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Flocculation process of fine-grained sediments by the combined effect of salinity and humus in the Changjiang Estuary

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Abstract

For the great amount of organic compounds and the variation of salinity in the Changjiang Estuary, the study on the flocculation process of fine-grained sediments by the combined effect of salinity and humus in the high-turbid system is of critical significance for the understanding of the mechanism of the formation of the turbidity maximum (TM). For the great amount of organic compounds and the variation of salinity in the Changjiang Estuary, the study on the flocculation process of fine-grained sediments by the combined effect of salinity and humus in the high-turbid system is of critical significance for the understanding of the mechanism of the formation of the turbidity maximum (TM). The effects of salinity and humus on the fine-grained sediments have been analyzed through the synthetic study of the aspects of flocculation/coagulation power (F), diameter (D) and zeta potential (Z). And the microcosmic configuration of the flocs has been analyzed by using a scan electron microscope and Fourier Transform Infrared Spectrometry. The results show that: (1) with the increase of salinity, F and D become greater and Z becomes smaller, and with the increase of the concentration of humus, F becomes smaller, but D and Z become greater; (2) the microcosmic configuration of the flocculation shows that humus packs on the fine sediments in the form of salt, and the flocculation model of C–P–OM (C stands for clay; P cations; OM organic materials) can successfully demonstrate the mechanism of the formation of the fine-grained sediments in the high-turbid area of the Changjiang Estuary.

Key words: Changjiang Estuary, fine-grained sediment, flocculation, salinity

1 Introduction

The flocculation of fine-grained particles is one of the main reasons for the estuarine deposition. With the combination of salt water and freshwater, fine-grained particles in estuaries will experience drastic changes: flocculation, settlement, resuspension, deflocculation, diffusion and aggradation. Flocculation, in particular, affects the transport and the fate of not only the sediments (Jiang and Yao, 2006; Shen et al., 1983; Pan et al., 1999; Zhang et al., 1995; Xie et al., 1998) but also the metallic and organic materials (Lin et al., 1995). Therefore, the study on the flocculation process of fine-grained sediments by the combined effect of salinity and humus in the high-turbid system is of great help in understanding the mechanism of the formation of TM and illustrating the deposition dynamics of sediments (Shen et al., 1982; Milliman et al., 1983). Up till now, studies on flocculation have mainly shown the effect of the dynamic condition (Zhang, 1992; Jiang et al., 2002; Shi, 2000) and of the exterior environment (Ruan, 1991; Partheniades, 1965; Matz, 1983; Van, 1988), while less re-

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search has focused on its intrinsic factors. Much research on the flocculation mechanism has reflected the importance of salinity (Jiang et al., 2002; Guan et al., 1992; Chen, 1987; Jiang et al., 1995); however, it is also held that the effect of organic matters is stronger than that of salinity (Dyer, 1988; Eisma, 1991; Berhane, 1997).

The sediments with organic matters take up 60 to 75 percent of the total sediments in quantity (Li et al., 2001), the salinity increases in the course of the river's flowing into the sea. The abundance of organic matter and the variation of the salinity in the Changjiang Estuary are two important factors that affect the sediment flocculation. So it is highly necessary to put the two factors together in the scientific study of the flocculation mechanism.

In this paper, the water and the sediments are all collected from the turbidity maximum (TM) of the Changjiang estuary. The variation of turbidity is applied to indicating the comparative change of the suspended sediments. And the change of flocculation power (F) may explain the effect of the two flocculation factors on the fine-grained particles (Osborne, 1978; Ozkan, 2003; Ozkan Yekeler, 2003; Ozkan et al., 2004). And the diameter and the zeta potential of floc are determined. After the study of each factor was carried out respectively, the combined effect was studied. The microstructure of flocs was also studied by an IR spectra and scan electron microscope. Through the close study of the different effects of the two factors, the flocculation mechanism of the fine-grained sediments in the Changjiang estuary was clearly illustrated.

2 Materials and methods

Water and sediment samples were saved at 4℃, which were collected in the TM of South Passage in the Changjiang Estuary in September 2004. At the same time, the pretreatment of samples was processed in the laboratory. In order to wipe off the organic matter, sediment samples were mixed with 30% H_2O_2 at the constant temperature 50℃ until no air bubble appears. After being dried at 100℃, sediment samples were filtered by the 54 μm filter (Fig. 1). And the water samples were filtered with acid precleaned by 0.45 μm pore-size acetate cellulose filters.

