Interaction between Nano TiO_2 and Simulacra of Dissolved and Colloidal Substances in the Process Water of a Paper Machine

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In the papermaking process, the removal and control of dissolved and colloidal substances (DCS) is a key issue for reducing the usage of fresh water. The use of nano TiO_2 for removal of dissolved substances (DS) and colloidal substances (CS) was investigated through monitoring the titration process of nano TiO_2 colloids to sodium laurate ($C_{11}H_{23}COONa$, DS simulacra) and stearic acid ($C_{17}H_{35}COOH$, CS simulacra) solution with COD (chemical oxygen demand), DLS (dynamic light scattering), SEM (scanning electron microscope), and zeta potential, respectively. The results indicated that most of the simulacra molecules could be removed from the aqueous solution by the flocculation with nano TiO_2 colloids. The removal of CS by nano TiO_2 colloid arose from heterocoagulation rather than from charge neutralization, in which nano TiO_2 was adsorbed onto the surface of CS particles and bridged CS to form flocs. While in the removal process of DS by nano TiO_2, the negative-charged portion of the DS molecule was adsorbed onto the surface of nano TiO_2 particles with a mono- or multilayer, eliminating the repulsive force between nano TiO_2 particles and resulting in their flocculation.

Keywords: Nano TiO_2; Dissolved and colloidal substances; Sodium laurate; Stearic acid; Simulacra

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INTRODUCTION

Wastewater from the paper industry is one of the major industrial pollutants. It is a viable option to implement the closed-water circuit of the paper machine (whitewater closure) in order to decrease wastewater pollution in paper mills. In addition, the whitewater closure can also reduce the cost of raw materials and energy consumption (Xu and Deng 2004). But, the main obstacle for improving the whitewater closure is the enrichment of dissolved and colloidal substances (DCS) (Liang *et al.* 2011), which can interfere with papermaking by weakening the effectiveness of the wet end chemicals (Zhang 2004; Nurmi *et al.* 2004), reducing the paper quality (Dunham *et al.* 2002), and degrading the runnability of the paper machine (Donat *et al.* 2003; Hubbe *et al.* 2012).

DCS originate from wood lipophilic extractives and various polymer additives from the secondary fibres, which can include a wide variety of chemical species, such as fatty acids, resin acids, triglycerides, sterol esters, hemicelluloses, lignans, and pectin substances (Sundberg *et al.* 1994; Thornton *et al.* 1994). Currently, the methods for controlling the enrichment of DCS involve physico-treatment (Falth *et al.* 2001), physico–chemical treatment (Shetty *et al.* 1994), bio-treatment (Zhang *et al.* 2000), and wet end controlling (Huang *et al.* 2006; Chen *et al.* 2011), of which the physico- and biotreatments are performed in the equipment outside the papermaking process, resulting in a large investment and secondary solid wastes. Wet end controlling is an alternative option for removing DCS from the whitewater, in which DCS are captured and retained in the paper sheet by the nano TiO_2 particles before the formation of stickies and carried out from the water circuits while the paper machine runs (Chen *et al.* 2006, 2009; Hulkko and Deng 1999). This route appears to be advantageous for both cost-effectiveness and protection of the environment, as it can fully exploit the raw materials, reduce the treatment load of wastewater, and avoid the cost of external equipment and over-running the machine. Researchers Cong and Pelton (2003) and Lu and Pelton (2002) have shown that DCS in whitewater could be flocculated by a PEO (polyethylene oxide)/cofactor dual-component system retention aid. Wågberg *et al.* (2007) used hyperbranched polymers (polyesteramides) as a cationic fixing agent to remove DCS. Gruber and Müller (2004) used dual-component systems in the paper industry to improve cellulose fiber formation and pigment retention in papermaking, in which the colloidal component in the dual retention aid is SiO_2.

In previous work, nano TiO_2 and its dual-component system displayed an obvious removal efficiency of DCS and a good retention and drainage capacity on DIP (deinked pulp) (Chen *et al.* 2009; Kou *et al.* 2008). It was discovered that when a DCS solution was titrated with a nano TiO_2 colloid, the flocculation of DCS did not correspond to the obvious change of the zeta potential, from which it was speculated that the flocculation arose from heterocoagulation rather than from charge neutralization (Chen *et al.* 2011). Therefore, more research results are needed to verify the flocculation mechanism. Gesenhues (2011) provided, for the first time, a quantitative understanding of the interplay of particle surface neutralization and bridging in colloid flocculation by polyelectrolytes.

