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Electrokinetic chemical characteristics of humic and dannic acids effecting on the natural water and its coagulation

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Abstract—— Taking streaming current (*SC*) as the electrokinetic parameter, this paper demonstrated the electrokinetic chemical characteristics of humic and dannic acids (HA and DA) in suspensions including turbid water, coagulated water and HA or DA contained water. Accordingly, the studies were carried out for determining the relationship between streaming current and zeta potential ζ (expressed by electrophoretic mobility EM) in above water conditions. In addition, the mechanisms of HA effecting on streaming current within or after coagulant addition and the electrokinetic detection principles for HA or DA were also investigated on experiments and theoretical analysis. The results indicated that the change of *SC* like ζ presented meaningful information concerning the degree for destabilization of a particulate suspension, and HA or DA in water could remarkably decrease the effect of inorganic coagulant upon streaming current, which is in accordance with their influence on coagulation.

Keywords: electrokinetic chemical characteristics; humic acid; dannic acid; natural water.

1 Introduction

Humic substances, dannic acid and other organic large-molecular substances in natural water possess the complex and stable structure and species. They can join the chemistry circle processes of earth and react with heavy metal cations, so they may influence, to a certain extent, the migration and transformation of some organic and inorganic pollutants. Simultaneously, they will make the water treatment more difficult (Gibbs, 1983).

Humus, dannic acid existing in natural water with their anions may not only react with the coexisting ions or molecules to become some kinds of high-molecular substances with the complex structure, but also can be adsorbed on the particles in water to strengthen the negative electrical, stable and dispersal properties of colloids. In fact, there is a certain relationship between viscosity of clay and flocculation and dispersion of clay (Jekel, 1986). Lahav (Lahav, 1970) noted that humic substances could reduce the dimensions of Kaolinite colloid particles in water. The research of Roy (Roy, 1971) confirmed that humus could lower the viscosity of Kaolinite suspension and break the natural structure formed in clay particles.

Thomas (Thomas, 1988) found that some important reactions happened between humic substances and aluminum salts. The research also proved, a certain quantity of humic and dannic acids in water being treated would weaken the effect of coagulants on colloid particles, thus the coagulation processes became more difficult and the coagulant consumption would be increased. However, the knowledge regarding the effect of humic substances and dannic acid on flocculation or coagulation is incomplete so far. This paper, taking streaming current (*SC*) as the eletrokinetic parameter, provides an initial attempt at predicting the acting principles in reaction of humic or dannic acid (HA or DA) with colloid particles and coagulants in natural water and the water treatment processes by using theorctical analysis and experiments.

2 Research method

2.1 Detection of electrokinetic parameter

SC is regarded as the electrokinetic parameter in this study. *SC* is detected successively by a Milon Roy-GFNπ-ED Streaming Current Detector, or SCD, which essentially consists of a sampling chamber, a sensor composed of a reciprocation piston in a cylinder, and a signal amplifier. The sampling chamber allows a continuous flow of sample to be characterized over time, but on SCD used in this research, this sampling chamber could be removed and a batch sample is placed so that the sensor was directly immersed in a fixed volume of water.

It is assumed that colloids in the fluid momentarily can adhere to the piston and cylinder surfaces. The piston imparts motion to fluid in the annular gap, which causes motion of counterions relative to the colloids. The resulting current, detected by ring-shaped electrodes at opposite end of the annulus, is transferred and amplified to give an useful output. Because this signal is proportional to electrical charge on the colloids, it indicates the extent of destabilization in a manner similar to zeta potential.

Theory predicts a direct proportionality between streaming current and zeta potential (Smith, 1967):

$$I_S = \frac{AP\varepsilon\zeta}{\eta l}, \tag{1}$$

where I_s is streaming current; A is capillary cross sectional area; P is applied pressure; ε is dielectric constant of water; ζ is zeta potential; η is viscosity of water; l is length of passage. Furthermore, the linear relationship between *SC* and ζ is still correct in SCD detection (Steven, 1989):

$$I_S = -4\varepsilon\omega SR^2\zeta/C^2, \tag{2}$$

where ω is rotational speed of the driving motor of SCD; S is piston stroke; R is radius of cylinder; C is radial clearance of piston or width of annulus. The electrical charge or potential of coagulated particles has usually been measured by electrophoresis or colloid titration, but both methods are tedious and impractical to perform on a continuous basis. The Equation (2) indicates that streaming current can provide a meaningful information concerning the electrical charges on colloid particles in natural water in a manner similar to zeta potential.

