Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1092889

57 (2016) 18817–18824
August

Taylor & Francis
Taylor & Francis Group

Sedimentation of TiO_2 nanoparticles in aqueous solutions: influence of pH, ionic strength, and adsorption of humic acid

Jing Lu[a], Dongmei Liu[a,*], Xiaonan Yang[a], Haixing Liu[a], Shiguang Liu[a], Huan Tang[a], Ying Zhao[a], Fuyi Cui[b,*]

[a]*State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China, Tel. +8618746015386; email: lujing8556@163.com (J. Lu), Tel. +86 451 86283008; emails: mei18@hit.edu.cn (D. Liu), Xeare@163.com (X. Yang), lhx_526@163.com (H. Liu), shiguang8556@163.com (S. Liu), 1103521546@qq.com (H. Tang), zhaoying@hit.edu.cn (Y. Zhao)*
[b]*School of Municipal and Environmental Engineering, Harbin Institute of Technology, Huanghe Road 73, Nangang District, Harbin, China, Tel. +86 451 86282098; email: hit_cuifuyi@hotmail.com*

Received 4 March 2015; Accepted 4 September 2015

ABSTRACT

With the development and industrial applications of nanotechnology, increasing productions of engineered nanomaterials enter the aqueous environments by several routes (i.e. remediation purpose and unintentional release). Due to the potential risk deriving from their higher surface activity and greater transferability, engineered nanoparticles bring a new challenge for the environmental systems and human beings. Under favorable particle–particle interactions, nanoparticles aggregate, form large clusters, and settle out from the environmental solutions. The settling process can reduce the mobility of nanoparticles in environmental systems. In the current study, sedimentation experiments were conducted under different environmental conditions to investigate the settling process of nanoparticles. The results indicated that the A/A_0 ratios of titanium dioxide (TiO_2) nanoparticles increased with increasing ionic strength. They also increased near the pH_{pzc} (point zero of charge). However, the increasing concentrations of humic acids in aqueous solutions reduced the A/A_0 ratios even near the pH_{pzc}. The measured zeta potentials revealed that the TiO_2 nanoparticles became less charged in the range of pH_{pzc} and at higher ionic strength. It was due to the double electric layers of TiO_2 nanoparticles compressed with increasing in ionic strength and charge screening effect. Therefore, the electrostatic repulsive force between nanoparticles significantly declined, which lead to favorable aggregation. The interaction energies calculated using the DLVO theory under different pH and ionic strength conditions were consistent with the experimental results from the sedimentation experiments. In addition, the steric interactions between humic acid absorbed on the surface of TiO_2 nanoparticles were responsible for the reduction in the A/A_0 ratios.

Keywords: Sedimentation; Titanium dioxide nanoparticles; Ionic strength; Humic acid

---

*Corresponding authors.

1944-3994/1944-3986 © 2015 Balaban Desalination Publications. All rights reserved.

1. Introduction

Due to its special structural, thermal, electronic, and optical properties, TiO_2 nanoparticles are widely used in paints, photovoltaic cells, and wastewater treatment [1–3]. TiO_2 nanoparticles have a potential toxicity to aquatic organisms and human beings when they enter into aquatic environments by intentional or unintentional release (i.e. remediation purposes or surface runoff). Therefore, understanding the mobility of TiO_2 nanoparticles in environmental solutions is essential and urgent for evaluation of the potential risk. Aggregation and deposition of engineered nanomaterials in aquatic systems have been extensively studied to understand their mobility in environmental systems [4–9]. They prove that properties of nanoparticles (i.e. size, shape, chemical composition, and surface charge), surrounding solution chemistry (i.e. pH, ionic strength, ionic composition, and natural organic matter), and hydrodynamic conditions impact the stability of nanoparticle suspensions [10]. The DLVO and extended DLVO theories are utilized to describe the mobility of nanoparticles in aqueous solutions, and indicate a good qualitative agreement with the results from aggregation and deposition experiments [11–15].

Brownian motion is regarded as the dominant mechanism in the transport of the primary nanoparticles in aqueous solutions [16,17], while the fluid shear and gravity sedimentation are generally neglected [4]. Aggregation induced by attractive interactions between primary nanoparticles results in clusters with larger diameters [18]. Therefore, the concentration of the nanoparticles in aqueous suspensions decreases due to gravitational sedimentation and interception, as well as the mobility of the nanoparticles in environmental systems. In general, the aggregation process of engineered nanoparticles in aquatic solutions determines the probability of occurrence of the sedimentation process. The aggregation process of nanoparticles has been extensively studied as discussed above. However, studies focusing on the sedimentation process of aggregated nanoparticles are rare.