The simulacra is often used for research on DCS due to the complexity of DCS components and the difficulty in separating dissolved substances (DS) and colloidal substances (CS) from the actual whitewater. Yuan and Dai (2011) chose negative-charged substances to simulate DCS in order to explore their impact on the wet end and paper properties. Qin (2004) and Mclean *et al.* (2005) obtained DCS mimesis by preparing samples in the laboratory and collecting processing pulp or water from the factory, such as resin acids, fatty acids, and triglycerides, which were used for discussing the effect of DCS on the papermaking system.

We think that the most harmful components in DCS are the lipophilic compounds, existing in the micelle particles (CS), and partially in the single molecules (DS). The formation of stickies mainly comes from the merging and aggregation of the micelle particles, which can be solid and also soft and gelatineous. The present research focuses on the interaction between nano TiO_2 particles and DCS, including the CS grains and DS molecules. In the experiment, stearic acid was dispersed in the water with a magnetic stirring apparatus at 1000 rpm and 80 °C, and then cooled to obtain the stearic acid colloidal solution, which was used for the simulation of the CS. The sodium laurate solution with a concentration below its critical micelle concentration (CMC) was used for the simulation of the DS. The flocculation and adsorption mechanisms between nano TiO_2 colloid and DCS simulacra were studied by COD, SEM, zeta potential, and DLS analysis.

EXPERIMENTAL

Materials

An aqueous suspension of nano TiO_2 (anatase) with mean size 30 nm, solid content 26.0%, positive charge 40 mV, and specific surface area 85~120 m^2/g, which was diluted to 0.1% for experiments, was provided by Hunan Titania Nano Science and Technology (China). The colloidal suspension has isoelectric point of 6.67 (pH) and zeta potentials between 14 mV and 30 mV at a pH between 4.5 and 6.0 in the presence of 5.0 m $mol \cdot L^{-1}$ $NaNO_3$ electrolyte. The particle size of nano TiO_2 was measured by a Malvern Instrument ZEN3600 (the minimum particle size measurable by this method is 1 nm). Stearic acid, sodium laurate, and sodium hydroxide were of analytical grade.

Methods

Preparation of CS simulacra (stearic acid colloid)

One to two grams of stearic acid was mixed with 1 L of distilled water in a 1-L beaker, and stirred for 1 h at 75–80 °C and 1000 rpm on the magnetic stirring apparatus. The mixing liquid was cooled to room temperature and filtered to obtain the stearic acid colloid, which was 4.5×10^{-4} mol/L from the calibration of 1.0×10^{-3} mol/L NaOH solution (calibrated with potassium hydrogen phthalate). The mean size of the stearic acid colloidal particle was about 550 nm and the zeta potential was −47 mV, detected by DLS analysis meter (Britain-Malvern Instrument ZEN3600). As the majority of the CS particle sizes in whitewater were larger than 0.22 μm (Zhang *et al.* 2006) and the negative zeta potentials of CS from the actual whitewater (Wang *et al.* 2003), it was reasonable for the stearic acid solution to be used as CS simulacra.

Preparation of DS simulacra (sodium laurate solution)

Sodium laurate, 0.15 g, was dissolved into 550 mL of distilled water and then diluted to 1 L. The concentration of the solution was 6.76×10^{-4} mol/L, which was smaller than its CMC (2.84×10^{-2} mol/L) (Xu *et al.* 1995) and promised that the sodium laurate was a single molecule without any formation of micelles.

For sodium laurate, there was no particle size distribution by DLS analysis (the minimum particle size measurable by this method is 1 nm), from which it was suggested that no micelle particle existed in the solution, in accordance with the demand of DS. So, it is reasonable for the sodium laurate to be used as DS simulacra.

Characterization of the interaction between nano TiO_2 and DCS simulacra

In this study, different dosages of nano TiO_2 were added into the 50 mL of DS or CS simulacra solutions by magnetic stirring to obtain the mixture system, which were characterized as follows.

