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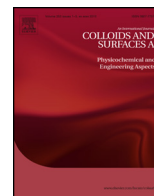
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## Effects of pH, ionic strength and humic acid on the removal of TiO<sub>2</sub> nanoparticles from aqueous phase by coagulation



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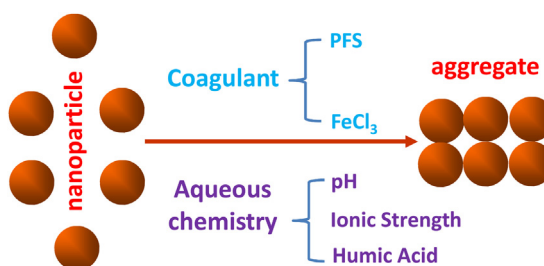
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### HIGHLIGHTS

- Iron-based coagulants (PFS and FeCl<sub>3</sub>) are effective to remove TiO<sub>2</sub> nanoparticles.
- Water chemistry influences TiO<sub>2</sub> nanoparticles removal.
- The effective pH range for PFS is broader than for FeCl<sub>3</sub>.
- Humic acid stabilizes TiO<sub>2</sub> nanoparticles and reduces removal by steric hindrance.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The increasing use of nanotechnology will most likely lead to the appearance of nanoparticles in aqueous phase. It is necessary to find effective methods to remove these nanoparticles from water. In this study, we found TiO<sub>2</sub> nanoparticles (NPs) could be removed effectively by poly-ferric sulfate (PFS) and ferric chloride (FeCl<sub>3</sub>) coagulants. The effects of pH, ionic strength and humic acid (HA) on the performance of these two coagulants in this application were investigated. The effective pH range of FeCl<sub>3</sub> is very narrow (9.5–10.6). For PFS, its effective pH range is broader (7–10.8). The behaviour of PFS is different from FeCl<sub>3</sub> for the removal of TiO<sub>2</sub> NPs. Liquid PFS contains many polymerization cations, which have the role of charge neutralization and bridging flocculation in the removal of TiO<sub>2</sub> NPs. The main mechanism for removing TiO<sub>2</sub> NPs by PFS is the formation of polymerization cations during the hydrolysis process. For both PFS and FeCl<sub>3</sub> coagulants, the increase of ionic strength can significantly improve the coagulation effect, although this effect is influenced by pH. For both coagulants, higher HA concentration makes the TiO<sub>2</sub> NPs suspension more stable, and the TiO<sub>2</sub> NPs removal rate decreased significantly because of the steric hindrance effect of HA molecules.

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## 1. Introduction

With an increasing flow of engineered nanomaterials through the world economy, the likelihood of finding them in aqueous phase is increasing [1]. For example, TiO<sub>2</sub> nanoparticles (NPs) can be released from textiles during washing [2]. The small size of nanoparticles increases the chances for interaction between the nanoparticles and biological tissue, and may have toxic effects on organisms [3]. As the ninth most abundant element in the earth's

crust, titanium has wide applications. High concentrations of TiO<sub>2</sub> NPs may exist in surface water and cause a serious threat or damage to aquatic ecosystem and human health [4–6].

In consideration of the potential hazard of TiO<sub>2</sub> NPs to aqueous ecosystem and their long-term effect on human health, it is necessary to explore efficient way to remove TiO<sub>2</sub> NPs from aqueous environment. Although it was reported that traditional wastewater treatment plants (WWTPs) are effective at removing low concentration of TiO<sub>2</sub> NPs (titanium concentrations ranging from 181 to 1233 µg/L) [7], it is still important to find rapid method to separate TiO<sub>2</sub> NPs from water. This is especially significant when there is unexpected leakage or accidental discharge of industrial wastewater containing high concentration of TiO<sub>2</sub> NPs to surface water. In addition, some researchers found that high concentrations of TiO<sub>2</sub> NPs are adverse to the biological treatment system (which is widely used in traditional WWTPs) in the long run [8]. Thus, physical–chemical treatment technologies, which are faster without causing side effect to the biological treatment system, might be good complementary options for the removal of TiO<sub>2</sub> NPs from aqueous environment.