Thus the value of streaming current detectors not only has the ability to continuously monitor an electrokinetic parameter for use in coagulant dose control, but also can perform as an effective electrokinetic parameter for studying some special properties and phenomena in water treatment processes that can hardly be done by zeta potential.

2.2 Experimental method

A simulated natural water was made up using fine mud that was taken and selected from Songhua River. Humic acid (HA) was extracted from the bottom mud of Songhua River, and dannic acid (DA) was a commercial reagent. Before HA and DA were used, both were dissolved respectively in 1 mol/L sodium hydroxide and distilled water to the concentrations of 5 mg/L and 10 mg/L as the applied solutions. The coagulant used was solid aluminum sulfate (alum, $Al_2(SO_4)_3 \cdot 18H_2O$) and its concentration was 2% (content of alum).

For experiments, the SCD was set at a sensitivity setting of 3. The sampling chamber surrounding the sensor was detached, and the probe was immersed in 8L test water that was filled in a 10L spherical polymethyl methacrylate trough. A stepless speed varying stirrer working at 240 r/min was used to mix the water sample well at all time. Equivalent readings were written down under different experiment conditions. At the same time, electrophoretic mobility (*EM*) values were measured by Micro-Electrophoretic Mobility Detector (made in Japan).

Several different particulate systems were used in experiment. (1) HA or DA was added to the distilled water or the simulated water (300 NTU). This system was used to assess the effect of HA and DA upon the streaming current. (2) The simulated raw water (300 NTU) was coagulated first by dosing 50 mg/L alum and then HA or DA was added. This system was used to determine the effect of HA and DA upon the streaming current under coagulating condition. (3) HA or DA was added to the raw water and then alum was dosed successively for coagulating. This system was used to study the effect of alum upon the streaming current in presence of HA and DA.

For obtaining reproducible results of streaming current, we found it was necessary to carefully clean the probe of SCD between experiments, particularly when samples contained supersaturated or surface active components. The cleaning by H_2O_2 and HCl solution was usually found satisfactory for the recovery of *SC* value as the beginning.

3 Results and discussion

3.1 Streaming current characteristics of humic and dannic acid

Relationship between *SC* values and concentration of HA or DA in simulated suspended natural water and distilled water are shown in Fig. 1 and Fig. 2. The *SC* values were obviously after a certain quantity of HA or DA was added into water, and their content increasing in water resulted in a continuously negative change of *SC*. In distilled water, the reason that *SC* value as an electrokinetic parameter alters with HA or DA addition may be the negative effect of their anions and negative colloids upon the probe surface of SCD and the water system. In suspension, the other key reason may be the coordinate effect between the two anions, colloids of HA or DA and suspended particles contained in raw water. This suggests that the negative electrical property of solids in water is strengthened due to the addition of the two substances, so it is believed that the colloids in water will appear more stable when there exists a certain quantity of HA or DA, which may also lead to a decrease of coagulation effect in water treatment.