The surface morphologies of the formed flocs were characterized with a scanning electron microscope (JEOL JSM-7600F, Japan) at a voltage of 5 kV in a vacuum. The samples were deposited on the slide and dried at room temperature, followed by coating with gold.

The zeta potential and particle size distribution were measured by a Britain-Malvern Instrument ZEN3600 (England) without any treatment of the mixture.

In order to analyze the chemical oxygen demand (COD) of the supernatants, the initial samples were placed for 24 h. For DS, the supernatants were obtained by centrifuging for 10 min at 4500 r/min and were used for the determination of COD, so as to characterize the residual concentration of DS in the system. For the mixture system of CS and nano TiO_2, the supernatant was directly filtered for the analysis. The COD measurements were carried out with a DR1200 COD tester (America, potassium dichromate method).

RESULTS AND DISCUSSION

Flocculation between Nano TiO_2 and DCS Simulacra followed by COD

The flocculation of nano TiO_2 acting on DCS was investigated by the titration of nano TiO_2 colloids to DS and CS simulacra solutions, respectively. When nano TiO_2 was added into the DCS solution, the flocculation gradually was generated, and the residual COD values of the supernatants of the flocculated DCS solutions were determined. The results are shown in Fig. 1, which characterizes the flocculating efficiency. As shown in Fig. 1, for the sodium laurate solution, the residual COD values of the supernatant decreased quickly with the increase of nano TiO_2 dosages and reached a constant, at approximately 60 mg/L, which declared that the maximum adsorption efficiency of nano TiO_2 (with a 1.40×10^{-2} g/L dosage) acting on sodium laurate occurred with the molar ratio of 1:3.5 (nano TiO_2: sodium laurate) and 84% removal ratio of sodium laurate.

For the stearic acid solution, CS simulacra, the residual COD values decreased with the increase of nano TiO_2 dosages and reached a constant at approximately 50 mg/L, with the molar ratio of 1:5.4 (nano TiO_2:stearic acid) and 86% removal ratio of stearic acid.

In short, there are interactions between nano TiO_2 and DS or CS simulacra, which induced the flocculation, resulting in the removal of most simulacra molecules from the aqueous solution. Theoretically, the simulacra molecules should be completely removed by nano TiO_2, but there were still residual COD in the supernatants when nano TiO_2 was excessive, which may be attributed to the retaining of nano TiO_2 particles that adsorbed sodium laurate molecules or stearic acid molecules, resulting into the disturbance to the COD analysis.

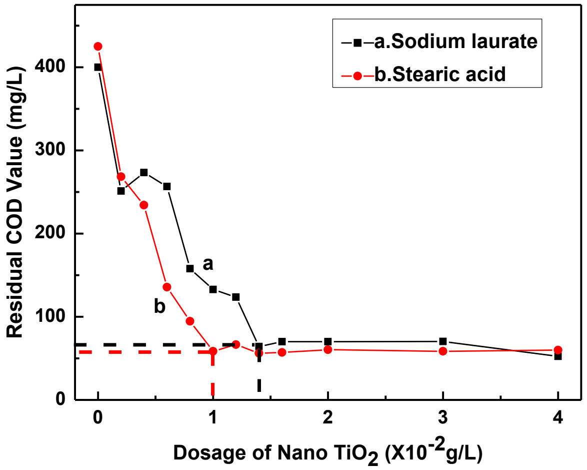


Fig. 1. The residual COD values with nano TiO_2 colloid titrating to the DS and CS simulacra solution

Interaction between Nano TiO_2 and DS Simulacra

Zeta potential and particle size of sodium laurate–nano TiO_2 system

The nano TiO_2 colloidal particles, which possess positive surface charges and plenty of surface hydroxyl groups, can interact with negative-charged DS simulacra. When nano TiO_2 was added into the sodium laurate solution, flocculation occurred, which resulted from the adsorption of sodium laurate molecules on the surface of nano TiO_2. This process was also investigated by the titration of nano TiO_2 colloid to sodium laurate solution, determining the changes of particle sizes and zeta potentials in the titration systems. As shown in Fig. 2, the particle sizes in the mixture solution increased with the increase of nano TiO_2 dosages and had a steep turning point (0.81×10^{-2} g/L), which indicated that the flocculation of nano TiO_2 acting on sodium laurate occurred at that moment. On the other hand, the zeta potentials of the system increased with the increase of nano TiO_2 dosage, then became relatively stable, but did not have the electrical reversion. The turning point in the zeta potential values appeared at 0.80×10^{-2} g/L nano TiO_2 dosage, in agreement with the turning point in the particle sizes. After the flocculation, few of the negative-charged molecules adsorbed onto the surface of the nano TiO_2 particles, and the formed composite particles brought about aggregation and flocculation, which resulted in less increase of particle potential in the mixture system.