Although membrane treatment is effective for removing nanomaterials from water [9], this technology is expensive and not applicable for the removal of high concentration of pollutants. As a widely used water treatment technology, coagulation can accelerate the aggregation and precipitation of colloids with easier operation and lower cost. Some studies have illustrated the possibility of separating nanomaterials from wastewater by coagulation, but most of the target pollutants have been carbon nanotubes and silicate nanoparticles [10–12]. There are few studies on the removal of TiO<sub>2</sub> NPs from aqueous solution by coagulation. In addition, there is very limited information about the interaction of TiO<sub>2</sub> NPs with different coagulants. Most current studies focus on the aggregation of TiO<sub>2</sub> NPs in natural surface waters [13,14], but there are few studies about the behavior of TiO<sub>2</sub> NPs in an enhanced reactor such as a coagulation process. Some researchers reported that alum coagulation could remove <80% of the total mass of commercial nanoparticles, including TiO<sub>2</sub> NPs [15]. However, it is not clear whether iron-based coagulant is useful for the removal of TiO<sub>2</sub> NPs from water. In addition, natural organic matter (NOM) has the ability to stabilize NPs in the water phase [13]. It is necessary to study the effects of NOM on the effectiveness of removal of TiO<sub>2</sub> NPs using different coagulants.

This study aims to investigate the feasibility of removing TiO<sub>2</sub> NPs from aqueous phase by iron-based coagulants, and to compare differences in behavior of two types of coagulants (PFS and FeCl<sub>3</sub>) as they interact with TiO<sub>2</sub> NPs at different pH, ionic strength and humic acid (representing NOM) conditions. We chose PFS and FeCl<sub>3</sub> as coagulants because they are widely used in drinking water treatment, and our previous study has indicated that PFS and FeCl<sub>3</sub> have better performance than other coagulants such as polyaluminum chloride (PACl) and alum (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) for the removal of TiO<sub>2</sub> NPs [16]. The finding of this study is expected to provide fundamental understanding of the reaction between TiO<sub>2</sub> NPs and coagulants, as well as to provide a practical solution for the separation of TiO<sub>2</sub> NPs from water.

## 2. Material and methods

Nano-TiO<sub>2</sub> (rutile) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. According to the manufacturer, these nanoparticles have the following characteristics: diameter × length = 10 nm × 40 nm; specific surface area = 130–190 m<sup>2</sup>/g; purity = 995%; size <100 nm; may contain up to 5 wt% silicon dioxide as a surface coating. In our recent publication [17], we presented SEM and TEM images of these TiO<sub>2</sub> NPs, which were

found to be aggregates from individual rod particles with primary sizes of tens of nanometers. This is consistent with the size range reported by the manufacturer. Humic acid (HA) was purchased from Sigma-Aldrich Trading Co., Ltd (Shanghai, China). The HA stock solution was prepared by dissolving a certain amount of HA powder into deionized (DI) water and adjusting the pH to 11 by adding 0.1 M NaOH, then stirring the solution for 24 h. The dissolved HA powder was filtered through a 0.45 µm membrane to remove the impurities and macromolecule particles, and the pH was readjusted to 7.5 using 0.1 M HCl. The total organic carbon (TOC) of HA stock solution was measured (Elementar Vario EL III, Germany). The HA stock solution was diluted to 0.5, 25, 11 mg/L, respectively. HA was added first to the TiO<sub>2</sub> NPs suspension, before the coagulants were added. Poly-ferric sulfate (PFS) and ferric chloride (FeCl<sub>3</sub>) were provided by Jiangsu Yijing Environmental Protection Co. Ltd., (China). PFS (solid) contains 213% Fe, and the concentration of FeCl<sub>3</sub> (liquid) is 28% (w/w as FeCl<sub>3</sub>). The dosage of coagulants was 0.3 mM Fe, corresponding to 79 mg/L PFS and 60 mg/L FeCl<sub>3</sub>. Stock solution of PFS and FeCl<sub>3</sub> were prepared in DI water.

Stock suspensions of 30 mg/L TiO<sub>2</sub> NPs were prepared by adding 3 mg TiO<sub>2</sub> nanopowder to 100 mL DI water. Although the TiO<sub>2</sub> NPs concentrations used in this research are much higher than what is expected in the municipal wastewater [7], such high concentrations of TiO<sub>2</sub> NPs are possible in industrial wastewater and waste effluent. TiO<sub>2</sub> NPs suspension was ultrasonicated with Ningshang Ultrasonic SY-180 (Shanghai, China) for 30 min before coagulation.

