ORIGINAL RESEARCH ARTICLE

Sedimentation of nanoparticle titanium dioxide in the presence of ammonium

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ABSTRACT

Due to its physicochemical properties, nanoparticles titanium dioxide ($nTiO_2$) is being put into mass production and widespread applications, which inevitably results in their increasing exposure to the water body. After it entering the water body, the chemical properties of $nTiO_2$ can be influenced by ion compositions, ion strength and pH, which affects their ecological risk. Excess of ammonium (NH^{4+}) fertilizer has contaminated soil and water environments. In this paper, the Zeta potentials and hydrodynamic radius of $nTiO_2$ were studied in NH^{4+} solution compared to those in Na^+ solution. In addition, the sedimentation rate of $nTiO_2$ was also investigated. The experiment results show that high pH inhibits the sedimentation of $nTiO_2$. Moreover, NH^{4+} increases the stability of $nTiO_2$ more than Na^+ at the same IS, which was attributed the more negative Zeta potentials and the smaller hydraulic radius. Our results provide a theoretical basis for evaluating the ecological risk of $nTiO_2$ in aqueous solution containing NH^{4+}.

Keywords: Ammonium; Chloride; Nanoparticles Titanium Dioxide ($nTiO_2$); Sedimentation; Zeta Potential

1. Introduction

Nanomaterials have small size effects, surface effects, quantum size effects, and macroscopic quantum tunneling effects, so that nanomaterials are widely used in medical[1], chemical[2], environmental[3], microelectronics[4] and other industries. Nanotitanium oxide ($nTiO_2$), as common nanomaterial, is heavily produced and widely used due to low production cost, good chemical stability and strong photocatalytic capacity[5]. In the production and consumption of $nTiO_2$, some $nTiO_2$ cannot be released into the natural environment[6,7]. After entering the environment, they will resemble other environmental pollutants and participate in the circulation of the biosphere, where complex migration and transformation processes occur, which will produce ecological effects. For example, Yamamoto *et al.* found that $nTiO_2$ increases the generation of reactive oxygen species in skin cells[8], which may damage DNA or mutation of the gene and eventually develop to cellular cancer[9,10]. It was found that the nanoparticles affect the properties of the particles themselves. Particle size, surface potential, ion species, ion concentration, and pH values all affect the aggregation and settling of nanoparticles in water, hence their reactivity and biotoxicity. Therefore, studying the sedimentation capacity of $nTiO_2$ in water bodies can

provide important theoretical support for assessing the potential ecological risk of nTiO$_2$.

At present, the global economy is developing rapidly, and science and technology are becoming more and more developed. In agricultural production, a large number of pesticides and fertilizers containing ammonia nitrogen are being used, and the phenomenon of ammonia nitrogen pollution in lakes, groundwater and rivers has become more and more serious. Therefore, preventing and controlling ammonia nitrogen pollution is an urgent task in Chinese agricultural science, and it is of great practical significance to study the harm of ammonia nitrogen pollution. For example, the fixation of phosphorus in soil was studied by Li Yanan *et al.* in the case of synthetic calcium magnesium carbonate, and high pH favored fixation of phosphorus by the material[11]. At the same time, Na$^+$ is one of the most widely distributed and abundant ions in groundwater, which is inevitably considered when studying the relevant water environment.

It has been shown that nTiO$_2$ can be used to remove ammonia nitrogen from sewage[12,13]. After entering the water environment, nTiO$_2$ causes aggregation and settlement under van der Waals force and electrostatic attraction, which may lead to short stay in water, but also reduce the specific surface area of the particles, affect nTiO$_2$ reactivity, reduce photocatalytic performance, and ultimately affect the ability of nTiO$_2$ to remove ammonia nitrogen. So far, most reports have been on the effect of nTiO$_2$ migration. For example, Liu Cheng *et al.* studied the effect of phosphate on nTiO$_2$ migration in soil[14], and Xu Xiaoting *et al.* studied the effect of phosphate and humic acid on nTiO$_2$ migration[15]. However, to date, no report has been reported on the impact of ammonia nitrogen on nTiO$_2$ settlement performance, so it is very important to study the aggregation and settlement capacity of nTiO$_2$ in water bodies containing ammonia nitrogen.

In view of this, the authors mainly studied the mechanism of NH^{4+} on nTiO$_2$ particle settlement, studied the settlement curve of pH values, calculated the settlement rate through Zeta potential and nanopularity, and then explained the influence and mechanism of NH^{4+} on the settlement rate of nTiO$_2$ particles in water bodies.