Sedimentation of particles has been an active area of research due to its significance in colloid system and the industrial applications [19–21]. Some theoretical and simulation methods (i.e. Brownian dynamic, Monte Carlo, etc.) are utilized to investigate the effect of particle size and interaction energy of suspending particles on the stability of the colloid suspensions [22,23]. However, the particle sizes in most of the studies are in the order of microns or above. The sedimentation process of aggregated nanoparticles is rarely investigated. In addition, environmental conditions (i.e. pH, ionic strength, and natural organic matter), which play an important role in the stability of nanoparticle suspensions were neglected. Therefore, it is essential to investigate the influence of pH, ionic strength, and adsorption of humic acid on the sedimentation process.

In the current study, the sedimentation process of TiO_2 nanoparticles in aqueous solutions were investigated over a wide range of pH, ionic strength, and humic acid content. Zeta potentials of TiO_2 nanoparticles were measured to interpret the electrostatic repulsive force between nanoparticles. The total interaction energy was calculated using DLVO theory. By integrating these results, there is the potential to gain a greater understanding of the sedimentation of nanomaterials in environmental systems, as well as their removal in drinking water treatment plant.

2. Experimental section

2.1. Materials

The TiO_2 nanoparticles (particle size: 21 nm; specific surface area: 50 cm^2/g) used in the current study were purchased from Degussa (Essen, Germany). The stock solutions (1.0 g/L) of TiO_2 nanoparticles were prepared in ultrapure water (18.2 MΩ/cm Millipore, Billerica, MA, USA) with sonication for 30 min (50 W/L at 40 kHz). The working solutions of TiO_2 nanoparticles were prepared immediately prior to diluting the stock solution with ultrapure water. The humic acid was purchased from Sigma–Aldrich. The stock solution of humic acid was prepared by dissolving humic acid powder (1 g/L) stirred in water for 24 h, and then filtering the solution through a 0.45 μm filter membrane. The working solutions of humic acid were maintained at 1, 5, and 10 mg/L of TOC during the TiO_2 nanoparticles sedimentation experiments. Analytical grade NaOH and HCl were used to adjust the pH of the TiO_2 nanoparticle suspensions. The ionic strength was varied by adding different amounts of 0.01 M NaCl stock solution.

2.2. Sedimentation experiments

A strong correlation between absorbance and concentrations for TiO_2 nanoparticles solutions were found at a wavelength of 320 nm using an all band scanning (from 200 to 800 nm). In addition, many studies have proved that UV_{254} is a good predictor for the concentration of metal oxide nanoparticles in aqueous solutions [11,24]. In the current study, ultraviolet spectrophotometer (UV759S) was used to measure the absorbance of TiO_2 nanoparticle solutions. The sedimentation experiments were started and monitored during a period of 120 min. An absorbance value was recorded every 5 min. All experiments were repeated three times for each condition to confirm the observations, and the A/A_0 ratios presented were the average results. Solution pH was measured using a Metrohm 744 pH meter and a Metrohm Pt 1,000 combination pH electrode, calibrated with standard NBS buffers. The Zeta potentials (ζ-potential) were studied in different media from the Zetasizer NS (Malvern instruments, UK). The particle size distribution (PSD) during the early stage of aggregation were analyzed using dynamic light scattering (DLS) on a Zetasizer Nano ZS instrument (Malvern Instruments, UK).

2.3. DLVO Theory

The classical DLVO theory can be utilized to calculate the total interaction energy (V_{Total}) of a nanoparticle experienced in the process of approaching another nanoparticle. The stability of nanoparticles in aqueous solutions was determined according to the sum of van der Waals (VDW) and electrical double layer (EDL) interactions [12]. The expressions for V_{VDW} and V_{EDL} are:

$$V_{\text{Total}} = V_{\text{VDW}} + V_{\text{EDL}} \tag{1}$$

$$V_{\text{VDW}} = -\frac{A\,a_1 a_2}{6h(a_1 + a_2)(1 + 14h/\lambda)} \tag{2}$$

where A is the Hamaker constant, h is the distance between the centers of the two particles, a_1 and a_2 are the radius for each of the particles, and λ is the characteristic wavelength. A value of 6.0×10^{-20} J was used for A [4].

$$V_{\text{EDL}} = 64\pi\varepsilon_0\varepsilon \frac{a_1 a_2}{a_1 + a_2}\zeta^2 \exp(-\kappa h) \tag{3}$$

$$\kappa^2 = \frac{4\pi e^2 \sum z_i^2 n_{i0}}{\varepsilon_0 \varepsilon k_B T} \tag{4}$$

where ε_0 is the dielectric permittivity in vacuum, ε is the permittivity of water, ζ is the zeta potential, κ is the inverse Debye length which is a function of e, the charge of an electron, ionic strength, n_{i0}, and counterion valence, z_i.

In the current study, the classical DLVO theory was utilized to describe the effects of the different pH and ionic strength conditions on the stability of TiO_2 nanoparticles. The interparticle interaction potentials between two nanoparticles were calculated as a function of their separation distances from Eqs. (1)–(4).