Since TiO<sub>2</sub> has low solubility [18], TiO<sub>2</sub> NPs concentration was monitored by measuring the turbidity of the supernatant. Our recent publication showed a good correlation of TiO<sub>2</sub> NPs concentration with turbidity [16]:

$$C = 0.1178 \times T - 25946, \quad R^2 = 0.9925 \quad (1)$$

where  $C$  = TiO<sub>2</sub> NPs concentration (mg/L) and  $T$  = supernatant turbidity (NTU). The removal rate of TiO<sub>2</sub> NPs by coagulation was calculated as:

$$R(\text{removal rate, \%}) = \left( \frac{1 - C_s}{C_i} \right) \times 100 \quad (2)$$

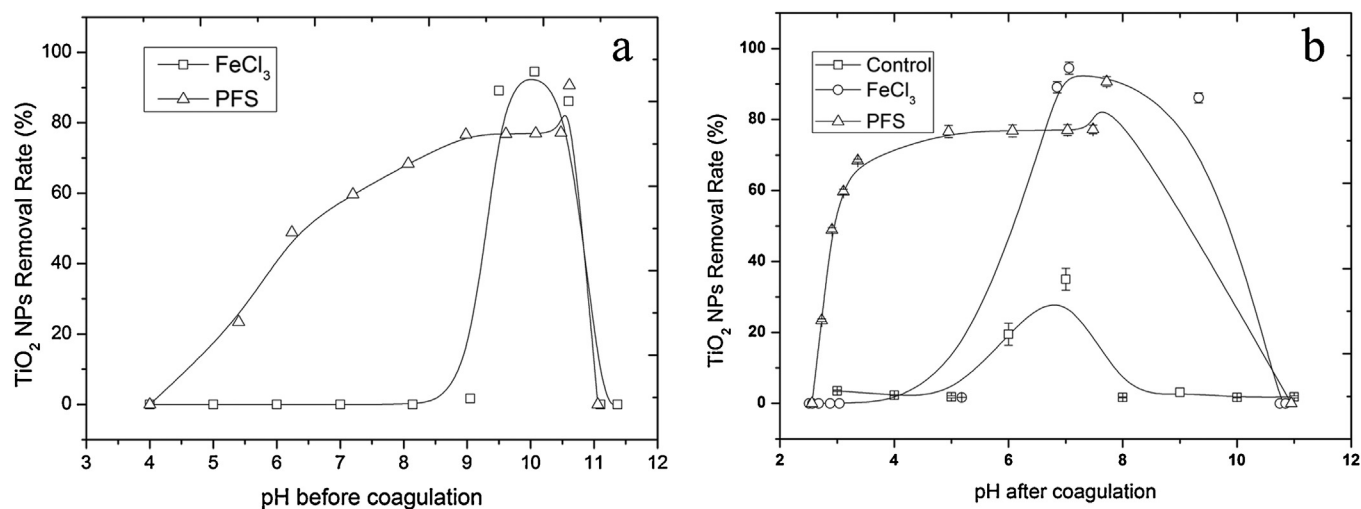
where  $C_i$  and  $C_s$  are TiO<sub>2</sub> NPs concentrations in the initial suspension and in the supernatant.

The effects of pH, ionic strength and HA on the removal of TiO<sub>2</sub> NPs using PFS and FeCl<sub>3</sub> were evaluated. The pH was adjusted using 0.1 M and 0.01 M HCl or NaOH. The ionic strength was adjusted using 0.03 M and 0.3 M NaCl. The NaCl solution was filtered through a 0.2 µm membrane. Coagulation was performed using the jar test procedure as follows: 1 min of rapid mixing (650 rpm); 15 min of slow mixing (150 rpm); and 30 min of settling. After coagulation, the zeta potential of TiO<sub>2</sub> NPs was measured by Zetasizer Nano (Malvern, England) at 25 °C, equilibrating for 2 min. The supernatant turbidity was measured by Turbidimeter (2100P, Hach). The volume weighted sizes (diameter) of the flocs were measured by an EyeTech instrument (Ankersmid, USA). Triplicate measurements were conducted and averaged for each sample.

