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RESEARCH ARTICLE

Effects of Cd(II) on the stability of humic acid-coated nano-TiO_2 particles in aquatic environments

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Abstract The stability of nanoparticles (NPs) in aquatic environments is important to evaluate their adverse effects on aquatic ecosystems and human health. Nanoparticle stability is known to be influenced by coexisting ions and dissolved organic matter. This study was designed to investigate the effects of coexisting low-level Cd(II) on the stability of humic acid-coated nano-TiO_2 (HA-TiO_2) particles in aquatic environments by measuring their aggregation kinetics through time-resolved dynamic light scattering (DLS) and monitoring suspended HA-TiO_2 concentrations via optical absorbance changes over time. The particles exhibited aggregation behavior consistent with the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. The results showed that Cd(II) concentration, pH, and ionic strength had various effects on the aggregation kinetics of the HA-TiO_2 NPs. The HA-TiO_2 particles aggregated faster as the Cd(II) concentration increased whereas the stability of the nanoparticles increased as the solution pH increased or ionic strength decreased regardless of the Cd(II) concentration. At the fixed pH and ionic strength conditions, the addition of Cd(II) promoted aggregation of nanoparticles, leading to higher attachment efficiencies. The enhanced aggregation of the HA-TiO_2 NPs in the presence of coexisting cadmium ions in aqueous solutions indicated that the fate and transport of nanoparticles could be greatly affected by heavy metals in aquatic environments.

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Introduction

Titanium dioxide nanoparticles (nano-TiO_2) are widely used in many fields because of their excellent dielectric and chemical properties, such as sunscreens, pigments, coatings, disinfectants, and photocatalysts (Chen and Mao 2007, Nowack and Bucheli 2007, Tong et al. 2013, Zhu et al. 2011). The extensive application of nano-TiO_2 has led to their ubiquitous distribution in aquatic environments, posing adverse effects to the ecosystem. They can accumulate in aquatic organisms and might threaten human health due to their high capability of conveying toxic substances (Baun et al. 2008, Limbach et al. 2005, Liu et al. 2009). Meanwhile, Cd(II) was recognized as a common pollutant in aquatic environments that could accumulate in animal and human bodies through the food chain and cause bone diseases (Belghith et al. 2016, Lin et al. 2005, Yasukawa et al. 2005). The environmental behaviors of nanoparticles have drawn increasing attention. The fate and transport of TiO_2 nanoparticles in aquatic environments might be strongly dependent on their size, surface properties, and their interactions with other pollutants in aquatic environments (Battin et al. 2009, Hofmann and von der Kammer 2009).

Once released into aquatic environments, nano-TiO_2 particles with strong surface activity will likely interact with the ubiquitously distributed natural organic matters (NOM), such as humic acids (HA). Once organic matter adsorbs onto the surface of nanoparticles, their stability could be much different from their bare counterparts (Ferretti et al. 1997, Li et al. 2015). Previous studies have reported that HA might alter the surface properties and significantly increase the stability of nano-TiO_2 NPs in aquatic environments through

complexation between the acidic functional groups (mainly carboxylic acid) of HA and the hydroxyl group of nano-TiO_2 NPs (Hajdu et al. 2009, Hyung et al. 2007). The interaction mechanisms between HA and nano-TiO_2 may include anion exchange, ligand exchange, hydrophobic interaction, entropic effect, hydrogen bonding, and cation bridging (Yang et al. 2009). On the other hand, the coexisting heavy metal ions in aqueous environments might affect the stability of nanoparticles and alter their environmental risks. Cd(II) can form stable complexes with HA by strong covalent force due to the ionic polarization effect of Cd(II) having different electronic configurations (Chen et al. 2012, Jia et al. 2008, Wu et al. 2012). Several researches have demonstrated that the colloidal stability of nanoparticles in aqueous environments depends on not only the amount of NOM such as HA present mainly in surface waters but also the pH and electrolyte conditions of aqueous environments (Brigante et al. 2009, Chowdhury et al. 2013, Godinez and Darnault 2011, Keller et al. 2010, Liu et al. 2011, Zhang et al. 2009). The solution pH and electrolyte composition/concentration can modify the surface charge of nanoparticles and significantly influence their colloidal stability (Chen and Huang 2017a,b), hence directly affecting their reactivity and potential biological toxicity (Ge et al. 2011, Jiang et al. 2012).

In the present study, we investigated the effects of cadmium on the surface charge, sedimentation, and aggregation kinetics of HA-TiO_2 particles. Results could provide insights on the interactions among heavy metal ions, NOM, and nanoparticles in aquatic environments for predicting their potential ecological hazards.

Materials and methods

Materials

Nano-TiO_2 (anatase) and cadmium chloride were purchased from the Aladdin Reagent Company, Shanghai, China. The purity, diameter, and specific surface area of the nano-TiO_2 were 99.8%, 40 nm, and 97.46 m^2/g, respectively. The purity of cadmium chloride was 99.9%. HA was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd., Shanghai, China. All other solutions were prepared by analytical grade chemicals (National Medicine Corporation Ltd., Shanghai, China).