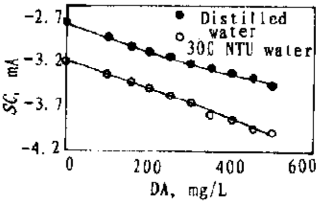


Fig. 1 Concentration of DA vs *SC* value

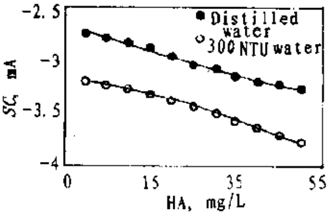


Fig. 2 Concentration of HA vs *SC* value

3.2 Electrokinetic characteristics of humic and dannic acid effecting on coagulation

3.2.1 Streaming current characteristics of HA and DA effecting on the coagulated water

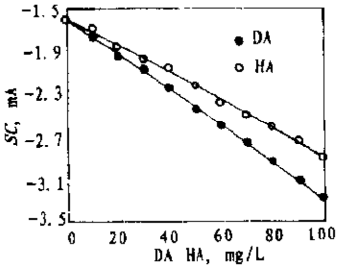


Fig. 3 Concentration of DA and HA vs *SC* value in coagulating water

Fig. 3 shows the *SC* results as the total concentration of HA or DA was increased from 10 to 100 mg/L at pH 7.2 in the water coagulated using 50 mg/L alum. In this process, the initial change of *SC* values brought about by alum addition implies that the originally negative probe surfaces of SCD were being affected by Al^{3+} and its hydrates, such as $Al(OH)^{2+}$, $AlOH^{2+}$, $Al_2(OH)^{5+}$, $Al(OH)_3$, etc., in the same manner that colloids in water experience charge neutralization. However, the positive property and neutralized ability of Al^{3+} and its hydrates will be reduced by the anions and their negative colloids after HA or DA addition. Besides, the two negative ions or particles in water will effect each other or be adsorbed on the probe of SCD, and then bring on a more negative *SC* value.

The experimental results proved that, the *SC* value was decreasing with HA or DA addition in the coagulated water. For example, the addition of 10 mg/L DA resulted in the *SC* value changing from −1.60 to −1.74, and when the concentration of DA reached to 50 mg/L, the *SC* value decreased to −2.44. If the content of DA was up to 100 mg/L, the *SC* value was even recovered almost to the initial value (−3.20) in raw water. This indicated that the positive effect of alum on streaming current was almost offset by the negative influence from DA. Although the tendency of *SC* value changed with the HA concentration increasing was similar to DA, their effect on streaming current was different. For instance, at their given concentration (50 mg/L) in water, HA and DA decreased the *SC* value by −0.68 and −0.47 mA respectively comparing with the initial value −1.57, the difference was about 0.2 mA. These imply that the negative ions or particles of DA in water had a greater negative effect on the electrokinetic property of colloids and probe surfaces than HA.

3.3.2 Effect of alum on streaming current in the water containing HA and DA

DA or HA was added to the simulated natural water to make up the experimental sample, then a given alum was dosed into the sample to assess the change of streaming current in the process. The results are shown in Fig. 4 and Fig. 5. It was found from the experiments that the presence of DA performed a certain influence on the efficiency of alum to increasing *SC* value, and the higher concentration was, the greater effect appeared. Comparing to the water condition without DA, the *SC* value increasing with alum dosing was weakened obviously by the addition of 20 mg/L DA. In the water containing 50 mg/L DA, the alum dose below 20 mg/L led to the *SC* values becoming more negative rather than positive. After that, the *SC* value was increasing slightly with the addition of alum. However, even if there was 50 mg/L alum dosed in water, the *SC* value only increased to −3.23 that was still more negative than the value of raw water (−3.20). HA also could strongly reduce the positive effect of alum upon streaming current. For instance, when there was 75 mg/L HA in the raw water, though the addition of alum reached to 20 mg/L, the *SC* results were still no any altering. This indicates that there must exist some special interactions between the natural organic large molecular and coagulant.

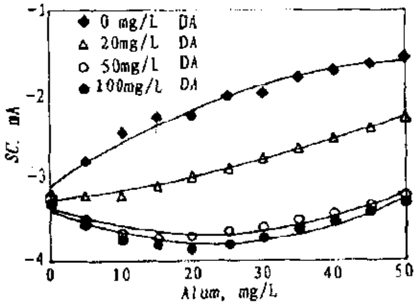


Fig. 4 Streaming current vs alum sulfate dosage in the water containing DA

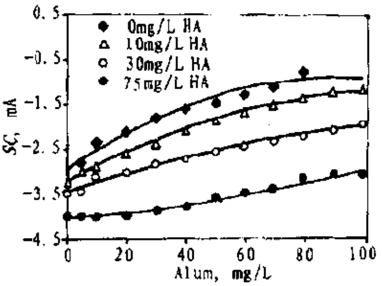


Fig. 5 Streaming current vs alum sulfate dosage in the water containing HA

It can be believed from above experimental results that the reduction of coagulant effecting on the electrokinetics of raw water is the essential relative characteristics between streaming current and HA or DA, and this must be one of the key reasons why HA and DA can lower the coagulation ability of alum.

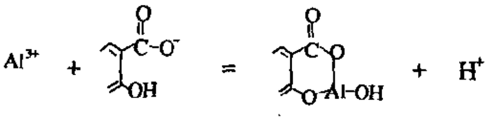
3.3.3 The mechanism of effect of HA and DA on *SC* in coagulation process

Take humic acid as the object studied here.