## 3. Results and discussion

### 3.1. Effect of pH on the removal of TiO<sub>2</sub> NPs

The effect of pH on the removal of TiO<sub>2</sub> NPs is shown in Fig. 1. Compared to the control (jar test without coagulant), both coagulants are more effective in removing TiO<sub>2</sub> NPs. It can be seen that the removal of TiO<sub>2</sub> NPs is strongly influenced by pH for these two coagulants. For FeCl<sub>3</sub>, it only removes TiO<sub>2</sub> NPs effectively in a narrow pH range (initial pH = 9.5–10.6 as shown in Fig. 1a, correspondingly final pH = 6.85–7.06 as shown in Fig. 1b). The Fe<sup>3+</sup> ion can hydrolyze



**Fig. 1.** Effect of pH on the removal rate of TiO<sub>2</sub> NPs. (a) initial pH; (b) final pH. (Coagulant dosage: 0.3 mM (as Fe), 1 mM NaHCO<sub>3</sub>, 30 mg/L TiO<sub>2</sub> NPs, DI water; control means the same jar test procedure in the absence of coagulant.)

into the hydroxide form only in alkaline conditions, removing TiO<sub>2</sub> nanoparticles by adsorption bridging and enmeshment effect. As has been reported by other researchers [19,20], the hydrolysis reaction process of ferric salt coagulants is directly affected by the pH of the solution.

As shown in Fig. 1, the effective pH range for PFS is relatively broader (initial pH=7.20–10.61 as shown in Fig. 1a, final pH=3.19–8.21 as shown in Fig. 1b). In aqueous solution, the polymer iron sulfate produces many polymerization cations available in a wide pH range, which participate in charge neutralization and bridging flocculation, resulting in the removal of TiO<sub>2</sub> NPs. In comparison, FeCl<sub>3</sub> does not flocculate TiO<sub>2</sub> NPs until cationic polymerization begins at higher pH [21].

The pH of the suspensions changed significantly when the coagulants were added (Table 1). In general there was a decrease of 1–3 pH units, with the effect generally increasing with increasing pH. The effect was more significant for FeCl<sub>3</sub> than for PFS, which also negatively affects the performance of FeCl<sub>3</sub> at lower pH.

### 3.2. Effect of ionic strength on the removal of TiO<sub>2</sub> NPs

#### 3.2.1. Effect of ionic strength on the removal of TiO<sub>2</sub> NPs by FeCl<sub>3</sub>

As can be seen from Fig. 2a, in comparison with the control (where there is no NaCl), the removal rate of TiO<sub>2</sub> NPs was improved with the addition of electrolytes, although it is pH dependent. Many studies have reported that the adsorption of ions on the surface of the NPs can lead to their aggregation [22,23]. These larger aggregates are thus easier to remove by coagulants. Although the higher ionic strength greatly improved the removal rate of TiO<sub>2</sub> NPs, there was almost no distinction between different salt concentrations (0.03 M and 0.3 M NaCl). It is likely that already at 0.03 mM NaCl there is enough aggregation to increase removal by FeCl<sub>3</sub> and adding more salts does not improve removal.

In some studies, zeta potential measurements have been used to provide an indication of the surface charge present on the particles

such as TiO<sub>2</sub> NPs when they were in aqueous suspension [13]. In this study, the zeta potential of the TiO<sub>2</sub> NPs was >+40 mV at pH 4, but decreased to <−20 mV at pH 11 (Fig. 2c). This indicated that the high removal rate of TiO<sub>2</sub> NPs at intermediate pH (7–10) is likely attributed to their surface charge. However, TiO<sub>2</sub> NPs removal rate at pH 11 was still near 90% under [NaCl] = 0.03 M or 0.3 M (Fig. 2a), while there was no removal in the control ([NaCl] = 0 M). This indicated that the efficient removal of TiO<sub>2</sub> NPs by coagulants at high pH (pH = 11) is not due to charge neutralization, but rather the compression of the double electric layer by the electrolytes [24].