Preparation of HA-TiO_2

The HA-TiO_2 complexes were synthesized according to the previous publications (Li et al. 2015, Yang and Xing 2009). Briefly, the HA-TiO_2 was prepared by introducing 5 g of nano-TiO_2 into 1-L 1-g/L HA solution. It was reported that the maximum HA content on the nano-TiO_2 was about 50 mg/g (Lin et al. 2012). The suspension was shaken at 150 rpm for 2 days, and then centrifuged at 4000 rpm for 30 min. The precipitated materials were then rinsed three times with Milli-Q water, freeze-dried, ground, and stored for use. The pH of supernatant was adjusted to 1 ± 0.5 by addition of HCl, and then the suspension was centrifuged at 4000 rpm for 30 min. The precipitated materials were then rinsed three times with Milli-Q water, freeze-dried, and stored for use, which was named as $HA_{treated}$.

Characterization of HA and HA-TiO_2

The HA and HA-TiO_2 were characterized using Fourier transform infrared spectroscopy (Vector 33, Bruker, Germany), and solid-state ^{13}C nuclear magnetic resonance spectroscopy (Avance AV 400, Bruker, Switzerland) was employed to investigate the functional groups.

Zeta potential and hydrodynamic diameter measurements

The suspensions were prepared by adding 0.03-g HA-TiO_2 into 250 ml of different solutions: 0–100-mg/L Cd(II) in 50-mM KNO_3 at pH 6.90–20-mg/L Cd(II) with 50-mM KNO_3 solutions in different pH values, and 0–20-mg/L Cd(II) in 0–100-mM KNO_3 solutions at pH 6.90. The suspensions were sonicated for 1 h. The zeta potential and hydrodynamic diameter (D_h) of HA-TiO_2 NPs suspension were measured using the Malvern Zetasizer Nano ZS-90 (Malvern, Westborough, MA).

Sedimentation experiments

To evaluate the effects of pH, ionic strength, and Cd(II) concentration on the stability of HA-TiO_2, sedimentation of HA-TiO_2 was studied by monitoring the suspended HA-TiO_2 concentrations via optical absorbance as a function of time (Godinez and Darnault 2011, Li et al. 2015). The suspensions were sonicated for 1 h after 0.03-g HA-TiO_2 was added into these background solutions. Then optical absorbance was measured at 350 nm with time intervals of 5 min over a 200-min period (Erhayem and Sohn 2014). The original absorbance of HA-TiO_2, C_0, and the absorbance at different time, C_e, were used to generate the reliable calibration curves for HA-TiO_2 versus absorbance (C_0/C_e), which shown the aggregation states.

Model fitting

The DLVO model was employed for analyzing the nanoparticle stability governed by inter molecular forces between particles (Chen and Huang 2017a, b, Chen and Elimelech 2007, Liu et al. 2012, Liu et al. 2011, Shih et al. 2012, Yang-hsin et al. 2012). The classical DLVO theory involves two major

forces: the van der Waals (vdW) attraction (F_{vdW}) and electrical double layer (EDL) repulsion (F_{EDL}). The sum of these two forces (V_{total}) can determine the stability according to the following expression (Liu et al. 1995):

$$V_{total} = 4.36{\cdot}10^{-9}\psi_0{}^2 r ln[1+\exp(-kx)] - \frac{A_H}{6}\left[\frac{2r^2}{x(x+4r)} + \frac{2r^2}{(x+2r)^2} + ln\frac{x(x+4r)}{(x+2r)^2}\right] \quad (1)$$

where ψ_0 is the zeta potential (V); r is the particle radius (m); k is the inverse of the Debye length (m^{-1}), $k = (2.17 \times 10^{19} I)^{1/2}$; I is the ionic strength ($mol{\cdot}L^{-1}$); x is the distance between two particles (m); and A_H is the Hamaker constant of particles in water (J).

Aggregation kinetics and attachment efficiency of HA-TiO_2

Time-resolved dynamic light scattering (TRDLS) was used to measure the increase in the hydrodynamic diameter (D_h) as a function of time at 15-s time intervals in different solution chemistries. At the initial aggregation stage, the aggregation rate constant (k_a) for HA-TiO_2 was proportional with time (t) for an initial particle concentration(N_0) (Chen and Huang 2017a, b, Chen and Elimelech 2007, Chen et al. 2006, Liu et al. 2012, Yang-hsin et al. 2012).

$$k_a \propto \frac{1}{N_0}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0} \quad (2)$$

The first measurement point was considered to be at time zero (t = 0), until the time at which D_h (t) reaches 1.25 D_{h0}, where D_{h0} was 515 nm. In the few cases, especially at lower electrolyte concentrations, where aggregation was changed extremely slow, the final D_h at the end of the linear regime less than 5% of D_{h0} (Chen and Elimelech 2006). This approach was usually conducted to analyze the initial linear regime and aggregation rates.