3. Results and discussion

3.1. Characteristics of the TiO_2 nanoparticles suspensions

In the current study, the TiO_2 nanoparticles in aqueous solutions were characterized firstly. The size distribution of the TiO_2 nanoparticles was measured using DLS at pH 7. As shown in Fig. 1, a wide distribution of 189–615 nm of the diameters of the TiO_2 nanoparticles in aqueous solutions is observed, with a peak at 300 nm. The diameters of the TiO_2 nanoparticles obtained using DLS measurements were much larger than the initial diameter of TiO_2 nanoparticles (21 nm). It indicated that the primary TiO_2 nanoparticles aggregated to clusters at pH 7. In addition, AFM images verified the DLS results. Therefore, it suggested that the aggregation of the TiO_2 nanoparticles in aqueous solutions have occurred during samples' preparation. The fast aggregation of engineered nanoparticles in aquatic solutions increased the probability of occurrence of the sedimentation process.

3.2. Effect of pH on the sedimentation process of the TiO_2 nanoparticles

The A/A_0 ratio (A, extinction at time = t mins; A_0, extinction at time = 0 min) was used to describe the sedimentation process. For stable nanoparticle suspensions, the A/A_0 ratio will be constant over the entire experiment. However, for unstable suspensions, the A/A_0 ratio will decrease due to the sedimentation of aggregated nanoparticles in aqueous solutions. The faster the change of A/A_0 ratios, the less stable the suspensions. Previous studies suggest that the TiO_2 nanoparticles in aqueous solutions can form large clusters near the pH_{pzc} [25,26]. To investigate the effect of the pH conditions on the sedimentation process of the TiO_2 nanoparticles in aqueous solutions, sedimentation experiments were conducted under different pH conditions (pH 5, 7, 9) at IS 0.01 M. The results are shown in Fig. 2. The A/A_0 ratios changed insignificantly at the first hour under all pH conditions. They changed to 87.3, 94.4, and 96.6% with a pH value of 5, 7, and 9, respectively, at end of the examinations.

The zeta potentials and average size of the TiO_2 aggregate were measured to reveal the mechanisms of the sedimentation process under different pH conditions. As shown in Fig. 3, the zeta potential plot shows that the zeta potential changed from 30.3 to −30.2 mV

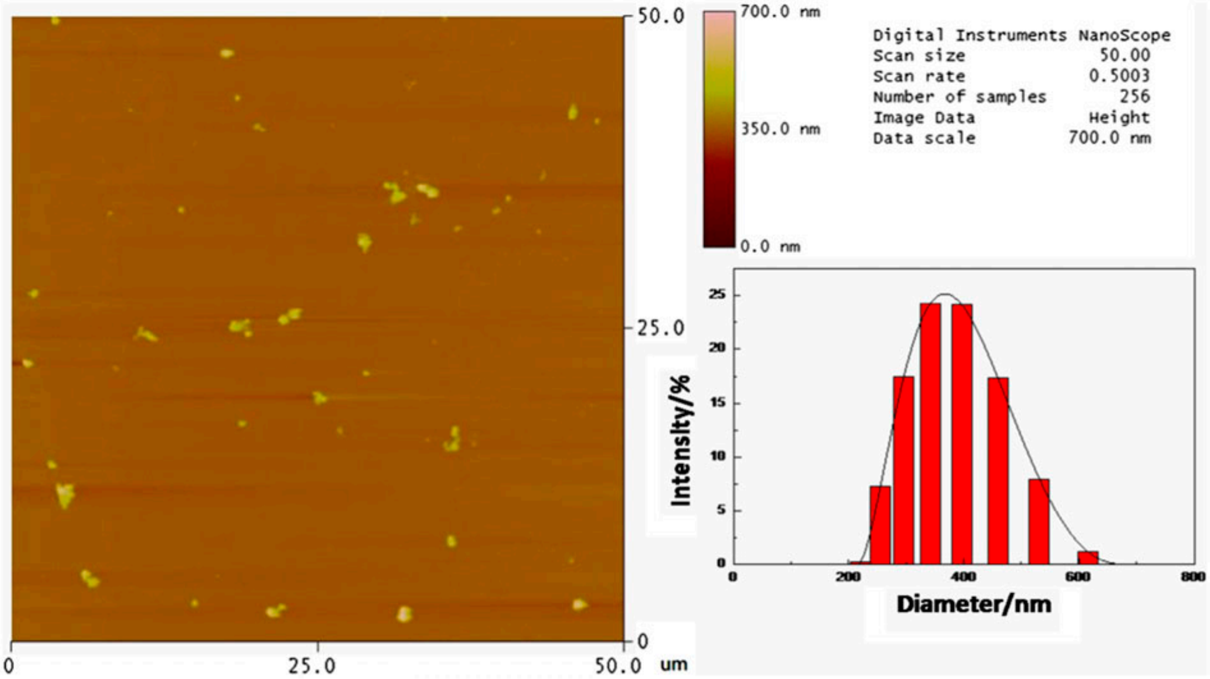

Fig. 1. Size distribution of the TiO_2 nanoparticles (pH 7, 10 mg/L, ultrasonitcated for 15 min).

