The effect of surfactant on the charge behavior and coagulation of TiO_2 nanoparticles suspension

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Abstract. In order to understanding of the fate and transport of TiO_2 nanoparticles (Nps) in the water treatment process, this study focus on the particle surface characteristics and coagulation process at different anionic surfactant sodium dodecylbenzene sulfonate (SDBS) and cationic surfactant cetyltrimethylammonium bromide (CTAB) concentration, using aluminum sulfate (AS) as a coagulant. Malvern Zetasizer nano-ZS measure the changes of zeta potential of TiO_2 Nps mixture and coagulation of flocs (Alu-TiO_2). Jar tests are conducted to evaluate the effect of surfactant on removal efficiency of TiO_2 NPs. Experimental results indicated that the adsorption of CTAB on TiO_2 Nps resulte in more positively charged surface. SDBS is more easily adsorbed on the surface of positively charged Alu-TiO_2 flocs. The presence of SDBS or CTAB have disadvantage of the removal of TiO_2 Nps during the coagulation process.

Introduction

With the rapid growth of nanotechnology during the past decade, engineered Nps have been extensively applied in commercial products. Among the engineered NPs, TiO_2 Nps have attracted special attention because of their particular chemical property, Such as photocatalysts, coatings, paints, and pigments[1]. The properties of TiO_2 Nps may enable them to make potential contributions to environmental applications. Significant research has been expended by environmental scientists in using TiO_2 NPs and So it is inevitable that a large amount of TiO_2 NPs will be discharged into environment.

TiO_2 Nps present in aquatic systems may also represent a pathway for human exposure, especially if these contaminated aquatic systems are used as source of potable water. Because of TiO_2 nanoparticles' tiny size and high reactivity, it can interact with biological macromolecule[2]. Based on these potential risks, the aggregation and stability in environment needs to be investigated. Surfactants are organic compounds consisting of both hydrophilic and hydrophobic portions, and have been widely used in improvement of the wetting ability, emulsifying, and the inhibiting properties of electrodeposition process, etc [3].

Surfactants exsit universally in the environment and play an important role in the interfacial reaction of contaminants. Wu et al.[4] research shows that SDBS can play as a bridge when the hydrous alumina coat on the organic pigment particle surface initially. Coagulation is a critical process used for the removal of turbidity particles at drinking water treatment works. Wang et al. [5] investigate the influences of CTAB on coagulation removal of turbidity using aluminum sulfate, coagulation removal of turbidity is enhanced at low CTAB concentration level, but interfered at high CTAB concentration. However, little thought is generally given to the influence of surfactant on the physicochemical characteristics and hydrodynamic properties of alum-TiO2 Nps flocs.

The objectives of this articles are to investigate the surface physicochemical characteristics of TiO_2 Nps with SDBS and CTAB, and A series of jar tests are performed to evaluate the effect of SDBS and CTAB on the removal efficiency of TiO_2 Nps by coagulaton with AS, and the surface physicochemical characteristics of alum-TiO2 Nps flocs.

Materials and methods

TiO_2 nanoparticles solution. TiO_2 Nps (99.8%, Hydrophile and Anatase, Aladdin) with a nominal size of 25 nm were used in all experiments. Adding 10 mmol TiO_2 Nps into Ultra Pure Water and sonicating for 30 min yielded 10 mmol/L nanoparticle stock suspensions.
Jar test procedure. Jar tests are conducted to evaluate the removal of aggregated TiO_2 Nps and investigated the effect of surfactant. A series of jar tests is conducted with constant TiO_2 Nps concentration (0.1mmol/L) and different surfactant concentrations (0.01mmol/L to 1mmol/L). The TiO_2 Nps suspensions with 1mmol/L NaCl and 100 mg/L $NaHCO_3$, the pH of the suspensions are adjusted to 7.50 ± 0.02 using 0.1 mol/L HCl or 0.1mol/L NaOH. Coagulation with aluminum sulfate ($Al_2(SO_4)_3$•$18H_2O$) in concentrations 40 mg/L. Coagulation use conventional water treatment processes. It can be divided into coagulation-flocculation-sedimentation three sections. Jar tests are conducted using these five steps: (1) rapid mixing for 1 min at 200 rpm ($G = 35.6\ S^{-1}$), (2) firstly slow mixing for 5 min at 70 rpm ($G = 8.7\ S^{-1}$), (3) secondly slow mixing for 5 min at 40 rpm ($G = 4.1\ S^{-1}$), (4) thirdly slow mixing for 10 min at 20 rpm ($G = 1.6\ S^{-1}$), and (5) settling for 30 min. After coagulation, all samples are collected at 2.2 cm above the bottom of the jars. The residual concentration of TiO_2 Nps are tested with ICP-AEX (Optima 5300DV, Perkin Elmer Inc).
Characterization of flocs. Zeta potential values are measured with a Zetasizer nano-ZS (Malvern Instruments, UK). Flocs are immediately collected from beaker after the rapid mixing phase of the jar test procedure.