Particle attachment efficiency (α) (i.e., inverse stability ratio, 1/W) was employed to quantify the aggregation kinetics of nanoparticles, and defined as the initial aggregation rate (k_a) constant of interest normalized by the rate constant derived under diffusion-limited (fast) aggregation conditions ($k_{a,\ fast}$) (Chen and Huang 2017a, b, Chen and Elimelech 2006, 2007, Liu et al. 2012, Miao et al. 2016, Yang-hsin et al. 2012).

$$\alpha = \frac{1}{W} = \frac{k_a}{k_{a,fast}} = \frac{\frac{1}{N_0}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0}}{\frac{1}{N_{0,fast}}\left(\frac{dD_h(t)}{dt}\right)_{t\to 0,fast}} \quad (3)$$

Eq. (3) is simplified by dropping N_0 since the initial HA-TiO_2 concentrations (N_0) are maintained constant at varying ionic strengths. α can be calculated from the ratio of the initial slope of linear regime at varying ionic strengths solution to the initial slope under diffusion-limit (fast) condition.

Results and discussion

FTIR spectra of HA and HA-TiO_2

The results of FTIR spectra for organic functional groups of HA and HA-TiO_2 surfaces are presented in Fig. 1. Different wave numbers had different assignment of adsorption bands (Li et al. 2004, Santos and Duarte 1998, Senesi et al. 2003). The common features of the HA and HA-TiO_2 included (a) the H-bonded OH stretching at 3450 cm^{-1}, (b) stretching vibration of conjugated C = C or H-bonded carbonyl C = O at 1625 cm^{-1}, O–H bending vibration of hydroxyl or carboxylic group, and C–O stretching of phenolic group at 1400 cm^{-1}. These features indicated that HA and HA-TiO_2 contained hydroxyl, phenolic, and carboxyl groups.

The different features of the HA and HA-TiO_2 included (a) a shoulder at 2925–2850 cm^{-1}, attributed to the C-H stretching of methyl or methylene groups of aliphatic chains, (b) the relative intensities of COOH stretching at 1625 cm^{-1} were stronger in the HA than in the HA-TiO_2 spectra, (c) a weak peak in the region of 1598–1509 cm^{-1} in the HA, generally attributed to aromatic C = C stretching, N-H deformation or C = N stretching of amides, but without in HA-TiO_2, (d) the O-H bending vibration of alcohol or carboxylic acids, and C-O stretching vibration

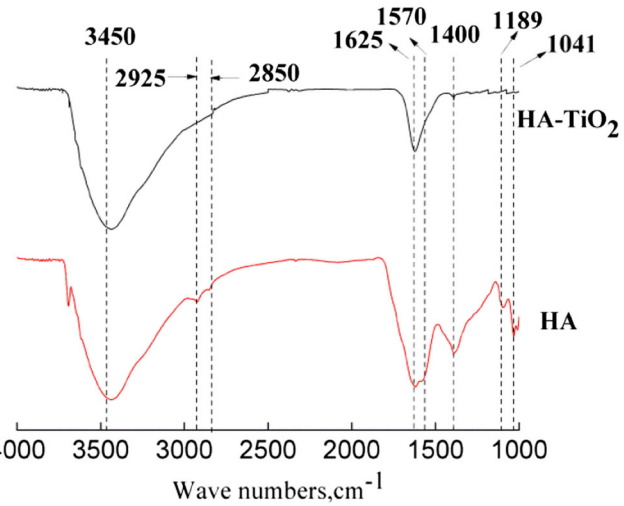

Fig. 1 FTIR spectra of HA and HA-TiO_2

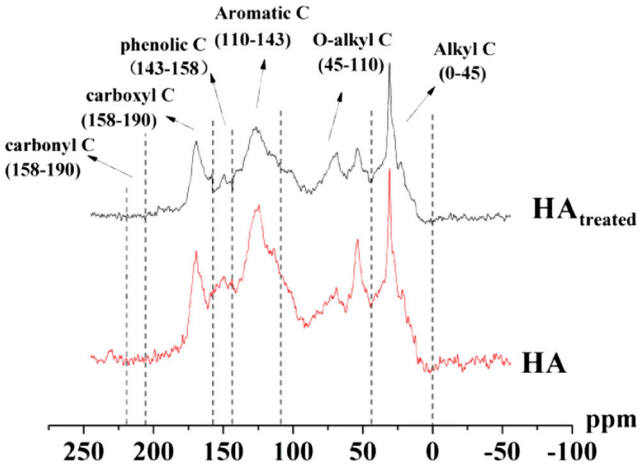

Fig. 2 Solid-state ^{13}C NRM spectra for two HAs

of phenols at 1400 cm^{-1}, whose relative intensities were strong in the HA spectrum but very weak in the HA-TiO_2 spectra, and (e) the weak peak at 1189 cm^{-1} and in the region of 1080–1030 cm^{-1}, respectively, due to the C-OH stretching of aliphatic OH and the C-O stretching of polysaccharide-like components or to the Si-O stretching of silicate impurities, which were only present in the spectra of HA. This suggested that the interactions of COOH, aliphatic OH groups, and phenolic group on the HA with nano-TiO_2 were significant, which was consistent with previous studies (Kang and Xing 2008, Yang et al. 2009, Yang and Xing 2009).