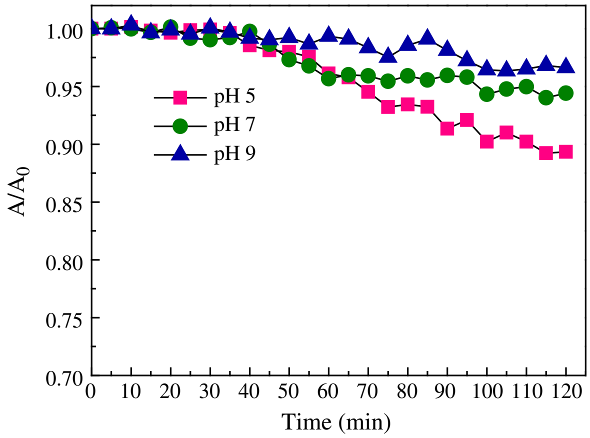

Fig. 2. Sedimentation curves of the TiO_2 nanoparticles under different pH conditions (IS 0.01 M).

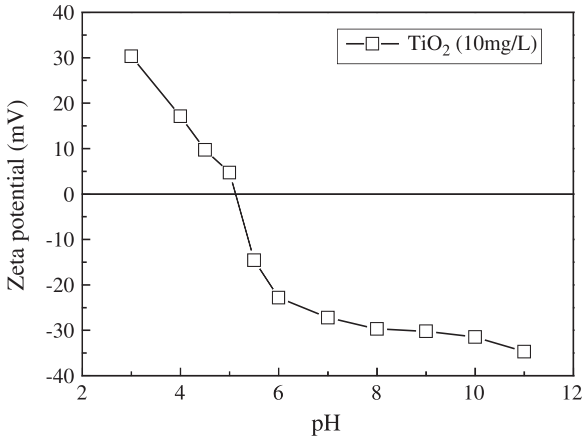

Fig. 3. Zeta potential of the TiO_2 nanoparticles under different pH conditions (IS 0.01 M).

with increasing pH (from 2 to 11). The pH_{pzc} of the 10 mg/L TiO_2 nanoparticles at IS 0.01 M was about 5.2. Therefore, the electrostatic repulsive force was approximately zero at pH 5. The TiO_2 nanoparticles suspensions were destabilized and aggregated favorably. The average size of TiO_2 nanoparticles under different pH conditions showed in Fig. 4 verified the results. A peak was observed at pH 5.2. Based on the discussion above, it suggested that the electrostatic repulsive interaction is the main mechanism for sedimentation process under different pH conditions.

The DLVO theory was utilized to interpret the sedimentation process of TiO_2 nanoparticle in the view of the interaction energy. The total interaction energy calculated by Eqs. (1)–(4) between TiO_2 nanoparticles under the different pH conditions are presented in Fig. 5. The DLVO calculations indicated that the total interaction energy of TiO_2 nanoparticles was negative (attractive) at pH 5. It was approximately zero with the increasing separation distance. At pH 3, 4, 6, 7, 8, and 9, repulsive barriers with

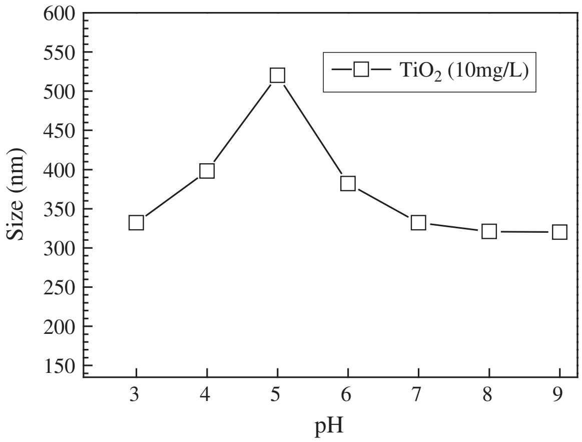

Fig. 4. Average size of the TiO_2 nanoparticles under different pH conditions (IS 0.01 M).

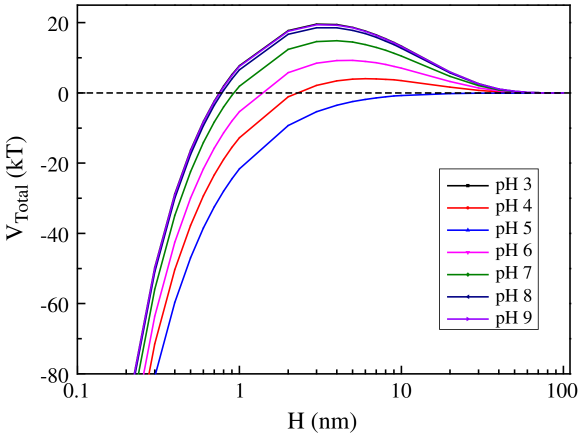

Fig. 5. DLVO curves of the TiO_2 nanoparticles under different pH conditions.

values of 19.56, 4.05, 9.27, 14.8, 18.56, and 19.39 k_BT were observed. There was a trend of increasing sedimentation rate as repulsive barriers decreases to near zero. The results calculated using DLVO theory were in good agreement with the results of sedimentation experiments under different pH conditions.