#### 3.2.2. Effect of ionic strength on the removal of TiO<sub>2</sub> NPs by PFS

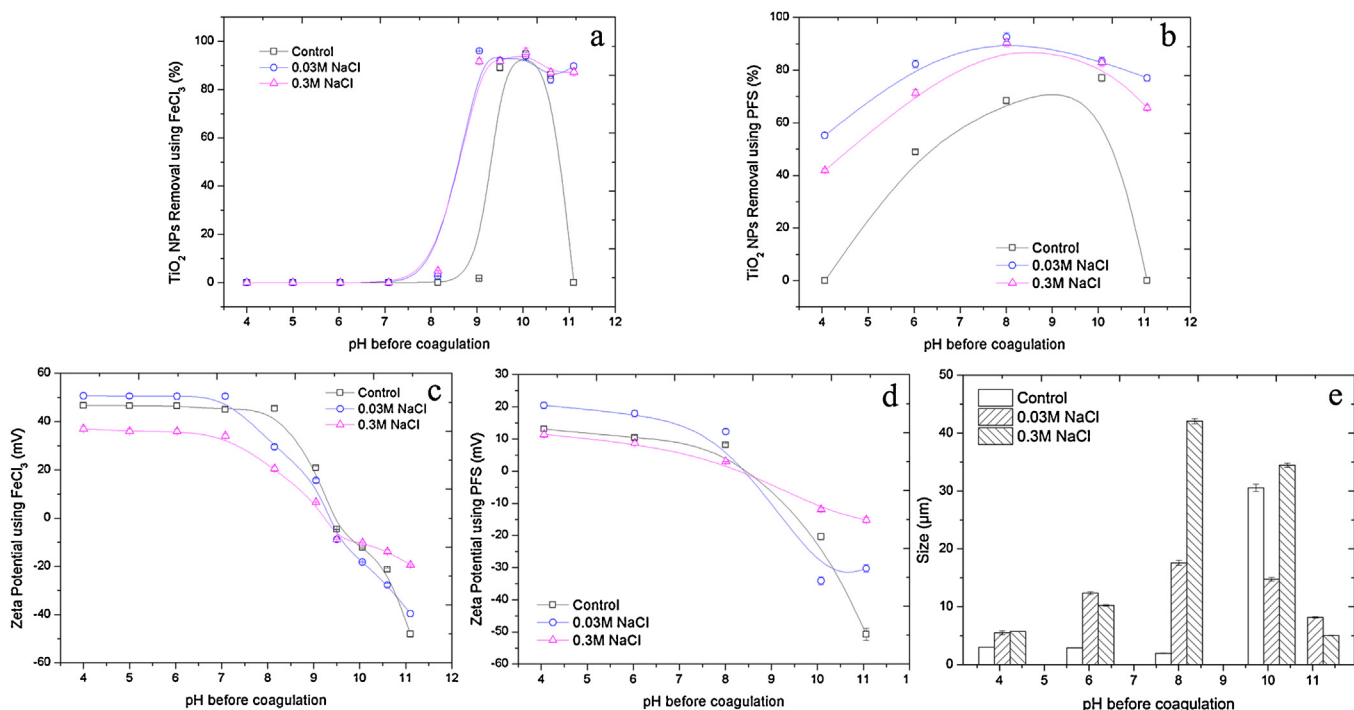
The effect of ionic strength on the removal of TiO<sub>2</sub> NPs by PFS is shown in Fig. 2b. The increase of ionic strength in a water medium can improve the effect of coagulation using PFS for the experimental pH range. At lower pH, especially at pH 4, the removal rate of TiO<sub>2</sub> NPs was increased from zero to nearly 50% even at 0.03 M NaCl, which was probably due to the compressed double electric layer effect. Similar to the results of FeCl<sub>3</sub>, the removal rate was increased from zero at 0 M NaCl to nearly 80% at 0.03 or 0.3 M NaCl at pH 11, which could also be due to the compressed double electric layer effect. In addition, there was a noticeable improved rate of TiO<sub>2</sub> NPs removal when NaCl concentration in the water medium was increased from 0.03 M to 0.3 M, particularly at lower pH (4–6).

As seen in Fig. 2d, when the initial pH (before coagulation) was increased to 11, the zeta potential of TiO<sub>2</sub> NPs after coagulation was decreased by the increasing ionic strength, which led the NPs to be destabilized and aggregate easily. This explains the increasing removal rate (Fig. 2b). The floc sizes (volume weighted diameter) after coagulation at different pH were also measured, which are shown in Fig. 2e. The increase of ionic strength was an advantage to floc growth, and it resulted in the increase of floc sizes. There was a strong correlation between zeta potential and size of flocs formed. The coagulation system was more stable with higher zeta potential, which led to smaller floc sizes and lower removal rates.