Results and discussion

Effect of surfactant on zeta potential of TiO_2 Nps.

The zeta potential of TiO_2 Nps with various concentrations SDBS and CTAB is comparatively investigated, as shown in Fig 1.

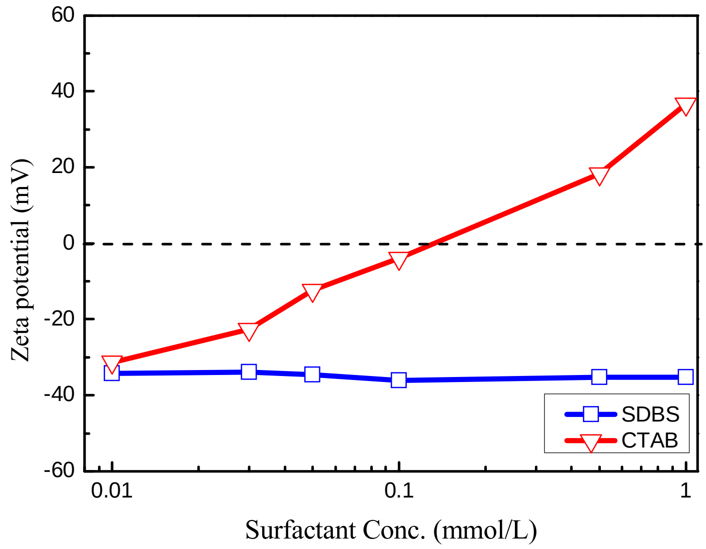

Fig 1. The effect of surfactant on the measured zeta potential of TiO_2 Nps
(temperature: 25°C, NaCl concentration: 1 mmol/L, initial Nps concentration: 10mg/L).

In alkaline raw water, TiO_2 Nps surface become negatively charged by deprotonation. CTAB can be adsorbed onto the surface of TiO_2 Nps through electrostatic attraction, and then change the surface chemical properties of nanoparticles. As the CTAB concentration increased, the zeta potential of TiO_2 shifted toward more positive values, which would enhance colloidal stability. On the contrary, similarly charged TiO_2 Nps and SDBS cannot agglomerate because of electrostatic repulsion, so the zeta potential of mixture remained about the same. It is can be defined using expression as follows:

$$TiO_2 + CTAB \rightarrow TiO_2 \cdots CTAB$$
$$TiO_2 + SDBS \rightarrow TiO_2 + SDBS$$

Effect of surfactant on zeta potential of Alu-TiO_2 flocs.
The zeta potential of TiO_2 Nps with various concentrations SDBS and CTAB after alum addition in the coagulation experiments is comparatively investigated, as shown in Fig 2.

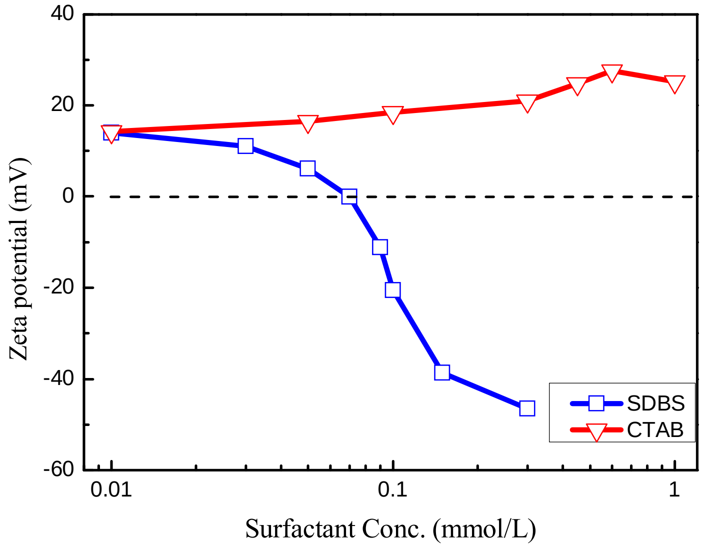

Fig 2. The effect of surfactant on the measured zeta potential of Alu-TiO_2 flocs
(temperature: 25°C, NaCl concentration: 1 mmol/L, initial Nps concentration: 10mg/L).