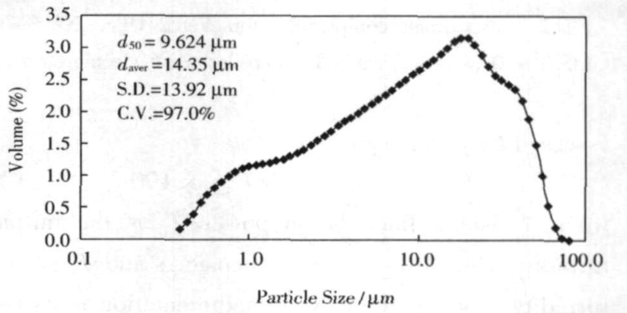


Fig. 1 Granularity distribution of fine-grained sediments in the experiments logarithm coordinate in X axis. S. D. represents standard deviation and C. V. cofficient of variation

Sodium chloride (GR), purchased from the Shanghai Chemical Reagent Factory (No. 4) in China and humus, obtained from the Zibo Tiande Chemical Factory in China, were used for flocculation experiments of fine-grained sediments.

As shown in Fig. 2, the flocculation experiments were carried out in a 50 dm^3 cylindrical cell by using 30 dm^3 water and 30 g fine-grained particles which were pretreated in the laboratory. The dispersed suspension, adjusted to the desired pH, was first conditioned at 500 r/m for 5 min and the flocculant was added to the suspension at an impeller speed of 500 r/m. After 5 min the stirring speed was reduced to 0 r/m for 15 min, to allow floc growth. At the same time, the turbidity of the supernatant was measured by an Endeco OBS-3a turbidity monitor. The flocculation size was recorded with LISST-100 and the zeta potential with JS94F micro electrophoretic-meter. The flocculation experiments were performed at around 20℃.

The performance of the flocculation process was

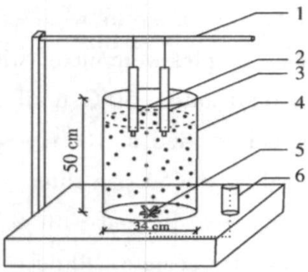


Fig. 2. experiment equipment. 1 bracket, 2 OBS-3A, 3 LISST-100, 4 cylindrical cell, 5 impeller and 6 electromotor

assessed by using a formula:

$$F = [(T_0 - T_f)/T_0] \times 100 \qquad (1)$$

where F is the flocculation power; T_0 is the initial turbidity of well dispersed suspension; and T_f is the turbidity of supernatant when sedimentation is assisted by flocculants.

After being dried at low temperature, the floc was scanned by NICOLET NEXUS670 Fourier transform infrared spectrometry and JSM-5610LV scan electron microscope to study the micro structure.

3 Results

3.1 Flocculation power

The variation of turbidity is attributable to the change of water color, particle size and its concentration, which is caused by the effect of sedimentation. And the sedimentation is closely related to the flocculation of fine-grained particles. So the flocculation power can directly reflect the flocculation capacity, and the change of the flocculation power at a certain time may show the alteration of the settling velocity of flocs. Figure 3 is an illustration of the effect of salinity and humus on the flocculation power of fine-grained particles. The flocculation power values of the fine-grained particles increased with the increase of salinity when the humus concentration equals 0 mg/L, but decreased with the increase of humus concentration when the salinity 0. By the combined effect of salinity and humus, the variation of flocculation power is complex. The isoline changed rapidly under the conditions of the higher salinity and lower humus concentration zone, as shown in the ichnography, which indicated that the flocculation power was affected greatly by salinity. On the contrary, the isoline changed slowly in the higher humus concentration and lower salinity zones, which showed the great influence of the humus concentration on the flocculation power of fine-grained particles. As a form of the macromolecule organic compound, humus can join together fine-grained particles with its functional group, and the low density of humus led to the decrease of the density of flocs. At the same time, the electrostatic repellency of flocs became bigger because of the increasing humus concentration with the negative electric charge.