2. Materials and methods

2.1 Experimental reagents

nTiO$_2$ was purchased from Shanghai Gaoquan Chemical Co., Ltd. All other reagents were analytical reagents (AR).

2.2 Aggregation experiment of nTiO$_2$

Accurately measure 1 g of TiO$_2$, transfer it to a 100 ml beaker, add 100 ml NH$_4$Cl solution and NaCl solution with different concentrations (1, 5 and 10 mmol·L^{-1}) respectively, adjust the pH value to 6.0 and 8.0 with HCl and NaOH respectively, place the TiO$_2$ suspension in the ultrasonic instrument for ultrasonic for 30 min, and then stand for interval sampling, sampling 2 ml each time. The measurement method of nTiO$_2$ was measured by diantipyrylmethane method, and the absorbance was measured at 390 nm by Shimadzu uv-2450 UV spectrophotometer[16]. Dilute 1000 mg·L^{-1} titanium standard solution to 1–5 mg·L^{-1} for measurement, and obtain the standard curve of nTiO$_2$ concentration (as shown in **Figure 1**).

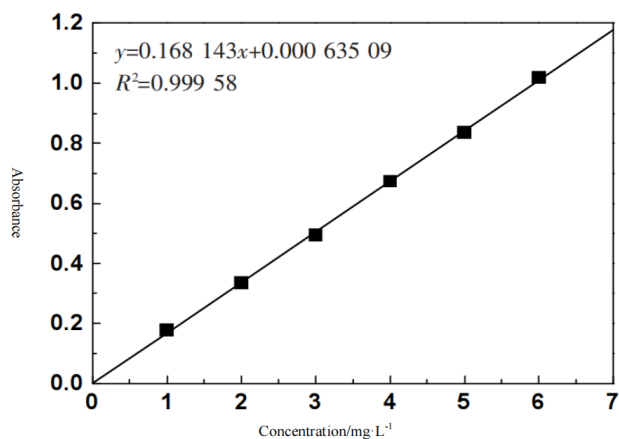$$y = 0.168\,143x + 0.000\,635\,09$$
$$R^2 = 0.999\,58$$

Figure 1. Curve for nTiO$_2$ concentration was determined by UV spectrophotometry.

2.3 The Zeta potential and hydraulical diameter measurements of nTiO$_2$

Accurately weigh 0.01 g of TiO$_2$, transfer it to a 100 ml beaker, add 100 ml of NH$_4$Cl solution and NaCl solution with different concentrations (1, 5 and

10 mmol·L^{-1}) respectively, and adjust the pH to 6.0 and 8.0 with HCl and NaOH respectively. Referring to the research method of Fang et al.[17], in order to promote the better dispersion of nTiO$_2$ in the solution, the suspension was placed in the ultrasonic instrument for ultrasonic for 10 min, and then each sample was sampled three times. The zeta potential and hydraulic diameter were measured by Malvin Nano-ZS90, and finally the average value was taken.

2.4 Settlement efficiency model

The sedimentation data were analyzed using the empirical model of Quik et al. and Velzeboer et al.[18,19]:

$$C_t = C_{res} + (C_0 - C_{res}) \times e^{-t \times V_s/h} \tag{1}$$

in which t is the settlement time, C_t is the colloidal concentration (g·L^{-1}) at the time t, Cres is the residual concentration (g·L^{-1}), C_0 is the initial concentration (g·L^{-1}), V_s is the sedimentation rate (mm·min^{-1}), h is the height of the water surface distance sampling point, aggregate V_s. According to equation (1), assuming not in each solution, the nTiO$_2$ samples were dissolved in ionic states.

