different conditions were summarized in Figs. 5 and 10. The strength factors and recovery factors under three DOC concentrations with 0.1 mmol/L under pH 5.0 were summarized in Table 2.

The results in Fig. 5A indicated that the floc size increased from 225 μm to 330 μm with increasing the amount of CNTs in coagulant from 0.0 g to 2.0 g. The results in Table 2 showed that the concentration of CNTs had no significant effects on the strength factors, and the recovery factors increased with increasing the concentration of CNTs. These results showed that the CNTs existed in the coagulants could bridge the flocs together, but the bridging effects were smaller than the effects of coagulants. But the bridging effects were significant in recovery period, so the recovery factors increased with increasing the concentration of CNTs. The results in Fig. 1 showed that when the solution pH was 5.0, the CNTs in the coagulants had positive charges. In the breakage period, the new exposed surfaces would have negative charges, so the CNTs which had positive charges would bridge

Fig. 7. Effects of different amounts of CNTs on the coagulation process (pH 9.0, coagulant dosage = 0.1 mmol/L calculated as Al, (A) DOC = 2.0 mg/L; (B) DOC = 4.0 mg/L; (C) DOC = 8.0 mg/L).

Table 2

Strength factors and recovery factors (pH 5.0, coagulant dosage = 0.1 mmol/L).

Coagulants		PACl(0)	PACl(1)	PACl(2)	PACl(3)	PACl(4)	PACl(5)
DOC = 2.0 mg/L	Strength factor	34.66%	34.13%	34.28%	35.12%	36.89%	35.31%
	Recovery factor	66.38%	66.67%	67.89%	75.27%	78.14%	80.67%
DOC = 4.0 mg/L	Strength factor	40.86%	40.54%	38.75%	38.53%	36.66%	35.61%
	Recovery factor	42.02%	38.64%	34.69%	31.74%	32.33%	31.74%
DOC = 8.0 mg/L	Strength factor	–	–	–	–	–	–
	Recovery factor	–	–	–	–	–	–

the broken flocs together. When the concentration of DOC was increased to 4.0 mg/L, the results were summarized in Fig. 5B. The results showed that the floc sizes increased from 350 to 455 μm . When the concentration of DOC was 2.0 mg/L, the solution had positive charges, so the floc sizes decreased due to the repulsion force. After increasing the concentration of DOC to 4.0 mg/L, there would be more HA molecules which had negative charges, so the

floc sizes increased larger. These mechanisms were also proved by strength factors, and the strength factors for flocs formed with 4.0 mg/L DOC were larger than flocs formed with 2.0 mg/L DOC. The results also showed that the amount of CNTs had no significant effects on the strength factors. The recovery factors decreased with increasing the concentration of CNTs, and this may be caused by the larger removal efficiency for HA (the floc sizes after re-growth

Fig. 8. Effects of different amounts of CNTs on the coagulation process (pH 5.0, coagulant dosage = 1.0 mmol/L calculated as Al, (A) DOC = 2.0 mg/L; (B) DOC = 4.0 mg/L; (C) DOC = 8.0 mg/L).

Table 3
Strength factors and recovery factors (pH 7.5, coagulant dosage = 0.1 mmol/L).

Coagulants		PACl(0)	PACl(1)	PACl(2)	PACl(3)	PACl(4)	PACl(5)
DOC = 2.0 mg/L	Strength factor	28.84%	31.75%	37.61%	36.62%	36.84%	40.75%
	Recovery factor	37.16%	36.11%	34.35%	42.96%	47.73%	55.21%
DOC = 4.0 mg/L	Strength factor	45.19%	43.82%	42.22%	40.23%	41.11%	40.48%
	Recovery factor	38.14%	39.00%	36.54%	36.44%	32.07%	33.6%
DOC = 8.0 mg/L	Strength factor	–	–	–	–	–	–
	Recovery factor	–	–	–	–	–	–

increased with increasing the concentration of CNTs). When the concentration of DOC was adjusted to 8.0 mg/L, there were no flocs formed using all coagulants. The strength factors and recovery factors under three DOC concentrations with 0.1 mmol/L under pH 7.5 were summarized in Table 3. When the concentration of DOC was 2.0 mg/L, the effects of amount of CNTs had no significant effects on the floc size after growth. The results in Table 3 showed that the strength factors and recovery factors increased with increasing the

concentration of CNTs, and the CNTs would bridge the flocs together in the coagulation process. The results of Figs. 5 and 6A showed that when the solution pH was 5.0, the concentration of CNTs had no significant effects on the strength factors. The effects of CNTs were affected by two mechanisms: (1) the interaction between HA molecules and CNTs; (2) the coagulation process in removing of HA molecules. The strength factors for flocs formed under pH 7.5 were smaller than flocs formed under pH 5.0, and these results may be

Fig. 9. Effects of different amounts of CNTs on the coagulation process (pH 7.5, coagulant dosage = 1.0 mmol/L calculated as Al, (A) DOC = 2.0 mg/L; (B) DOC = 4.0 mg/L; (C) DOC = 8.0 mg/L).