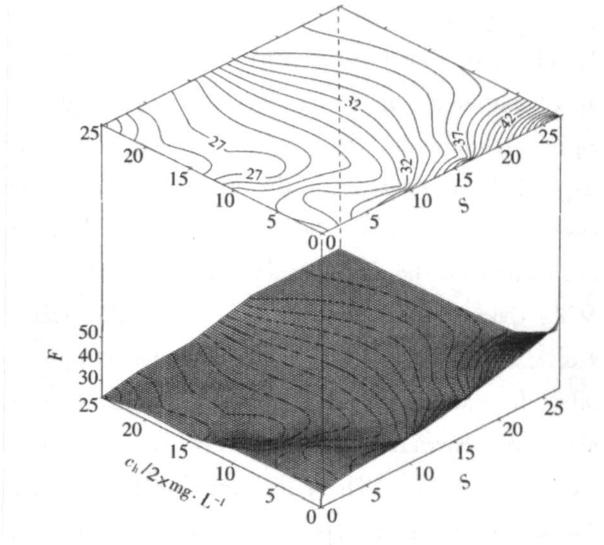


Fig. 3. Effect of satinity (S) and humus concentration (c_h) on the flocculation power of fine-grained particles

3.2 Diameter of flocs

Figure 4 is the illustration of the effect of salinity and humus concentration equals on the diameter of flocs. The diameter of flocs increased appreciably with the increase of salinity when the humus concentration 0 mg/L, but decreased rapidly with the increase of humus concentration when the salinity equals 0. By the combined effect of salinity and humus, the variation of flocs' diameter shows an increased trend. This indicates that humus concentration is the main influencing factor on the diameter of flocs. As the ichnography shows, the isoline is denser in the low humus concentration area (0~5 mg/L), and the diameter of flocs becomes bigger (50~80 μm) with the increase of the humus concentration; however, the diameter of flocs has little change (80~90 μm) in the environment of high humus concentration. When the humus concentration exceeds 5 mg/L, the humus concentration became saturated, wrapping the surface of the fine-grained particles. So the big flocs cannot be formed by the static repulsion effect and the volume restriction effect of humus concentration. Though the salinity alone has little effect on the diameter, the higher salinity in the water with humus concentration supplies a large amount of electrolyte, which decreases the static repulsion of flocs. Thus, the big flocs can be formed by combined effect of salinity and humus, especially in the higher salinity area.

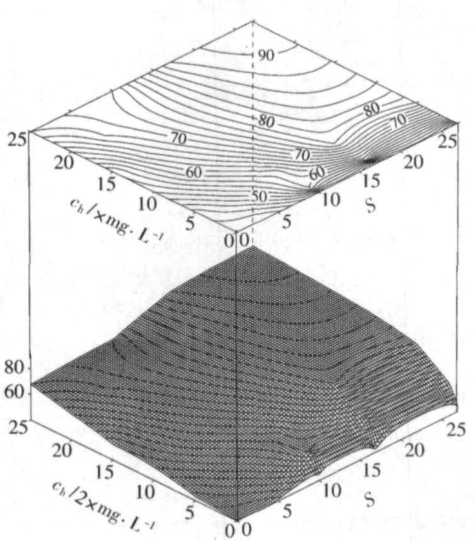


Fig. 4 Effect of salinity and humus concentration on the diameter (d) of flocs

3.3 Zeta potential of flocs

The flocculation power signifies the effect of the flocculants on the fine-grained particles, the diameter of the flocs denotes the superficial phenomena, and the zeta potential is the essence of flocculation. According to the DLVO theory (Sato and Ruch, 1980), the increase of the electrolytes can lead to the decrease of the static repulsion of the flocs, which can in turn cause the fine-grained particles to hang together more easily, and accordingly the flocculation occurs. As Fig. 5 shows, the absolute value of the zeta potential decreases with the increase of salinity when the humus concentration equals 0 mg/L, but increases a little with the increase of the humus concentration when the salinty equals 0. By the combined effect of salinity and humus, the variation of flocs' zeta potential is complex. This indicates that the two factors have different effects on the flocculation of fine-grained particles. The increase of salinity will compress the electrical double layer, and then decrease the absolute value of zeta potential; while humus, packing on the surface of the fine-grained particles with its functional group, increases the negative electric charge of the flocs and causes the increase of the absolute value of zeta potential. As the ichnography shows, the flocculation of fine-grained particles is affected greatly by humus in the low sa-