3. Results and discussion

3.1 Zeta potential and hydroechanical diameter of nTiO$_2$ in NaCl solution

In **Figure 2**, it studied the Zeta potential (a) and hydroechanical diameter (b) of nTiO$_2$ at pH = 6.0 and 8.0, in NaCl solution.
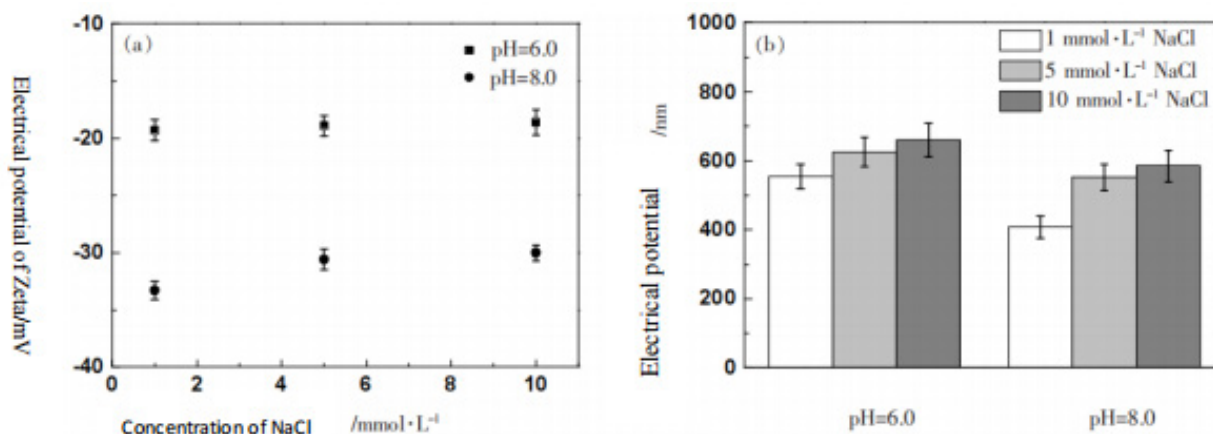
In **Figures 2(a)** and **2(b)**, the Zeta potential becomes slightly less negative with Na$^+$ concentration, with particle size (hydroechanical diameter) larger and prone to reunion. When the pH value continues to increase to 8.0, the Zeta potential of nTiO$_2$ in the water environment becomes more negative and the hydraulical diameter decreases. For specific pH values, both Zeta potentials become less negative with increasing Na$^+$ concentration, mainly because the charge shielding effect and electrostatic bielectric layer on the nTiO$_2$ surface are compressed resulting in reduced net negative charge and reduced Zeta potention the particle surface[20,21].

3.2 Zeta potential and hydroechanical diameter of nTiO$_2$ in NH$_4$Cl solution

In **Figure 3**, it studied The Zeta potential (a) and hydroechanical diameter (b) of nTiO$_2$ at pH = 6.0, were studied in NH$_4$Cl solution 8.0.

In **Figure 3(a)**, the Zeta potentials of nTiO$_2$ at pH = 6.0 and 8.0 are all negative. At the same NH$_4$Cl concentration, the Zeta potential at pH = 6.0 is less negative than that at pH = 8.0; in **Figure 3(b)**, at the same NH$_4$Cl concentration, the particle size of nTiO$_2$ decreases with increasing pH values. The possible mechanism leading to this phenomenon is that, Zeta, with less than a negative potential. This results in a smaller electrostatic repulsion between the nTiO$_2$ particles, making it easier to reunite between nTiO$_2$ particles and then leading to a larger particle size. In **Figure 3(a)**, the Zeta potential of nTiO$_2$ becomes less negative with increasing ion concentrations for spe-
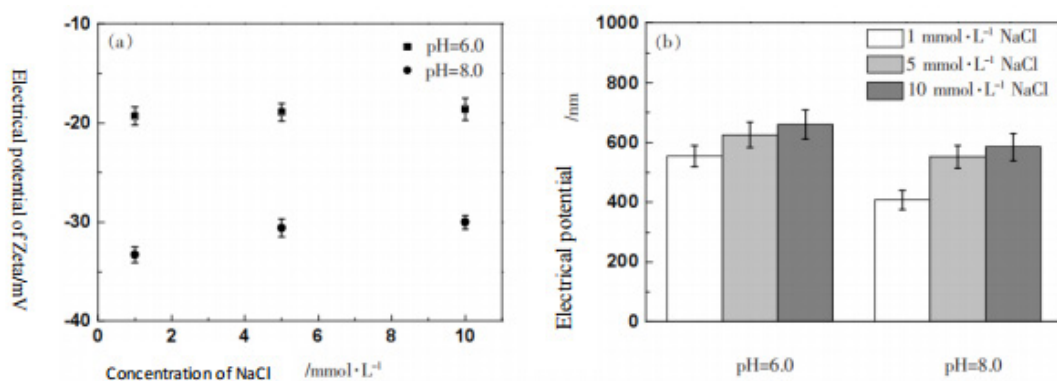

Figure 2. Zeta potentials **(a)** and Hydraulical diameter **(b)** of nTiO$_2$ in different concentrations of NaCl solution under pH= 6.0 and 8.0.