3.3. Effect of ionic strength on the sedimentation process of the TiO_2 nanoparticles

Previous studies reveal that the aggregation of TiO_2 nanoparticles is strongly dependent on the ionic strength of aqueous solutions [11,25,26]. It suggests that the sedimentation process of the TiO_2 nanoparticles may change with the variation of the ionic strength. The sedimentation curves of the TiO_2 nanoparticles were obtained for a wide range of ionic strength conditions at pH 9. As shown in Fig. 6, the A/A_0 ratios reduced with the increasing ionic strength during the entire sedimentation experiments. They changed to 96.6, 87.0, and 73.3% with an ionic strength of 0.01, 0.03 and 0.1 M, respectively, at end of the examinations. In comparison to the effects of pH conditions, ionic strength impacted the sedimentation process of the TiO_2 nanoparticles more severely. The sedimentation process under different ionic strength conditions occurred within a few minutes, while sedimentation process under different pH conditions took at least 60 min to observe a measurable sedimentation rate.

The measured zeta potentials of 10 mg/L TiO_2 nanoparticles suspensions at pH 9 are presented in Fig. 7. The results showed that the TiO_2 nanoparticles became less negatively charged with the increasing ionic strength. The double electric layers of TiO_2 nanoparticles compressed with the increase in ionic strength, and charge screening effect impacted the sedimentation process of the TiO_2 nanoparticles. Therefore, the electrostatic repulsive force between the TiO_2 nanoparticles significantly declined. The TiO_2 nanoparticles aggregated and settled out from the TiO_2 suspensions. The zeta potential results are consistent with the variation of the A/A_0 ratios from the sedimentation experiments. The results reported by Bian indicated that the double electric layers of TiO_2 nanoparticles compressed with the increase in ionic strength, and charge screening effect was the dominant mechanism for the aggregation of the ZnO nanoparticles [11].

As shown in Fig. 8, the total interaction energies between TiO_2 nanoparticles are negative (attractive) at IS 1 and 0.1 M. A repulsive barrier emerged with the

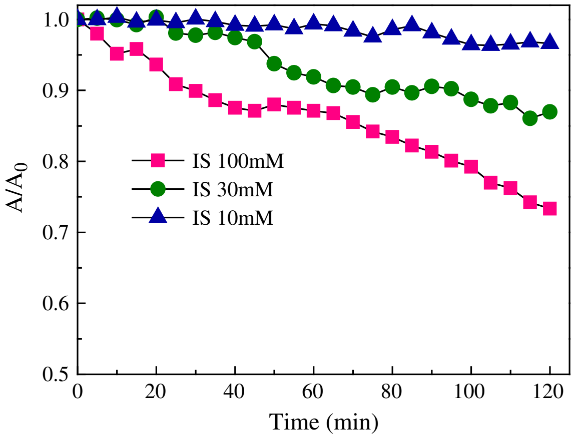

Fig. 6. Sedimentation curves of the TiO_2 nanoparticles under different IS conditions (pH 9).

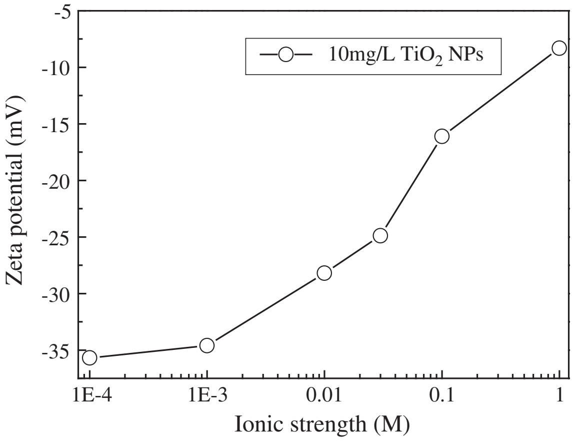

Fig. 7. Zeta potentials of the TiO_2 nanoparticles under different IS conditions (pH 9).