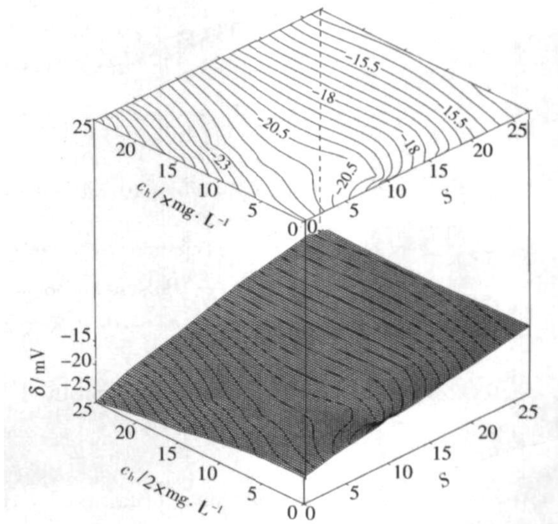


Fig. 5 Effect of salinily and humus concentration on the zeta potential (ζ) of flocs (Z: Zeta potentialmv).

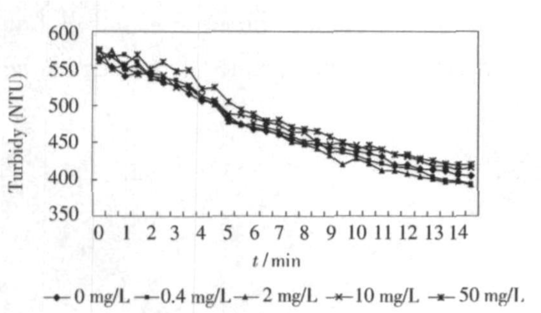
linity area. In the area of low salinity and low humus concentration, because of the opposite effect mechanism of the two factors, there is little change of the zeta potential of flocs, while in the area of high salinity, even the humus concentration increases, there is still little change of the zeta potential, which shows that the salinity is the main factor to influence the flocculation.

4 Discussion

4.1 Effect of humus on the fine-grained particles in saltwater and freshwater

As Fig. 6 shows, the flocculation of fine-grained particles in freshwater can be divided into two categories. With the increase of humus, when the humus concentration is low (0 ~2 mg/L), the turbidity of the flocs decreases rapidly; while when the humus concentration is high (>2 mg/L), the turbidity decreases slowly. The flocculation power first rises and then falls with the increase of humus concentration. When there is little humus packed on the fine-grained particles, the hydrophobic groups of humus direct outwards, causing the increase of the hydrophobic property. And consequently, the settling rate of the flocs accelerates. When the humus concentration is high, the surface of the flocs is packed with the hydrophilic groups (Chen et al., 1993) and the density of the flocs becomes lower for the humus concentration is always low in density. And as a result, the settling rate of flocs decreases.

As Fig. 7 shows, with the increase of humus concentration, the flocculation power goes down in saltwater ($S=10$). Because of the existence of the electrolyte in high salinity water, the humus reacts with cations more easily, which leads to the change in the layout of the hydrophobic groups and hydrophilic groups. The cations can connect fine-grained particles with humus, and as a bridge, can neutralize the charge, which may cause the decrease of the static repulsion of the flocs. Hence the big flocs can be formed and the settling rate can be accelerated.



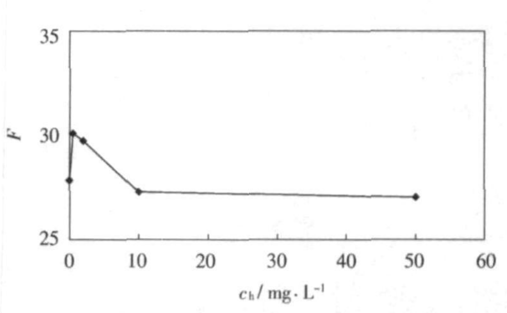
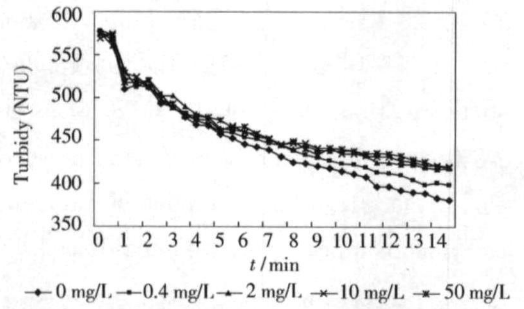