Figure 3. Zeta potentials **(a)** and Hydraulical diameter **(b)** of nTiO$_2$ in different concentrations of NH$_4$Cl solution under pH = 6.0, and 8.0.
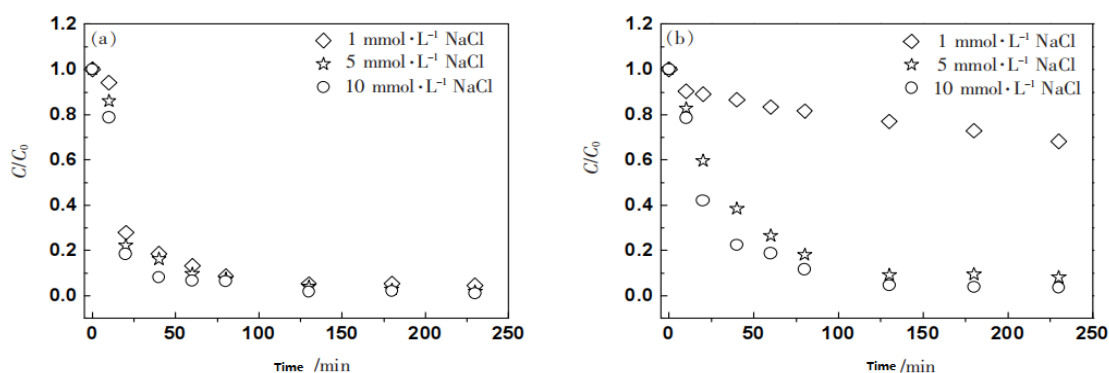

Figure 4. Settlement curves of nTiO$_2$ in different concentrations of NaCl solution pH = 6.0 (a) and 8.0 (b).

cific pH values, consistent with the phenomenon in Na$^+$. The increase in the hydrotomechanical diameter in **Figure 3(b)** is consistent with the less negative of the Zeta potential in **Figure 3(a)**. Compared to **Figures 3** and **2**, the Zeta potential of nTiO$_2$ is more negative and smaller particle size in NH$_4$Cl electrolyte solution at the same pH values and the same ion concentration. For example, under the condition of pH = 6.0, the Zeta potential and hydroechanical diameter of nTiO$_2$ in 1 mmol·L^{-1} NaCl solution are –19.3 mV, 554 nm, and the corresponding value becomes -20.6 mV, 472 nm. When the electrolyte solution is 1 mmol·L^{-1} NH$_4$Cl, the corresponding values are changed to –20.6 mV, 472 nm.

3.3 Settlement of nTiO$_2$ in the NaCl solution

Figure 4 is the settlement curve of nTiO$_2$ in NaCl solution in pH = 6.0 and 8.0.

The abscissa represents the settling time, and the ordinate represents the ratio of the concentration of nTio$_2$ (c) in the sampled liquid to the initial concentration of nTio$_2$ (C_0) under the corresponding settling time. The smaller the ratio, the lower the concentration of nTiO$_2$ in the representative sample, and the more nTiO$_2$ settled in the corresponding solution. **Figure 4(a)** shows that under the condition of pH = 6.0, although the concentration of NaCl solution has no obvious effect on the sedimentation performance of nTiO$_2$, on the whole, the higher the ion concentration, the faster the sedimentation rate and the worse the suspension stability. The increase of ion concentration is conducive to the sedimentation of particles, but this effect is not very obvious. According to the sedimentation rate (V_s) simulated and calculated according to formula (1), it is found that with the increase of ion concentration, V_s only increases from 0.507 mm·min^{-1} to 0.534 mm·min^{-1}. In **Figure 4(b)**, under the condition of pH = 8.0, low NaCl concentration (1 mmol·L^{-1}) has obvious sedimentation effect on nTiO$_2$, which significantly enhances the suspension stability of nTiO$_2$ in water environment. Comparing **Figure 4(a)** and **Figure 4(b)**, under the condition of 1 mmol·L^{-1} NaCl, pH

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value is an important factor affecting the sedimentation performance of nTiO$_2$ in water environment; at higher ion concentration, the inhibition effect of high pH value on sedimentation is not obvious.