Humic substances are acid, heteodisperse, polymeric, colored, chemically complexed macromolecules in soil, sediment and water. They contain phenol hydroxy and a few of fatty hydroxyl. Because of its peculiarity in structure, we propose that the followings may be the important aspects for the mechanism of effect of HA and DA on *SC* in coagulation process.

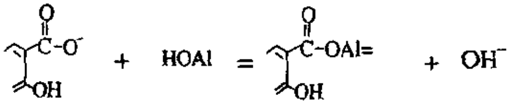
(a) Complex reactions

There are some complex reactions taking place in water between the free metal ion Al^{3+} and the soluble HA, in which Al^{3+} replaces some hydrogen ions from HA and a kind of complex precipitated compound will be developed in the processes.

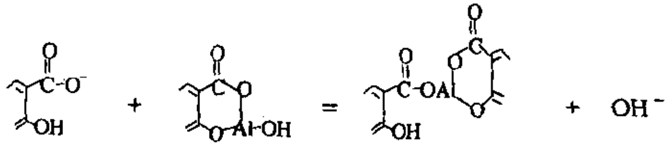


Al^{3+} is compounded into the molecular structure of HA after complexing. The influences of spatial obstruction and complex precipitation in the new produced Al-HA complex compound will greatly lower the positive efficiency of Al^{3+} as the electrolyte cation in neutralizing the surface charges of colloids in water and probe in SCD, and then the effect of alum in altering streaming current is reduced reasonably in this case.

In addition, the following reaction taking place between HA and hydroxyl aluminum will also influence the electrokinetic chemical behavior of alum in water:



In which AlOH=hydrated aluminum hydroxide. This kind of complex reactions can also take place between complex compounds and the anions of humic substances:



Al^{3+} will be compounded further in the complexing formation in the second stage reaction, and thus it can not act as a positive ion influencing streaming current but producing some anions like OH^- to increase the negative property of the system in water, which may be one of the reasons for appearing as more negative *SC* result by a lower dosage of alum in the water containing a higher content of HA.

(b) Adsorption effect

The adsorption of HA onto surfaces of colloids and SCD probe in water results from physical or chemical forces. Bonds that form can include van der Waals interactions, H-bonding, hydrophobic bonding, ligand exchange, anion exchange, or dipole interaction (Bottero, 1981). Simultaneous precipitation can be considered to be the simultaneous reaction of different HA molecules with both soluble Al or $Al(OH)_3$. Therefore, by the adsorption, the charged surfaces of colloids in the water and probe of *SCD* must become more negative, so that a more amount of alum will be needed for gaining the same electrokinetic effect as in the water without HA. On the other side, some soluble Al or $Al(OH)_3$ may be combined with the insoluble or soluble HA, thus an extra alum will be consumed directly by the adsorbing processes. These are believed to be another important reason for the influence of alum upon the *SC* values .

(c) Neutralization

As mentioned above, HA exists in water as a sort of negative charged insoluble colloids and soluble anions. Those negative colloids will be neutralized and coagulated by alum dosed in water, so more amount of alum must be necessary to match the coagulation effect to water condition without HA, which must be displayed by streaming current.

3.4 Streaming current vs electrophoretic mobility in the water containing HA or DA

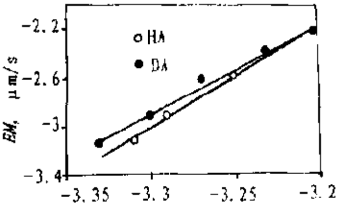


Fig. 6 *SC* values vs *EM* as adding HA and DA into the simulated water

In the water containing humic or dannic acid, there still exists the linear relationship presented in Equation (2) between streaming current and zeta potential (expressed by electrophoretic mobility, *EM*), which was assessed by the experimental results shown in Fig. 6, Fig. 7 and Fig. 8. When 75, 30, 20, 10, 0 mg/L HA and/or 100, 80, 50, 20, 0 mg/L DA were added to the simulated raw water, the *SC* values vs *EM* was increasing linearly as shown in Fig. 6. In addition, after the same quantities of DA or HA as in the Fig. 6 were dosed into the coagulated water containing 50 mg/L alum, the two electrokinetic parameters were also varying proportionally as shown in Fig. 7. Although the experiment process in Fig. 8 was different from Fig. 6 and Fig. 7, the change of *SC* vs *EM* still exhibited a linear tendency, in which both the *SC* results and *ME* were positively altering as increasing alum concentration from 10 to 50 mg/L in the water containing 100 mg/L DA or HA. This indicates that in a wide range, both streaming current and zeta potential perform the same electrokinetic tendency for evaluating the water quality change caused by humic substances and dannic acid.