**Table 1**  
pH change before and after TiO<sub>2</sub> NPs coagulation using FeCl<sub>3</sub> and PFS.

FeCl <sub>3</sub>	pH(i)	401	501	603	708	815	905	95	10.06	10.6	11.1
	pH(f)	226	257	268	288	304	518	685	706	9.33	10.75
PFS	pH(i)	406	54	624	72	807	898	961	10.08	10.48	10.61
	pH(f)	256	281	312	319	336	494	613	703	7.42	8.21

Note: pH(i) is pH before coagulation (initial pH); pH(f) is pH after coagulation (final pH).



**Fig. 2.** Effect of NaCl concentration on: (a) TiO<sub>2</sub> NPs removal using FeCl<sub>3</sub> (coagulant dosage: 0.3 mM (as Fe), 1 mM NaHCO<sub>3</sub>, 30 mg/L TiO<sub>2</sub> NPs suspension, DI water; control: 0 M NaCl) (b) TiO<sub>2</sub> NPs removal using PFS (coagulant dosage: 0.3 mM (as Fe), 1 mM NaHCO<sub>3</sub>, 30 mg/L TiO<sub>2</sub> NPs, DI water; control: 0 M NaCl) (c) zeta potential using FeCl<sub>3</sub> (FeCl<sub>3</sub> coagulant dosage: 0.3 mM (as Fe), 1 mM NaHCO<sub>3</sub>, 30 mg/L TiO<sub>2</sub> NPs suspension concentration, DI water; control: 0 M NaCl) (d) zeta potential using PFS (PFS coagulant dosage: 0.3 mM (as Fe), 1 mM NaHCO<sub>3</sub>, 30 mg/L TiO<sub>2</sub> NPs suspension concentration, DI water; control: 0 M NaCl) (e) floc particle size using PFS (PFS coagulant dosage: 0.3 mM (as Fe), 1 mM NaHCO<sub>3</sub>, 30 mg/L TiO<sub>2</sub> NPs suspension concentration, DI water).

The bigger floc size and higher removal rate of NPs were achieved when the zeta potential of the system was lower.

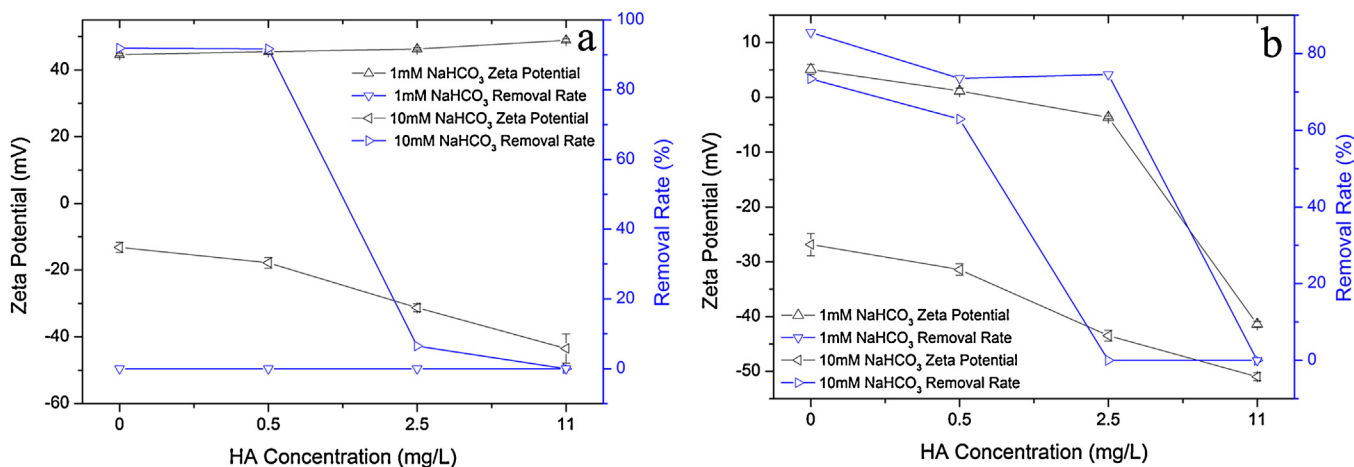
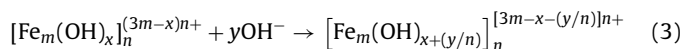
### 3.3. Effect of HA on the removal of TiO<sub>2</sub> NPs