3.4 Settlement of nTiO$_2$ in the NH$_4$Cl solution

As shown in **Figure 5(a)**, nTiO$_2$ settles at pH = 6.0 with increasing NH^{4+} concentration, indicating that nTiO$_2$ sedimentation performance is affected by NH^{4+} concentration, and higher sedimentation rate and worse suspension stability, mainly due to the charge shielding effect of the nTiO$_2$ surface and electrostatic double electric layer compression theory, and enhanced electrostatic repulsion between particles[19,20].When the pH value increased to 8.0, the suspension stability of nTiO$_2$ still weakened with increasing NH^{4+} concentration. The data in **Table 1** explain this well: it does increase with ion concentration. This suggests that NH^{4+} concentration is an important factor influencing the settling properties of nTiO$_2$. By comparing **Figures 5(a)** and **5(b)**, we also found that when the pH increases at the same

NH^{4+} concentration, the smaller the settlement rate, the better the suspension stability. This is consistent with previous Zeta potential and hydroechanical diameter results: the Zeta potential of nTiO$_2$ is more negative and smaller hydraulical diameter at high pH. Moreover, the data in **Table 1** indicate values at pH = 6.0 higher than those at pH = 8.0, indicating that increased high pH improves the suspension stability of nTiO$_2$ in the water environment. Comparing **Figures 4(a)** and **5(a)**, it is not difficult to find that NH^{4+} inhibited the aggregate deposition of nTiO$_2$ compared to Na$^+$ under the same ionic strength at pH = 6.0. If settlement equilibrium is reached, the value of C/C_0 is 0.029 in 10 mmol·L^{-1} NaCl solution, and the ratio is 0.011 in NaCl solution. This phenomenon still applies when pH increases to 8.0. The Zeta potential and hydraulical diameters in **Figures 2** and **3** also show that a more negative Zeta potential and a smaller hydraulical diameter will make the nanoparticles difficult to settle and enhance stability. It can be seen that NH^{4+} is conducive to improve the suspension stability of nTiO$_2$ in the water environment.
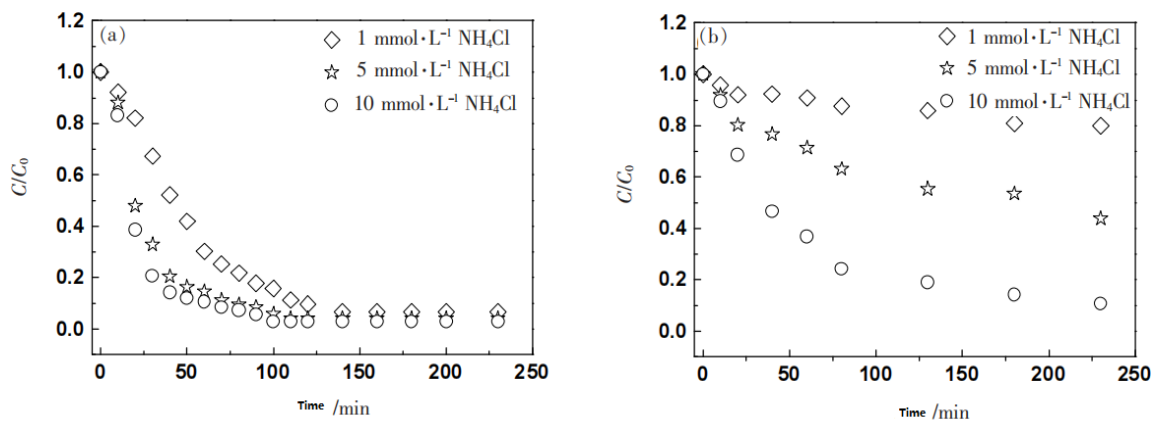

Figure 5. Settlement curve of nTiO$_2$ at pH = 6.0 **(a)** and 8.0 **(b)** in different concentrations of NH$_4$Cl solution.

Table 1. Settlement rates of nTiO$_2$ (10 g·L^{-1}) in different electrolyte solutions

PH of solution	Concentration of NH$_4$Cl /mmol·L^{-1}	Settlement rate V_s / mm·min^{-1}	PH of solution	Concentration of NaCl /mmol·L^{-1}	Settlement rate V_s / mm·min^{-1}
6.0	1	0.570	6.0	1	0.507
	5	0.688		5	0.524
	10	0.782		10	0.534
0.4598.0	1	0.142	8.0	1	0.214
	5	0.196		5	0.459
	10	0.363		10	0.466

4. Conclusion

Experimental results show that high pH helps to improve nTiO$_2$ stability in the electrolyte solution because the increased pH leads to more negative particle surface potential, larger electrostatic repulsion between particles, causing particles to reunite and eventually lead to settle. In the same pH and ionic strength, NH^{4+} in water than Na$^+$ can improve particle stability and suspension, and the settlement rate of nTiO$_2$ increases with NH^{4+} concentration.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgements

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