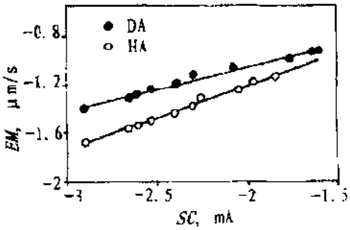


Fig. 7 *SC* values vs *EM* as adding HA and DA into the water coagulated by 50 mg/L alum

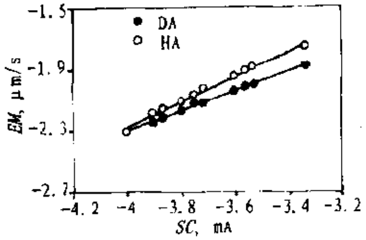


Fig. 8 *SC* values vs *EM* as dosing alum into the water containing HA and DA

3.5 The electrokinetic detection principles of humic substances and dannic acid

According to the character of absorption on the probe surface of SCD (Qu, 1994), while the water containing HA or DA is flowing on the surfaces of probe, streaming current may be varied in two ways: (1) the free anions of HA or DA together with other ions directly are adsorbed temperately on the probe surface to set up the new electrical double layers that is based on the electrical property of the piston and cylinder surfaces, where the background current (I_{sb}) will be developed; (2) the anions of HA or DA adhering to the suspended colloids in water will also adsorbed temperately on the probe surfaces following the colloids to set up another sorts of electrical double layers that is based on the electrical property of colloids, where the non-background current (I_{SC}) can be produced. Thus, the total streaming current is

$$I_s = I_{sb} + I_{sc}, \tag{3}$$

In accordance with the principles of SCD detection, the anions of HA or DA adhering to the probe regardless their ways to realize adsorption must be desorbed into solution and the places will be occupied by the new charged ions or particles to form new electrical double layers and produce streaming current. Because the process is successive, the streaming current produced can also be detected continuously by SCD. If there are electrical charge density σ_b and σ_c which are formed by the negative ions or colloids adhering to the probe in water respectively, their electrical double layers can be described as:

$$k_b = \frac{\varepsilon\zeta_b}{4\pi\sigma_b} \tag{4}$$

and

$$k_c = \frac{\varepsilon\zeta_c}{4\pi\sigma_c}. \tag{5}$$

Equation (6) can be deduced from Eq. (2) to (5)

$$I_s = \frac{4\pi G}{\varepsilon}(\sigma_b + \sigma_c). \tag{6}$$

If $\sigma = \sigma_b + \sigma_c$, and

$$\sigma = \frac{q}{A}, \tag{7}$$

where q is the total electrical charge of DA or HA in all species on the probe of SCD; A is the effective surface area of the probe. Combining this with Eq. (6) gives

$$I_s = \frac{4\pi Gq}{\varepsilon A}. \tag{8}$$

Equation (8) expresses that the more the negative ions of DA or HA adsorbed on the probe, the stronger the negative streaming current becomes, which is identical with the results of the experiments in this report.

4 Conclusions

The data presented in this paper confirm that the streaming current provides meaningful information concerning the effect of humic acid and dannic acid on the electrokenitic characteristics in the natural or coagulated water. Streaming current decreasing remarkably after addition of HA or DA suggests that the presence of humic substance and dannic acid would lead to an increase of negative charges on the surface of suspended particles in the natural water. In addition, when the water contained or was dosed by HA or DA, the efficiency of alum as the positive coagulant was weakened obviously which resulted in the alteration of electrokinetic property on colloid particles. This indicates that HA or DA can not only neutralize the cations but also combines with some species of alum, thus more amount of inorganic coagulant must be needed to realize a good coagulation result in the presence of humic substances and dannic acid.

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