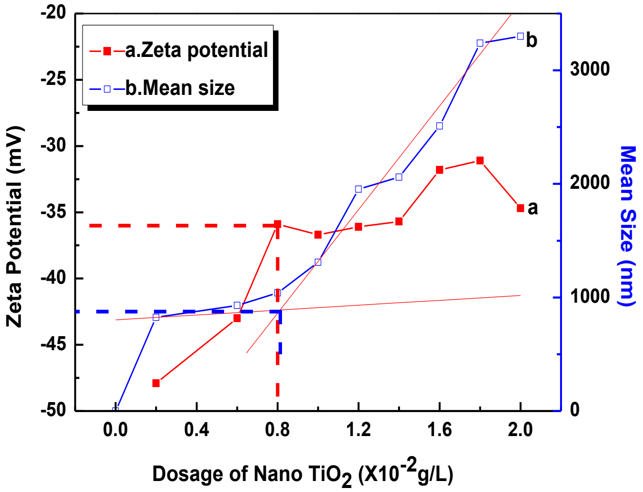
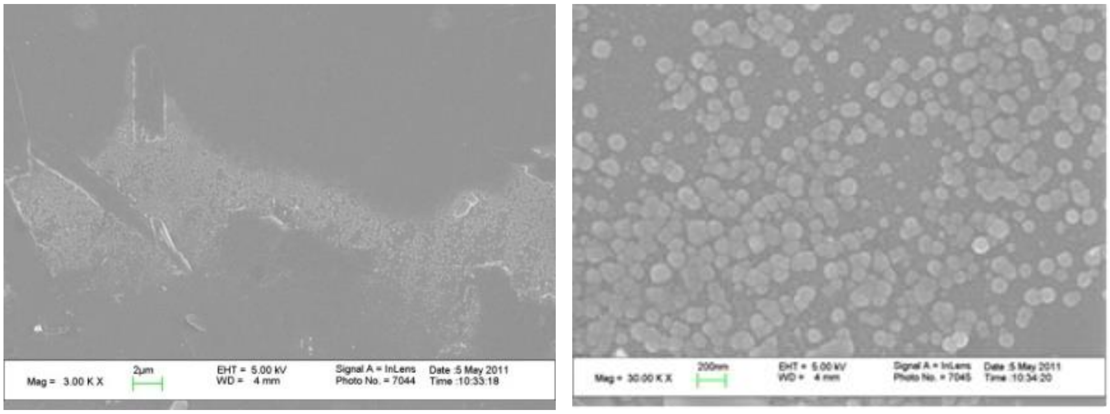


Fig. 2. The changes of zeta potentials and particle sizes with nano TiO_2 colloid titrating to the sodium laurate solution

SEM observation of composited particles of sodium laurate and nano TiO_2

The morphology of the flocs of sodium laurate and nano TiO_2 was observed using a scanning electron microscope and compared with sodium laurate.