Fig. 6 Effect of humus on the fine-grained particles in freshwater. a. turbidity variation with time and b. change of flocculation power with humus concentration

4.2 Effect on the diameter of flocs of combined effect

According to the diameter data obtained by the LISST-100, the diameter of combined effect of salinity and humus can be divided into two categories. The first changes between 100 μm and 200 μm, and the second ranges from 30 to 50 μm. This is because the flocs, which are small at the beginning of the flocculation, have a high tension and combine together tightly. At the same time, the electrolyte supported by high salinity decreases the static repulsion and brings about the formation of big flocs. As Curve a in Fig. 8 displays, there appear double apexes for



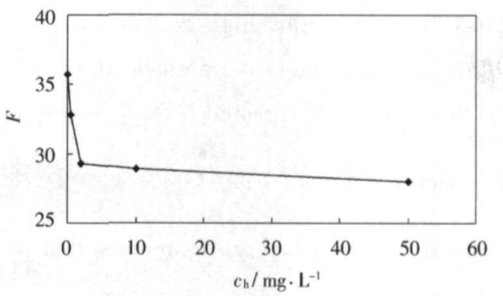


Fig. 7. Effect of humus on the fine grained particles in saltwater (S=10). a. Turbidity variation with time and b. flocculation power change with humus concentration.

the diameter of the flocs in the static water, while Curve b shows that there is just one apex in the dynamic water. The experiments suggest that large flocs formed in the static water can be broken up by the turbulent flow. Therefore, the diameter of flocs detected by the LISST-100 in the dynamic water of the Changjiang Estuary ranged from 50 to 60 μm (Cheng et al., 2005).

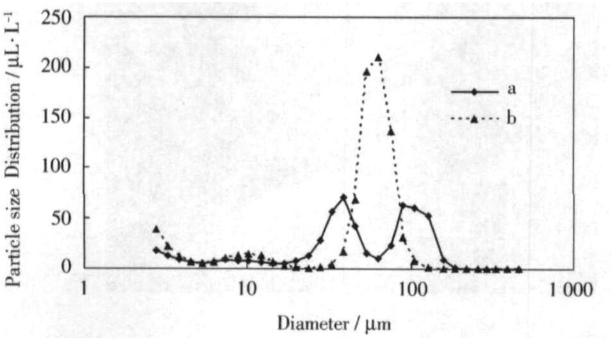


Fig. 8. Diameter distribution of flocs when humus concentration is 50mg/L and salinity is 27 (logarithm coordinate in x axis). a. flocs in static water and b. flocs in dynamic water

4.3 Microcosmic configuration of the flocs

Figure 9 shows the microcosmic configuration of flocs. The diameter of the flocs in the fresh-water formed by the fine-grained particles with humus being wiped off by H_2O_2 is comparatively equal, about 30 μm, as indicated in Fig. 9a. After being magnified further, the microcosmic configuration can be observed clearly in Fig. 9b. The surface of the flocs is relatively smooth, and big flocs cannot be formed for the weak effect between the particles.

As it is shown in Fig. 9c, the floc in the salt water is rather dense, and its diameter is about 40 μm, while the floc in the fresh water with humus is loose, and its diameter is about 90 μm, as Fig. 9d shows. These results indicate that both salinity and humus can increase the floc diameter of the fine-grained sediments and humus is the main factor affecting the floc diameter, which has been justified in Fig. 4.

Figure 9e shows the microcosmic configuration of flocs in the saltwater ($S=27$) with humus ($c_h = 50$ mg/L). The average diameter of flocs can be divided into two categories: one is the large flocs, about 180 μm in diameter and loose in structure; the other is the small flocs, about 50 μm in diameter and dense in structure, which are the same as the data observed by the LISST-100. What has been discussed in 3.2 further proves that the large flocs tend to break up in the dynamic water, which is again similar to the case of the loose flocs and dense flocs detected at the Jiaojiang Estuary (Li et al. 1993). It can be inferred that the formation of the large flocs is under the influence both of humus and salinity. The existence of humus induces the fine-grained particles to stick together to form relatively big and loose flocs, while the function of salinity lies in supplying electrolyte and condensing the electric double layer to form dense flocs and the high-concentration cations can attract many negative electric flocs. Then the large flocs are to be formed.