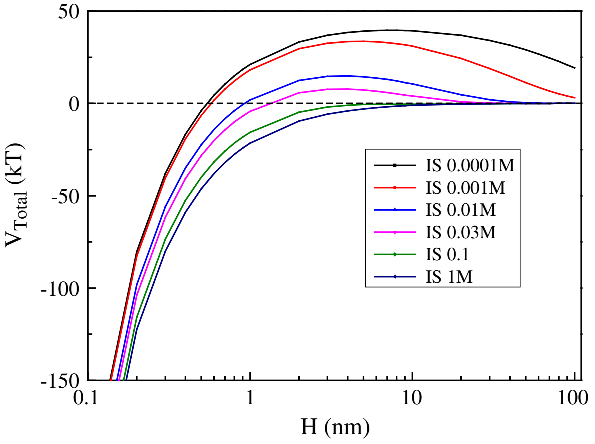

Fig. 8. DLVO curves of the TiO_2 nanoparticles under different IS conditions.

decreasing ionic strength. The values of the repulsive barrier were 14.88 and 33.59 k_BT, respectively, at IS of 0.01 and 0.001 M. The results indicated that the lower the ionic strength, the more repulsive the interactions between the TiO_2 nanoparticles. The results calculated using DLVO theory verified the results of sedimentation experiments.

3.4. *Effect of humic acid on the sedimentation of the TiO_2 nanoparticles*

Natural organic matter (humic acids, fulvic acids, etc.) is one of the widely existing matter in aqueous environments, which can absorb onto the surface of metal oxide nanoparticles [27]. The effects of humic acid on the sedimentation process of the TiO_2 nanoparticles at pH 5.5 and IS 0.01 M are shown in Fig. 9. The results showed that the A/A_0 ratios decreased with the increase in humic acid concentration after 60 min. They changed to 89.3, 92.9, and 95.7% with a humic acid concentration of 0, 1 and 5 mg/L, respectively, at end of the examinations. The results suggested that the humic acid adsorbed onto the particle surfaces, providing a barrier to aggregation. Under these conditions, the nanoparticles aggregated for a longer time. Previous studies indicate that humic acid enhances the stability of nanoparticles suspensions, even at high ionic strength [28,29].

Zeta potentials of the TiO_2 nanoparticles under different IS and HA concentrations at pH 5.5 are shown in Fig. 10. The TiO_2 nanoparticles were negatively charged over the entire range of ionic strength and humic acid conditions examined. The zeta potential of the TiO_2 nanoparticles increased with the increase in humic acid concentrations (from 0 to 5 mg/L). It suggested that the absorbed humic acid enhanced the negative surface charge of TiO_2 nanoparticles due to their carboxylic acid groups. As the surface of the TiO_2 nanoparticle was coated with humic acid, the charge on the particle was dominated more and more by the charge of the humic acid. Thus, the electrostatic repulsive interactions and steric interaction impeded the aggregation of nanoparticles. The zeta potentials increased insignificantly when the humic acid concentration varied from 5 to 10 mg/L. It suggested that the adsorbing capacity of humic acid onto the TiO_2 nanoparticles was limited. As shown in Fig. 11, the results of the adsorbed amount of humic acid on the surface of the TiO_2 nanoparticles verified it. The humic acid adsorption onto the TiO_2 nanoparticles was investigated under different humic acid concentrations (1.0, 5.0, and 10.0 mg/L) and IS at pH 5.5. The

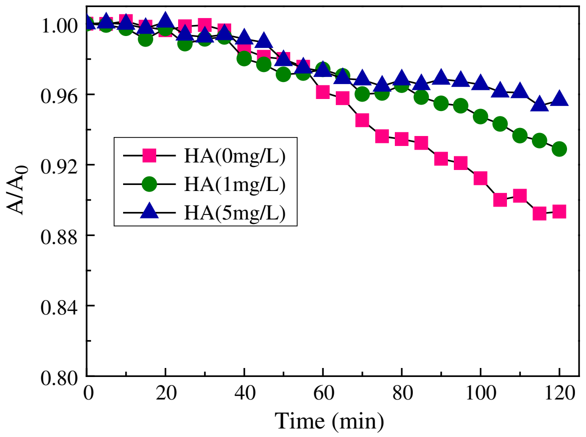

Fig. 9. Sedimentation curves of the TiO_2 nanoparticles under different HA concentrations (pH 5.5, IS 0.01 M).

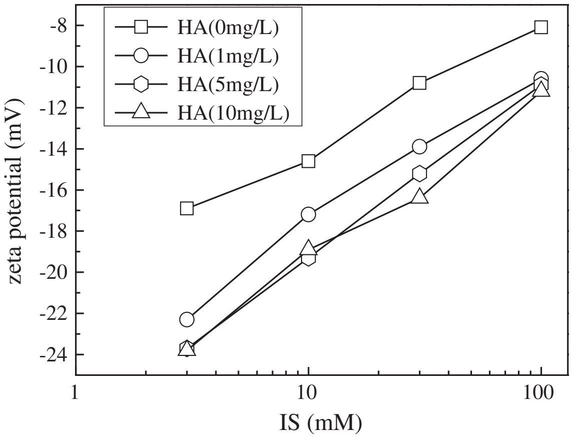

Fig. 10. Zeta potentials of the TiO_2 nanoparticles under different IS and HA concentrations (pH 5.5).