Solid-state ^{13}C NMR spectra

The solid-state ^{13}C NMR spectra are shown in Fig. 2 for two HA samples. Two HAs were obtained as original Ha and $HA_{treated}$. The peaks were generally assigned to aliphatic carbon (0–45 ppm), oxygenated aliphatic carbon (45–110 ppm), aromatic carbon (110–143 ppm), phenolic C (143–158 ppm), carboxylic carbon (158–190 ppm), and carbonyl carbon (190–220 ppm). The assigned peak areas are listed in Table 1. The ratios of the aliphatic carbon, phenolic C, and carboxylic carbon of HA were larger than that of $HA_{treated}$, which suggested that the COOH, aliphatic OH groups, and phenolic groups had the greatest contribution to the interaction of HA with nano-TiO_2. The $HA_{treated}$ contained higher contents of aromatic carbon and higher aromaticity compared with HA (Table 1), which shown $HA_{treated}$ had higher hydrophilicity. Li (Li et al. 2004) has pointed out that the fractions with lower molecular weight had more heterogeneous functional groups and higher contents of oxygen structure, whereas the higher molecular weight HA had lower contents of oxygen and aromatic structure. The higher molecular weight HA adsorbed by Nano-TiO_2 would keep the surface hydrophobic.

Aromaticity: aromatic C (110–158 ppm)/(aliphatic C (0–110 ppm) + aromatic C (110–158 ppm)).

The influence of Cd(II) concentration on the stability of HA-TiO_2 nanoparticles

The effect of Cd(II) on the sedimentation of HA-TiO_2 particles was investigated by measuring the time evolution of their absorbance change (Fig. 3 a). The aggregation of HA-TiO_2 particles increased with the increasing Cd(II) concentration, which was because Cd(II) neutralized the negative surface charge of HA-TiO_2 particles, causing the reduced repulsive force between particles and enhanced aggregation. The zeta potentials of HA-TiO_2 particles are listed in Fig. 3b. Compared with nano-TiO_2 particles, the HA-TiO_2 particles had higher negative zeta potential due to deprotonation of the acidic groups (mainly carboxylic and phenolic hydroxyl) from HA, which were preferentially adsorbed on the nano-TiO_2 surfaces (Tombacz et al. 2000). The zeta potential of HA-TiO_2 particles became less negative upon the addition of Cd(II) and caused reduction in repulsive force between the particles, which could be verified by calculating the DLVO interaction energy between particles (Fig. 3c).

The results of DLVO theory fitted on the net energy between HA-TiO_2 particles are shown in Fig. 3c. Before the addition of Cd(II), the HA-TiO_2 NPs had a high EDL repulsive energy as there was a high negative zeta potential on particles. Thus, the net energy barrier prevented the sedimentation of particles. The EDL repulsive energy between particles was reduced with the addition of Cd(II), which might be due to the neutralization of negative surface charge on the HA-TiO_2 particles by electrostatic attraction of Cd(II) and reduction of the repulsive force between particles. Moreover, Cd(II) might bridge through to form TiO_2-Cd-HA ternary complexes in the particles and then promote aggregation, which was similar with the literatures (Jia et al. 2008). Chen had reported that Cd(II) could be bonded with the acidic groups (mainly carboxylic and phenolic hydroxyl) of HA coated onto nano-TiO_2 through covalent bonds and form TiO_2-HA-Cd complexes (Chen et al. 2012). To further investigate the effects of Cd(II) on the aggregation of the HA-TiO_2 particles, TRDLS was employed to gain insight into the aggregation kinetics in different

Table 1 Structural group analysis from solid-state ^{13}C NMR spectra for three HAs

Sample	Distribution of C chemical shift (ppm), %						Aromaticity
	0–45	45–110	110–143	143–158	158–190	190–220	
HA	22.73	25.48	21.60	8.87	14.43	6.89	38.1
$HA_{treated}$	22.37	26.64	24.85	7.15	13.89	5.10	39.4