4.4 IR spectra of flocs

IR spectra of flocs in Fig. 10 denotes that the peaks of medium intensity at 3 520 – 3 450 and 3 640 – 3 630 cm^{-1} are stretching vibration adsorption of N—H and O—H. The adsorption of alkane stretching vibration (—CH_2—) is weak at 2 920 – 2 850 cm^{-1}. There is a peak of weak intensity at 1 710 cm^{-1}, belonging to the adsorption of carbonyl (C=O), and there is a peak of strong intensity at 1 4 0 0 cm^{-1},

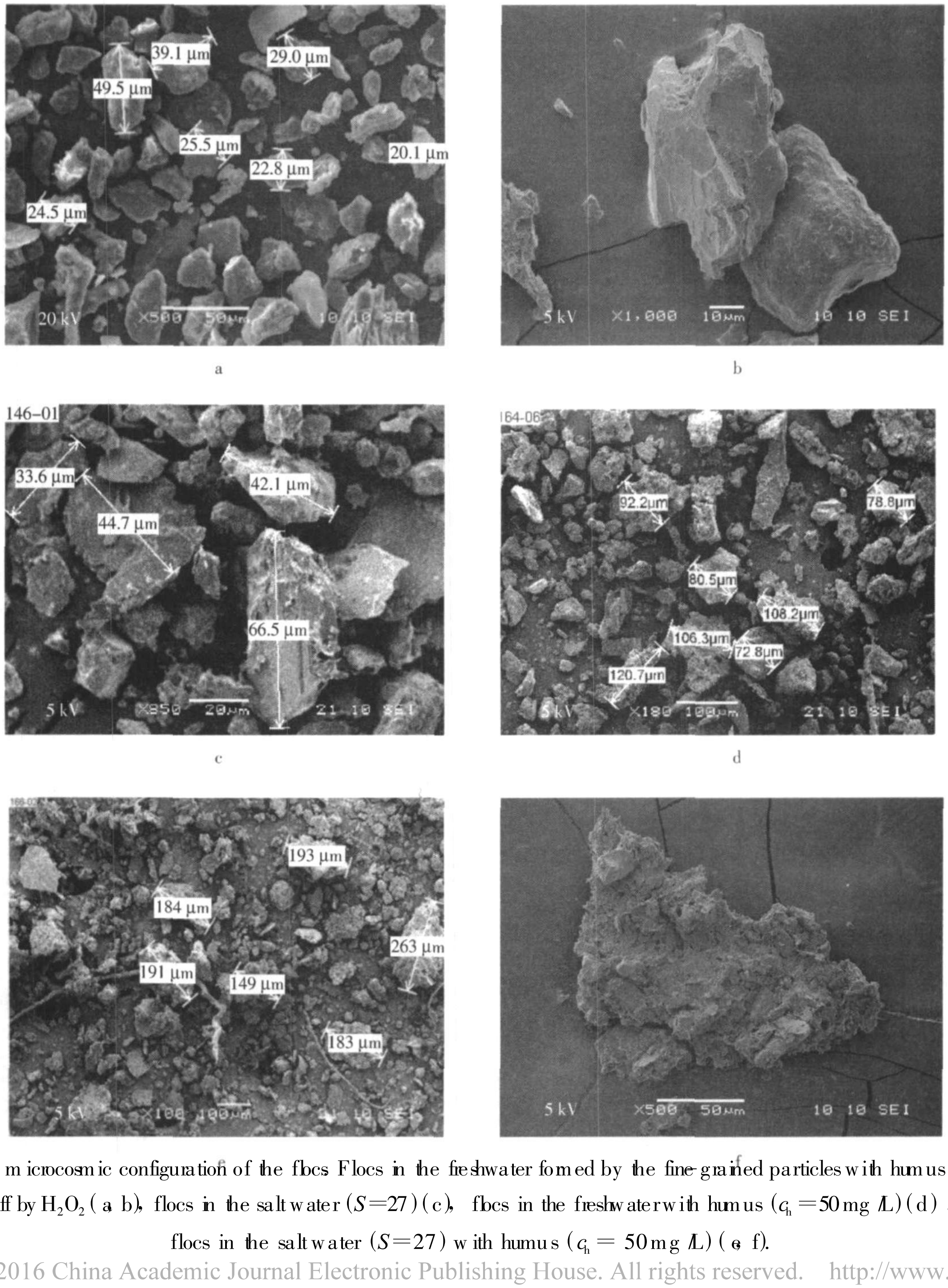


Fig. 9. microcosmic configuration of the flocs. Flocs in the freshwater formed by the fine-grained particles with humus being wiped off by H_2O_2 (a, b), flocs in the saltwater (S=27) (c), flocs in the freshwater with humus (c_h =50 mg/L) (d) and flocs in the saltwater (S=27) with humus (c_h = 50 mg/L) (e, f).

belonging to the stretching vibration of carboxylic acid salt (COO^-). Siloxane (Si-O) tends to absorb considerably at about 1 040 cm^{-1}. It can be concluded that the functional groups of hydroxyl, carboxyl and carbonyl found in humus are able to determine the property of their reactions with many other substances.

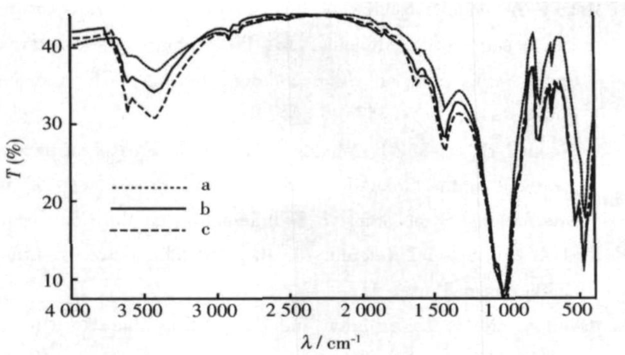


Fig. 10. IR spectra of flocs (Curve c). IR spectra of flocs in the freshwater formed by the fine-grained particles with humus being wiped off by H_2O_2 (Curve a), IR spectra of flocs in the Changjiang Estuary (Curve b) and IR spectra of flocs in the salt water ($S = 27$) with humus ($c_h = 50$ mg/L). T represents transparency.

The three spectra are extremely alike, and are almost identical at 500 ~ 1 200 cm^{-1}, which indicates that the compositions of the three flocs resemble, especially in their inorganic composition. Because the water used in the experiment is all filtered from the Changjiang Estuary with much colloid organic matter (Wang, 1998), there appear organic peaks in Curve a, but smaller than the peaks in Curves b and c, which shows that the absorptive strength of