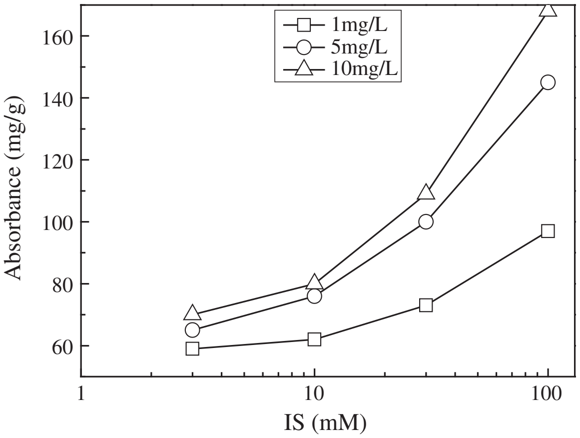

Fig. 11. Adsorbed amount of HA on the surface of the TiO_2 nanoparticles under different IS and HA concentrations (pH 5.5).

adsorption of humic acid onto the TiO_2 nanoparticles increased with increasing ionic strength for a given initial humic acid concentration. It also changed insignificantly with the increasing humic acid concentrations for a given ionic strength concentration.

4. Conclusion

In the current study, the effects of pH, ionic strength, and adsorption of humic acid on the sedimentation process of the TiO_2 nanoparticles in aqueous solutions were investigated using the measured A/A_0 ratios. The findings from the current study suggest that the sedimentation process was enhanced near the pH_{pzc} and with the increase in ionic strength. However, the increase in humic acid concentration caused a more stable TiO_2 nanoparticle suspension due to electrostatic and steric interactions. The zeta potentials were measured to interpret the electrostatic interaction under different conditions (pH, ionic strength, and humic acid content). The results indicated that the absolute zeta potential reduced near the pH_{pzc} or with increasing ionic strength. However, it indicated that the steric interaction between humic acid absorbed on the TiO_2 nanoparticles enhanced the negative surface charge of the TiO_2 nanoparticle. The DLVO theory was utilized to describe the sedimentation process of the TiO_2 nanoparticles quantitatively. The interaction energies were calculated under different pH and ionic strength conditions. The results were found to be in good agreement with the experimental results. The current study is useful to better understand the mobility of nanoparticles in a diverse array of real environmental media.

Acknowledgements

This work was financially supported by the Funds for Creative Research Groups of China (51121062), the National Natural Science Foundation of China (51278147).

Symbols

ζ — zeta potential, V
z_i — counterion valence
n_{i0} — ionic strength, m^{-3}
e — electron charge, 1.60×10^{-19} C
κ — inverse Debye length
k_B — Boltzmann constant, 1.38×10^{-23} J/K
T — absolute temperature
A — Hamaker constant
a_1,a_2 — particle radius
h — surface-to-surface separation distance
ε — relative dielectric permittivity of aqueous solutions
ε_0 — dielectric permittivity in vacuum

References

[1] Y. Bai, I. Mora-Seró, F. De Angelis, J. Bisquert, P. Wang, Titanium dioxide nanomaterials for photovoltaic applications, Chem. Rev. 114(19) (2014) 10095–10130.

[2] J. Bai, B. Zhou, Titanium dioxide nanomaterials for sensor applications, Chem. Rev. 114(19) (2014) 10131–10176.

[3] X. Qu, P.J.J. Alvarez, Q. Li, Applications of nanotechnology in water and wastewater treatment, Water Res. 47(12) (2013) 3931–3946.

[4] A.R. Petosa, D.P. Jaisi, I.R. Quevedo, M. Elimelech, N. Tufenkji, Aggregation and deposition of engineered

nanomaterials in aquatic environments: Role of physicochemical interactions, Environ. Sci. Technol. 44 (17) (2010) 6532–6549.

[5] X. Ren, J. Li, X. Tan, W. Shi, C. Chen, D. Shao, T. Wen, L. Wang, G. Zhao, G. Sheng, X. Wang, Impact of Al_2O_3 on the aggregation and deposition of graphene oxide, Environ. Sci. Technol. 48(10) (2014) 5493–5500.

[6] X. Li, J.J. Lenhart, Aggregation and dissolution of silver nanoparticles in natural surface water, Environ. Sci. Technol. 46(10) (2012) 5378–5386.

[7] X. Huangfu, J. Jiang, J. Ma, Y. Liu, J. Yang, Aggregation kinetics of manganese dioxide colloids in aqueous solution: Influence of humic substances and biomacromolecules, Environ. Sci. Technol. 47(18) (2013) 10285–10292.

[8] R.F. Domingos, N. Tufenkji, K.J. Wilkinson, Aggregation of titanium dioxide nanoparticles: Role of a fulvic acid, Environ. Sci. Technol. 43(5) (2009) 1282–1286.

[9] I.G. Godinez, C.J.G. Darnault, A.P. Khodadoust, D. Bogdan, Deposition and release kinetics of nano-TiO_2 in saturated porous media: Effects of solution ionic strength and surfactants, Environ. Pollut. 174 (2013) 106–113.