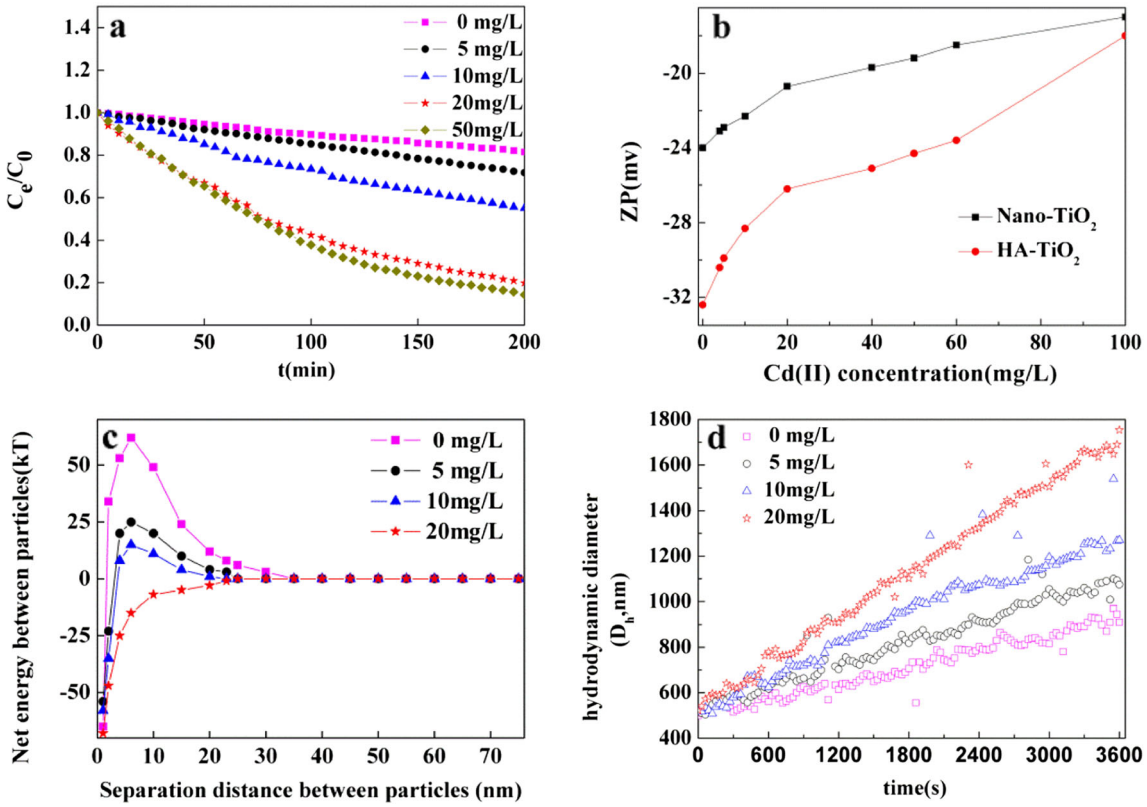

Fig. 3 The influence of Cd(II) concentration on the stability of nanoparticles (**a** sedimentation, **b** zeta potential, **c** DLVO interaction energy between particles, and **d** aggregation profiles)

Cd(II) concentrations (Fig. 3d). The aggregation rate of the nanoparticles increased with Cd(II) concentration, which might be related with the reduction of electrostatic repulsion. This was consistent with the trend from DLVO predictions in Fig. 3c. Besides, the form of TiO_2-HA-Cd or/and TiO_2-Cd-HA ternary complex might also increase the aggregation kinetics of the nanoparticles (Chen et al. 2012, Jia et al. 2008, Wu et al. 2012).

The influence of pH on the stability of HA-TiO_2 nanoparticles

Sedimentation studies of HA-TiO_2 as a function of pH are shown in Fig. 4a. The particles all gradually gathered and precipitated at three pH values. The sedimentation rate of HA-TiO_2 particles was the highest at pH 2, which was closed to the PZC of particles (Fig. 4b, pH_{PZC} = 2.9) where a marked decrease in the electrostatic repulsion between particles occurred (Thio et al. 2011). The sedimentation rate of HA-TiO_2 particles decreased with increasing pH, which might be related to the reduced zeta potential of HA-TiO_2 particles (Fig. 4b). Our results were consistent with those of previous studies, which reported that the electrostatic repulsion decreased with increasing pH (Godinez and Darnault 2011). At the same pH values, Cd(II) neutralized the negative surface charge that HA imparted to nano-TiO_2 particles, resulting in the decrease of repulsive force and contributing to the sedimentation of HA-TiO_2 particles. In addition, more acidic groups (mainly carboxylic and phenolic hydroxyl) were dissociated at higher pH, providing more complexation sites for Cd(II) so that more TiO_2-HA-Cd or/and TiO_2-Cd-HA ternary complexes might be formed (Chang et al. 2015, Jia et al. 2008, Wu et al. 2012), which promoted the aggregation of HA-TiO_2 particles.