the functional groups is low and there is fewer organic matter in the flocs. Therefore, there are a certain quantity of organic matter in the flocs of the Changjiang Estuary, and the emergence of the carboxyl salt peaks also proves that the flocculation mode of C-P-OM (C stands for clay; P, cations; OM, organic matter) under the combined effect of humus and salinity fits well for the flocculation of fine-grained particles in the Changjiang Estuary (Thurman, 1985; Xia and Esina, 1991).

5 Conclusions

(1) The experiments of complex flocculation show that with the increase of salinity, the flocculation power and the diameter of flocs become greater and the zeta potential becomes smaller, while with the increase of the humus concentration, the flocculation power becomes smaller, but the diameter of flocs and the zeta potential become greater.

(2) As shown by a scan electron microscope, complex flocculation affects greatly the diameter of flocs. The diameter of flocs in the freshwater is about 30 μm, while it is around 180 μm in the complex flocculation.

(3) IR spectra manifests that humus packs on the fine-grained sediments in the form of salt, and the flocculation model of C-P-OM can demonstrate the mechanism of the formation of the fine-grained sediments in the high-turbid area of the Changjiang Estuary.

(4) As the main influencing factors on flocculation, humus and salinity have different mechanisms in effect. Under the condition of combined effect, humus, through its functional groups, tends to pack on the surface of the fine-grained particles and connects with other flocs to form relatively big and loose flocs, while the function of salinity lies in supplying electrolyte and condensing the electric double layer to form dense flocs and the high-concentration cations can attract many negative electric flocs. Then the large flocs are to be formed.

Acknowledgements

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