[10] G.V. Lowry, K.B. Gregory, S.C. Apte, J.R. Lead, Transformations of nanomaterials in the environment, Environ. Sci. Technol. 46(13) (2012) 6893–6899.

[11] S.-W. Bian, I.A. Mudunkotuwa, T. Rupasinghe, V.H. Grassian, Aggregation and dissolution of 4 nm zno nanoparticles in aqueous environments: Influence of pH, ionic strength, size, and adsorption of humic acid, Langmuir 27(10) (2011) 6059–6068.

[12] Y. Zhang, Y. Chen, P. Westerhoff, K. Hristovski, J.C. Crittenden, Stability of commercial metal oxide nanoparticles in water, Water Res. 42(8–9) (2008) 2204–2212.

[13] J. Jiang, G. Oberdörster, P. Biswas, Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies, J. Nanopart. Res. 11(1) (2009) 77–89.

[14] Z. Ji, X. Jin, S. George, T. Xia, H. Meng, X. Wang, E. Suarez, H. Zhang, E.M.V. Hoek, H. Godwin, A.E. Nel, J.I. Zink, Dispersion and stability optimization of TiO_2 nanoparticles in cell culture media, Environ. Sci. Technol. 44(19) (2010) 7309–7314.

[15] Y. Hong, R.J. Honda, N.V. Myung, S.L. Walker, Transport of iron-based nanoparticles: Role of magnetic properties, Environ. Sci. Technol. 43(23) (2009) 8834–8839.

[16] Y. Li, Y. Wang, K.D. Pennell, L.M. Abriola, Investigation of the transport and deposition of fullerene (c60) nanoparticles in quartz sands under varying flow conditions, Environ. Sci. Technol. 42(19) (2008) 7174–7180.

[17] A.M. El Badawy, A. Aly Hassan, K.G. Scheckel, M.T. Suidan, T.M. Tolaymat, Key factors controlling the transport of silver nanoparticles in porous media, Environ. Sci. Technol. 47(9) (2013) 4039–4045.

[18] T. Phenrat, N. Saleh, K. Sirk, R.D. Tilton, G.V. Lowry, Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions, Environ. Sci. Technol. 41 (1) (2006) 284–290.

[19] S. Ganguly, S. Chakraborty, Sedimentation of nanoparticles in nanoscale colloidal suspensions, Phys. Lett. A 375(24) (2011) 2394–2399.

[20] W. Jiang, G. Ding, H. Peng, H. Hu, Modeling of nanoparticles' aggregation and sedimentation in nanofluid, Curr. Appl. Phys. 10(3) (2010) 934–941.

[21] J.T.K. Quik, D. van De Meent, A.A. Koelmans, Simplifying modeling of nanoparticle aggregation–sedimentation behavior in environmental systems: A theoretical analysis, Water Res. 62 (2014) 193–201.

[22] A.A. Markus, J.R. Parsons, E.W.M. Roex, P. de Voogt, R.W.P.M. Laane, Modeling aggregation and sedimentation of nanoparticles in the aquatic environment, Sci. Total Environ. 506–507 (2015) 323–329.

[23] H.N. Unni, C. Yang, Brownian dynamics simulation and experimental study of colloidal particle deposition in a microchannel flow, J. Colloid Interface Sci. 291(1) (2005) 28–36.

[24] A.A. Keller, H. Wang, D. Zhou, H.S. Lenihan, G. Cherr, B.J. Cardinale, R. Miller, Z. Ji, Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices, Environ. Sci. Technol. 44(6) (2010) 1962–1967.

[25] X.N. Yang, F.Y. Cui, Stability of nano-sized titanium dioxide in an aqueous environment: Effects of pH, dissolved organic matter and divalent cations, Water Sci. Technol. 68(2) (2013) 276.

[26] R.A. French, A.R. Jacobson, B. Kim, S.L. Isley, R.L. Penn, P.C. Baveye, Influence of ionic strength, pH, and cation valence on aggregation kinetics of titanium dioxide nanoparticles, Environ. Sci. Technol. 43(5) (2009) 1354–1359.

[27] S.P. Yang, O. Bar-Ilan, R.E. Peterson, W. Heideman, R.J. Hamers, J.A. Pedersen, Influence of humic acid on titanium dioxide nanoparticle toxicity to developing zebrafish, Environ. Sci. Technol. 47(9) (2013) 4718–4725.

[28] X. Qu, P.J.J. Alvarez, Q. Li, Impact of sunlight and humic acid on the deposition kinetics of aqueous fullerene nanoparticles (nC_{60}), Environ. Sci. Technol. 46 (24) (2012) 13455–13462.

[29] K.L. Chen, M. Elimelech, Influence of humic acid on the aggregation kinetics of fullerene (C_{60}) nanoparticles in monovalent and divalent electrolyte solutions, J. Colloid Interface Sci. 309(1) (2007) 126–134.