The zeta potential of the mixture with 0.01mmol/L surfactant and TiO_2 Nps is -35mV, those shift toward positive to 15mV with addition of the alum. The positively charged alum neutralize the surface charge on TiO_2 particle, change the surface charge of the particles in the synthetic water. With increasing surfactant concentration, the flocs zeta potential of SDBS solution decrease dramatically. However, the flocs zeta potential of CTAB solution remained about the same. It is believed that the action of charge neutralization played a key role in mixture coagulation, as follows:

$$TiO_2\cdots CTAB + [Alu] \rightarrow TiO_2\cdots[Alu] + CTAB$$

$$TiO_2 + SDBS + [Alu] \rightarrow TiO_2\cdots[Alu]\cdots SDBS$$

Removal efficiency of TiO_2 NPs in the presence of surfactant.
Experimental results shown in Fig.3. suggest that TiO_2 Nps can be effectively removed by a suite of coagulation in the low pollution concentration raw water. On this condition, the removal effciency of TiO_2 NPs reach up to 95%.

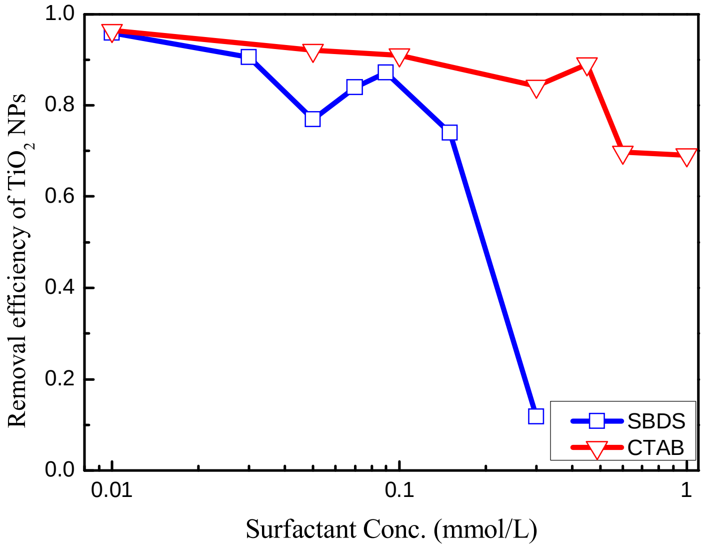

Fig 3. Removal efficiency of TiO2 NPs in the presence of surfactant.
(temperature: 25°C, NaCl concentration: 1 mmol/L, initial Nps concentration: 10mg/L).

The observed decrease in the removal of TiO_2 Nps in the presence of plenty of CTAB might be due to the competitive interaction between of CTAB and the coagulant.The presence of SDBS change the removal of TiO_2 Nps during the coagulation processes. With increase of SDBS concentrations, the removal of TiO_2 Nps dramatically decrease, this result suggest that high concentration of SDBS can enhance the stability of Alu-TiO_2 flocs. With increase of SDBS in raw water, SDBS adsorbed on surface of Alu-TiO_2 flocs will corresponding increase, in the circumstance, abundant SDBS will reduce the flocs surface tension and hinder coagulation of TiO_2 Nps.

Conclusions

(1) Surface characteristics of TiO_2 Nps are changed by adsorbe CTAB through electrostatic attraction. The adsorption of CTAB on TiO_2 Nps resulte in more positively charged surface. (2) The action of charge neutralization played a key role in mixture coagulation, SDBS is more easily adsorbed on the surface of positively charged Alu-TiO_2 flocs. (3) The presence of SDBS or CTAB have disadvantage of the removal of TiO_2 Nps during the coagulation processes.

Acknowledgements

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