The influence of HA on the removal of TiO<sub>2</sub> NPs is shown in Fig. 3. In consideration of the alkalinity consumption during coagulation process, NaHCO<sub>3</sub> was used in this study to provide alkalinity. The addition of NaHCO<sub>3</sub> makes the system more similar to natural water bodies. As can be seen from Fig. 3a, at a lower alkalinity of 1 mM NaHCO<sub>3</sub> (pH<sub>initial</sub> = 796 and pH<sub>final</sub> = 239) the FeCl<sub>3</sub> coagulant did not remove TiO<sub>2</sub> NPs in the entire HA concentration range, and the zeta potential remained very high (+40 mV). The removal rate

of TiO<sub>2</sub> NPs increases significantly at a higher alkalinity of 10 mM NaHCO<sub>3</sub> (pH<sub>initial</sub> = 856, pH<sub>final</sub> = 671) and low HA concentration. When HA concentration was high, the TiO<sub>2</sub> NPs in suspension remained stable and were not removed by the coagulant, because of the steric hindrance effect of HA.

In contrast, PFS was effective in removing the NPs even at lower alkalinity (NaHCO<sub>3</sub> = 1 mM, initial pH = 767) for HA up to 25 mg/L (Fig. 3b), as PFS contains large amount of iron hydroxyl polymer. There are two reaction processes for PFS in HA solution [25]:

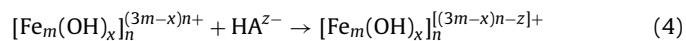
Hydrolysis:



**Fig. 3.** Effect of HA on TiO<sub>2</sub> NPs removal. (a) FeCl<sub>3</sub>, 1 mM and 10 mM NaHCO<sub>3</sub> (b) PFS, 1 mM and 10 mM NaHCO<sub>3</sub>. (Coagulant dosage: 0.3 mM (as Fe), 30 mg/L TiO<sub>2</sub> NPs, DI water; pH unadjusted, for FeCl<sub>3</sub>: when NaHCO<sub>3</sub> = 1 mM, pH<sub>initial</sub> = 796, pH<sub>final</sub> = 239; when NaHCO<sub>3</sub> = 10 mM, pH<sub>initial</sub> = 856, pH<sub>final</sub> = 671; for PFS, initial and final pH was shown in Table S1) (partially adapted from Wang et al. [16]).



Complex-formation:



As seen in Eq. (4), the polynuclear species of PFS ( $[\text{Fe}_m(\text{OH})_x]_n^{(3m-x)n+}$ ) will be changed when it is hydrolyzed or associated with HA, which will impact the coagulation removal process of  $\text{TiO}_2$  NPs. As the HA concentration increases, the solution pH decreases to the acidic range (Table S1). When the concentration of hydroxide ion decreases, the hydrolysis of PFS declines (Eq. (3)), and the complex-formation process improves since the negative charge on HA ( $\text{HA}^{z-}$ ) preferably combines with PFS. Hence, it can be concluded that the performance of PFS to remove  $\text{TiO}_2$  NPs improves because of the PFS-HA complex formation at lower pH (Fig. 3b). However, the formation of the PFS-HA complex is inhibited under high alkalinity conditions, which allows free HA molecules to cover the surface of  $\text{TiO}_2$  NPs and reduces the removal efficiency via PFS coagulation.

#### 4. Conclusions

This study shows that it is practical to remove  $\text{TiO}_2$  NPs by coagulation. Widely-used iron-based coagulants (PFS and  $\text{FeCl}_3$ ) are effective at removing  $\text{TiO}_2$  NPs from aqueous phase, and the removal rate can be up to ~90%, based on the regular jar test. This is higher than previously reported <80% of removal of nanoparticles, including  $\text{TiO}_2$  NPs, using an aluminum based coagulant. The mechanisms and behaviors of PFS and  $\text{FeCl}_3$  are different, based on the hydrolysis and polymerization species of PFS and  $\text{FeCl}_3$ . The removal of  $\text{TiO}_2$  NPs is strongly influenced by solution chemistry, including pH, ionic strength, and natural organic matter. The effective pH range for PFS is relatively broader than for  $\text{FeCl}_3$ . Increasing electrolyte concentration improves the removal rate of  $\text{TiO}_2$  NPs by coagulation, although it is pH dependent. HA stabilizes the  $\text{TiO}_2$  NPs by steric hindrance. These iron-based coagulants provide a solution for emergent treatment of industrial wastewater or effluent discharge which might contain high concentrations of  $\text{TiO}_2$  NPs, although the presence of organic matter may complicate the removal of the nanoparticles.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.03.029>.

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