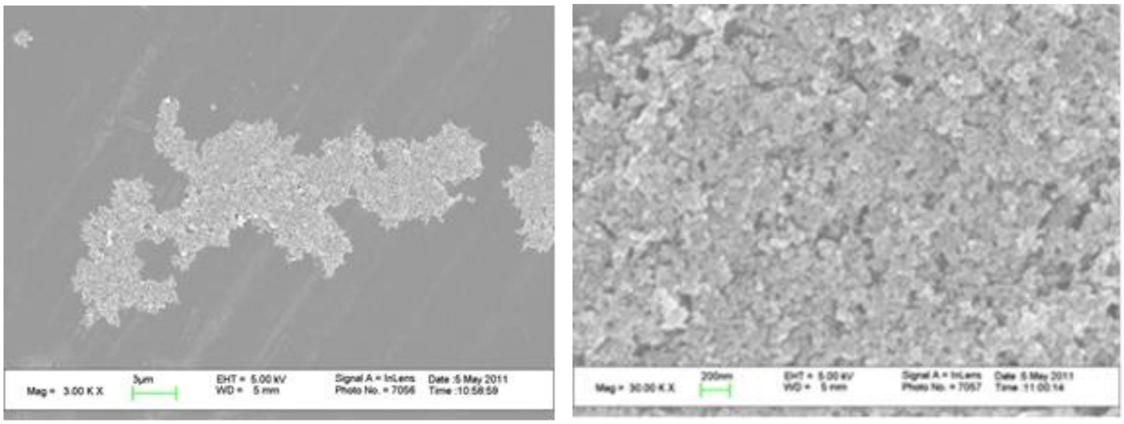
The SEM photos of sodium laurate under different magnifications are displayed in Fig. 3, which shows two kinds of particles with sizes of 50–100 nm and several nanometers (Fig. 3b). Those particles were formed when the solution was evaporated at sampling (Nizri and Magdassi 2005). It could be deduced that the former was the composited particles of the sodium laurate micelles and the latter was the image of the single micelle.



(a) (b)

Fig. 3. SEM images of sodium laurate. (a) Mag = 3000 x; (b) Mag = 30,000 x

The morphology of the formed flocs of sodium laurate and nano TiO_2 is displayed in Fig. 4. When the sodium laurate molecules mixed with nano TiO_2, they were adsorbed on the surface of the nano TiO_2 particles. Therefore, there were neither micelles nor merged micelles in the SEM photos, only the flocs that composited with complex particles of sodium laurate and nano TiO_2 with sizes of about 50 nm.



(a) (b)

Fig. 4. SEM images of the formed flocs of nano TiO_2 and sodium laurate. (a) Mag = 3000 x; (b) Mag = 30,000 x

From the above information, the flocculation process of nano TiO_2 acting on DS can be summarized as follows. When nano TiO_2 mixed with the DS solution, the negative-charged portion of the DS molecule was adsorbed on the surface of nano TiO_2 particles with a mono- or multilayer, which eliminated the repulsive force between nano TiO_2 particles and resulted in the flocculation of the mixture system. The originally strong negative electrode may be a result of the double adsorption that forms in a small amount of nano-particles, in which the negatively charged groups are exposed. This subject needs further investigation. The process is illustrated in Fig. 5.

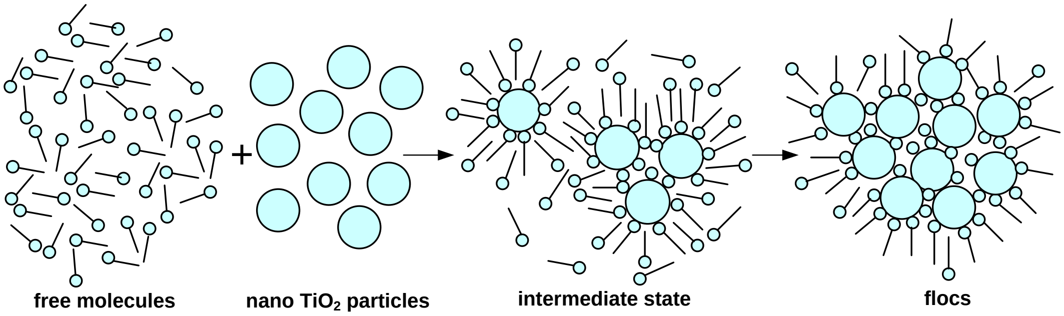


Fig. 5. The adsorption diagram as nano TiO_2 colloid titrates to sodium laurate solution

Interaction between Nano TiO_2 and CS Simulacra

Zeta potential and particle size of the stearic acid–nano TiO_2 system

Similarly, the flocculation process of CS by nano TiO_2 was investigated by the titration of nano TiO_2 colloid to stearic acid solution, determining the changes of particle sizes and zeta potentials in the titration systems. As shown in Fig. 6, the particle sizes in the mixture solution increased rapidly with the increase of nano TiO_2 dosages, and had a steep turning point (1.01×10^{-2} g/L), in agreement with the turning point in the residual COD values (1.00×10^{-2} g/L). But there was no significant change in zeta potential values, from which it was speculated that the flocculation arose from the bridging agglomeration activated by the adsorbing action between nano TiO_2 and stearic acid rather than by charge neutralization. The same conclusion was drawn in the interaction between the nano TiO_2 colloid and the actual DCS solution (Chen *et al.* 2011).