The influence of pH on the stability of HA-TiO_2 was examined by measuring its zeta potentials at different pH conditions (Fig. 4b). The negative charge on the particles was screened at lower solution pH due to dissociation of more acidic groups on HA-TiO_2, whereby the isoelectric point of HA-TiO_2 NPs was determined to be approximately pH 2.9. The acidity constants of HA were given as 4–6 for pK_{a1}(due to carboxyl groups) and 8–10 for pK_{a2}(due to phenolic groups) in the literature (Hizal and Apak 2006, Martinez et al. 2002, Ren et al. 2013, Xu et al. 2007, Zhou et al. 2005). At the same pH, the zeta potentials increased with the increasing Cd(II) concentration, which could be explained by two predominant factors. Firstly, when pH was below 2.9, the surface of the adsorbent was surrounded by H^+ ions such that the increase in competition between H^+ and Cd(II) for the limited active surface sites led to a lower adsorption percentage as the covalent bonds acted as an important role in the adsorption process. At pH beyond 2.9, the HA-TiO_2 surface was deprotonated so there was an electrostatic attraction between HA-TiO_2 and Cd(II) leading to a higher adsorption percentage (Abate and

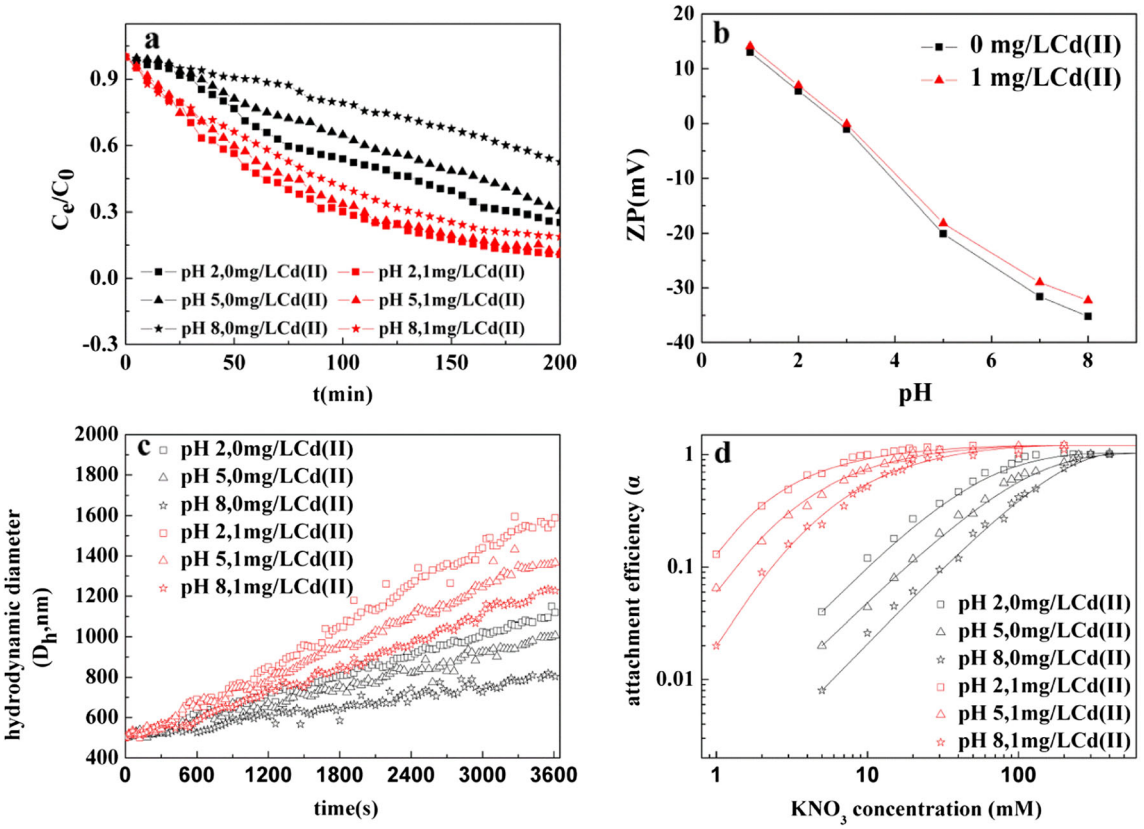

Fig. 4 The influence of pH on the stability of nanoparticles (**a** sedimentation, **b** zeta potential, **c** aggregation profiles, and **d** attachment efficiencies)

Masini 2005, Bayazit and Inci 2014, Wang et al. 2013). Secondly, the conformations of HA coated on nano-TiO_2 was condensed at higher pH, which resulted in more available adsorption sites exposed for Cd(II) (Chen et al. 2012, He et al. 2016). The negative charge of HA-TiO_2 particles was decreased upon the addition of Cd(II), resulting in weaker repulsive force between the particles and thus faster aggregation.