caused by the electrostatic patch effects. When the concentration of DOC was 2.0 mg/L, the flocs may have positive charges. After the breakage, the positive positions may attract with other negative positions, so the recovery factors were larger than pH 7.5. When the concentration of DOC was adjusted to 4.0 mg/L, the concentration of CNTs had no significant effects on the strength factors and recovery factors. This is maybe caused by the increase of the ratio of the amount of HA molecules to the amount of CNTs. When the concentration of DOC was adjusted to 8.0 mg/L, there were also no flocs formed in the coagulation process. When the solution pH was adjusted to 9.0 (Fig. 7), there were no flocs formed in the all conditions. Al_a is the most reactive species out of the three Al species (Al_a , Al_b , Al_c), and it is less efficient in the coagulation process. In previous studies, people have found that at acid region, the aluminum monomers (Al_a) were the dominant species in AS. Al_a decreased abruptly and reached a minimum at neutral pH condition. However, the variation of Al_b presented a sharp increase, followed by a rapid decrease when the pH moved away from neutral pH conditions. When the solution pH was adjusted to 9.0, the coagulation

process may be affected by the solution pH due to the different Al species distribution.

When the coagulant dosage was increased to 1.0 mmol/L calculated as Al under pH 5.0, there were no flocs formed in the coagulation with three DOC concentrations because the flocs had large positive charges (Fig. 8). When the solution pH was adjusted to 7.5 with DOC 2.0 mg/L, there also would be no flocs formed. When the concentration of DOC was increased to 4.0 mg/L or 8.0 mg/L under pH 7.5, there would be large flocs (Fig. 9, 1000 μ m) formed at the beginning of slow mixing period, and the floc size decreased with increasing the coagulation period. These results maybe also caused by electrostatic patch effects, and once the coagulant was added to the HA solution, the positions which had positive charges would attract with other positions which had negative charges to produce larger flocs. In the slow mixing period, the flocs re-arranged, and the floc size decreased. After breakage, the new exposed surfaces which had negative charges would attract Al species coagulants in the solution, so the broken flocs would have positive charges to repel with each other (the flocs would not

Fig. 10. Effects of different amounts of CNTs on the coagulation process (pH 9.0, coagulant dosage = 1.0 mmol/L calculated as Al, (A) DOC = 2.0 mg/L; (B) DOC = 4.0 mg/L; (C) DOC = 8.0 mg/L).

regrow). The results in Fig. 9B and C showed that the largest flocs decreased when the concentration of DOC was 8.0 mg/L. The largest floc size was about 1000 μm with concentration of DOC 4.0 mg/L, and the floc size decreased to about 800 μm when the concentration of DOC was increased to 8.0 mg/L. When the concentration of DOC was 8.0 mg/L, there would be more HA molecules in the solution, so the effects of electrostatic patch effects would not be significant. The results in Fig. 10 showed that when the solution pH was increased to 9.0, there would be large flocs formed at the beginning of slow mixing period under three concentration of DOC. The largest floc sizes had no significant differences at the beginning of slow mixing period, but the floc sizes after re-growth decreased with increasing the concentration of DOC. All the flocs had no re-growth abilities in the re-growth period due to different Al species distribution compared with other two pH values.

4. Conclusion

Although there were no standards about humic acid clarification, as one of the major portion of dissolved organic matter, humic acid was ubiquitous in the aquatic environment. Humic acid molecules in raw water could react with chlorine to form disinfection by-products (DBPs) and the DBPs may cause cancer or other hazards to humans. Thus, how to remove high concentration of humic acid was important to ensure the water quality. The former studies also indicated that Humic acid was the decision factor for residual aluminum in the water treatment process, and decreasing the concentration of HA had significant effects on the decreasing the concentration of residual aluminum. So in this study, t carbon nanotubes (CNTs)/polyaluminum chloride (PACl) composites coagulants were used to treat HA solution, and the DOC removal efficiency, the floc size in the coagulation process were investigated. The main conclusions from this work were listed as the following:

1. The removal efficiency for DOC decreased with increasing the concentration of DOC, and these results may be caused by the saturation of functional groups due to the large amount of HA molecules. When the concentration of DOC was fixed at one concentration, the removal efficiency for DOC increased with increasing the concentration of CNTs.
2. The concentration of CNTs had no significant effects on the strength factors, and the recovery factors increased with increasing the concentration of CNTs. The effects of CNTs on the coagulation process were affected by two mechanisms: (1) the interaction between HA molecules; (2) the coagulation process in removing of HA molecules.
3. When the coagulant dosage was increased to 1.0 mmol/L calculated as Al under pH 5.0, there were no flocs formed in the coagulation with three DOC concentrations because the flocs had large positive charges. When the concentration of DOC was increased to 4.0 mg/L or 8.0 mg/L under pH 7.5, there would be large flocs formed at the beginning of slow mixing period, and the floc size decreased with increasing the coagulation period. These results maybe also caused by electrostatic patch effects.

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