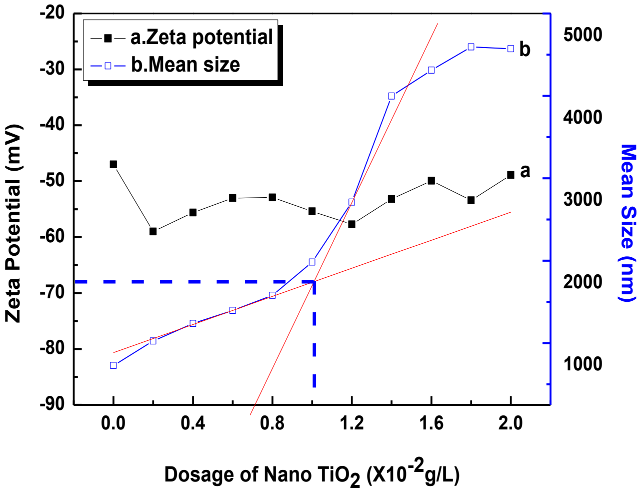
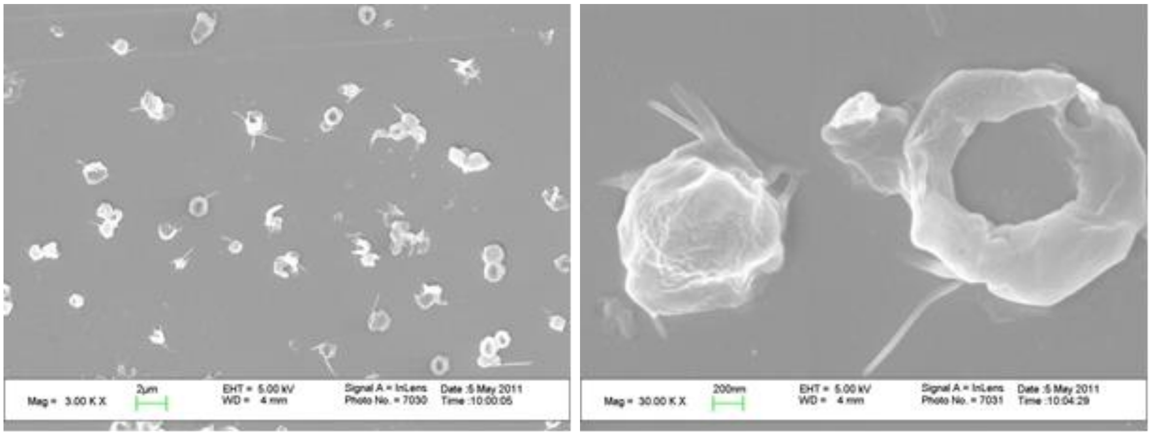


Fig. 6. The changes of zeta potentials and particle sizes as nano TiO_2 colloid titrates to the stearic acid solution