In Fig. 4c, the aggregation kinetics of HA-TiO_2 NPs decreased with the increasing pH. At the same pH, the aggregation kinetics of HA-TiO_2 NPs were higher in the presence of Cd(II). The pH effects on the attachment efficiencies of HA-TiO_2 NPs as a function of electrolyte concentration are quantitatively shown in Fig. 4d. At pH 2, 5, and 8, the attachment efficiencies were 0.58, 0.37, and 0.22 at 50 mMKNO_3 concentration, respectively; the critical coagulation concentrations (CCCs) were 123.6, 158, and 263.9-mM KNO_3 in the absence of Cd(II). In the presence of Cd(II), however, the attachment efficiencies were all about 1 and the respective CCCs were15.6, 19.2, and 27.4-mM KNO_3. The increase in stability of HA-TiO_2 NPs with pH was consistent with prior reports for negatively charged particles such as fullerene NPs (Brant et al. 2005, Ma and Bouchard 2009). In addition, Cd(II) might reduce the stability of HA-TiO_2 NPs at the same pH by reducing the electrostatic repulsion between particles and forming TiO_2-HA-Cd or/and TiO_2-Cd-HA ternary complexes (Chen et al. 2012, Wu et al. 2012).

The influence of ionic strength on the stability of HA-TiO_2 nanoparticles

Different sedimentation curves for HA-TiO_2 particles are presented in Fig. 5a. The sedimentation rate of HA-TiO_2 particles increased with the KNO_3 concentration. In the absence of Cd(II), the concentrations of suspended particles decreased by only approximately 30% after 200 min at relatively lower ionic environment. When Cd(II) concentration was 1 mg/L, the 20-mM solution decreased the suspended particles concentration by more than 80% in 200 min. This may be explained by the changed zeta potentials of particles which affected the DLVO interaction energy between particles as discussed later in this paper (Fig. 5c).

The zeta potentials of HA-TiO_2 particles are presented in Fig. 5b. The zeta potential of HA-TiO_2 particles increased with the KNO_3 concentration. The EDL was compressed at higher KNO_3 concentration, leading to more counter ion in the EDL that neutralized the negative surface charge on particles. Thus, the repulsive force between particles was weakened and resulted in sedimentation of HA-TiO_2 particles (Zhang et al. 2008, Zhou and Keller 2010). In addition, the zeta potential of HA-TiO_2 particles increased when Cd(II) concentration increased to 1 mg/L at the same KNO_3 concentration. This was probably due to the electrostatic adsorption between Cd(II) and HA-TiO_2 (Chen et al. 2012). It was reported that the compression of the diffusive EDL and the reduction of