SEM observation of the adsorption of nano TiO_2 on the surface of stearic acid

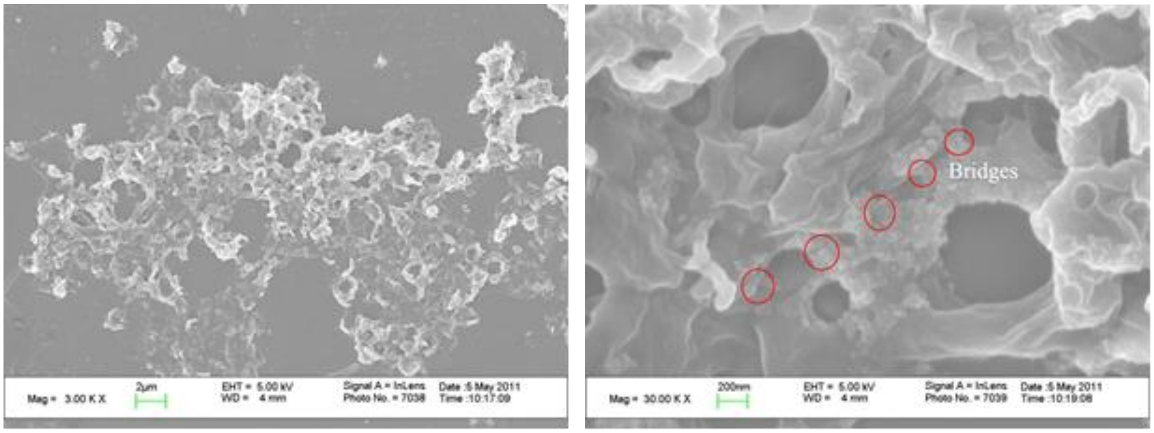
Figure 7 displays the SEM images of the stearic acid with particle sizes of about 400–500 nm, which was in agreement with the result obtained by the DLS analysis. There were two kinds of fine particles in the stearic acid, one was solid spherical and the other was circle ring (Fig. 7b).



a b

Fig. 7. SEM images of stearic acid. (a) Mag = 3000 x; (b) Mag = 30,000 x

The morphology of the formed flocs in the mixture of stearic acid and nano TiO_2 is displayed in Fig. 8, in which the flocculation is obvious (Fig. 8a), compared with Fig. 7. The TiO_2 colloidal particles on the flocs were observed by amplification (Fig. 8b). This indicated that nano TiO_2 particles were adsorbed on the surface of the stearic acid grains and bridged them to form flocs, which confirmed the previous assumption that the flocculation of stearic acid by nano TiO_2 arose from the bridging mechanism.



a b

Fig. 8. SEM images of the formed flocs of nano TiO_2 and stearic acid. (a) Mag = 3000 x; (b) Mag = 30,000 x

In the same way, we could summarize the flocculation process of CS by nano TiO_2 as follows. When the nano TiO_2 was titrated into CS solution, it was adsorbed on the surface of the CS grains with the negative-charged and bridged the CS grains to form flocs. The process can be illustrated in Fig. 9.

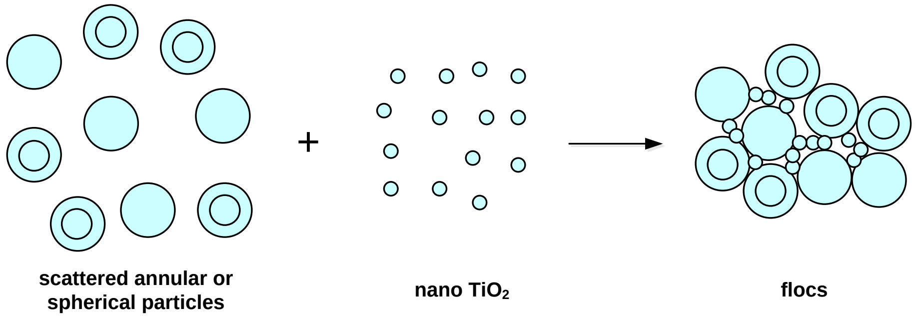


Fig. 9. The flocculation diagram with nano TiO_2 colloid titrating to stearic acid solution

CONCLUSIONS

1. Most of the DS, CS simulacra molecules could be removed from the aqueous solution through flocculation by their interaction with nano TiO_2 colloids, judging from the residual COD values of the supernatants of flocculated DCS solutions.
2. The removal of CS by nano TiO_2 colloid arose from heterocoagulation rather than from charge neutralization. When the nano TiO_2 was titrated into the CS solution, it was adsorbed on the surface of the CS grains with the negative-charged and bridged the CS grains to form flocs.
3. In the removal process of DS by nano TiO_2, the negative-charged portion of the DS molecule was adsorbed on the surface of nano TiO_2 particles with a mono- or multilayer, eliminating the repulsive force between nano TiO_2 particles and resulting in the flocculation of the mixture system.

ACKNOWLEDGMENTS

The reported work was supported by the Grand Science and Technology Special Plan Projects of Guangdong Province of PR China (No. 2008A090300016).

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Article submitted: April 1, 2013; Peer review completed: May 5, 2013; Revised version accepted: May 21, 2013; Published: May 22, 2013.