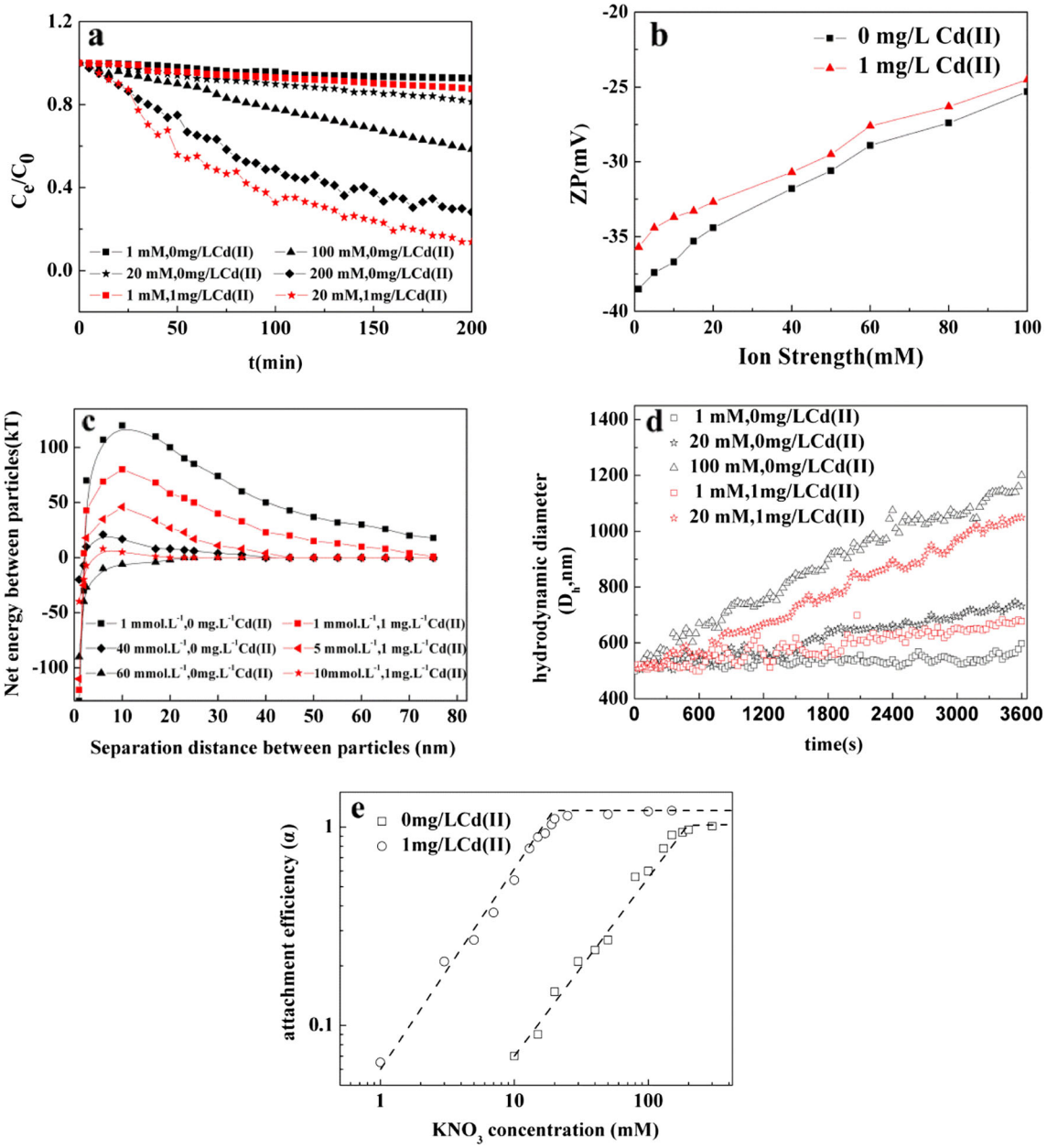

Fig. 5 The influence of ionic strength on the stability of nanoparticles (**a** sedimentation, **b** zeta potential, **c** DLVO interaction energy between particles, **d** aggregation profiles, and **e** attachment efficiencies)

repulsion forces at increasing salinity would help to facilitate the formation of covalent bonds between the acidic groups on HA and Cd(II) (Filius et al. 2000). Cd(II) could increase the sedimentation rate of the nanoparticles by reducing the repulsive force between particles and forming TiO_2-HA-Cd or/and TiO_2-Cd-HA ternary complexes with HA-TiO_2 (Chen et al. 2012, Jia et al. 2008, Wu et al. 2012). Figure 5c shows the DLVO calculations for HA-TiO_2 particles at different KNO_3 concentrations. The EDL repulsive energy reduced as the KNO_3 concentration increased, which could promote the aggregation of particles. In the absence of Cd(II), the EDL repulsive energy was relatively small at 200 mM of KNO_3 and the HA-TiO_2 particles were susceptible to aggregation. The addition of Cd(II) at 20 mM of KNO_3 completely screened the net energy barrier between the nanoparticles, leading to fast sedimentation of HA-TiO_2 particles. This indicated that Cd(II) could decrease the stability of nanoparticles by lowering the net energy barriers between particles.

The effect of ionic strength on the aggregation rate of HA-TiO_2 particles is presented in Fig. 5d. The increased KNO_3 concentration resulted in the faster aggregation of HA-TiO_2, which could be attributed to the decreased electrostatic repulsion as was consistent with the trend from DLVO predictions in Fig. 5c (Chen and Elimelech 2006, 2009). Moreover, at higher

KNO_3 concentration, the increased electrolyte concentration did not further increase the aggregation rate of HA-TiO_2 particles because the energy barrier was completely eliminated in this diffusion-limited aggregation regime (He et al. 2008). At the same KNO_3 concentration, the aggregation kinetics of HA-TiO_2 were higher in the presence of Cd(II), which was relevant to the weaker electrostatic repulsion due to the adsorbed Cd(II) on the HA-TiO_2 particles (Chen and Elimelech 2009, Chen et al. 2012). The attachment efficiencies at different KNO_3 concentrations are calculated in Fig. 5e. The CCCs were 190.8 mM in the absence of Cd(II) and 19.4-mM KNO_3 in the presence of Cd(II), indicating that Cd(II) could reduce the stability of HA-TiO_2. As has been widely reported in other literature, the aggregation behavior of HA-TiO_2 was consistent with the DLVO theory (Chen and Elimelech 2007, Chen et al. 2006).

Conclusion

In the present study, the influence of Cd(II) on the stability of HA-TiO_2 particles under the different environmental conditions were investigated. The aggregation behavior of HA-TiO_2 particles followed the classic DLVO theory, allowing for construction of predictive models for quantifying the transport of HA-TiO_2 NPs in an aquatic environment. The results showed that the stability of HA-TiO_2 NPs decreased with increasing Cd(II) concentrations, which was due to the formation of TiO_2-HA-Cd or/and TiO_2-Cd-HA complex with HA coated onto TiO_2 nanoparticles and the reduced energy barrier between the particles. In the absence of Cd(II), the stability of HA-TiO_2 increased with pH from 2 to 8, where the CCC increased from 58.6 to 170.9-mM KNO_3. This was possibly attributed to the deprotonation of functional groups from particle surface and the increased repulsive force between the particles. At the same pH, Cd(II) could promote the aggregation of HA-TiO_2 NPs, as CCCs were > 50-mM KNO_3 in the presence of Cd(II) and were < 30-mM KNO_3 in the absence of Cd(II). The stability of HA-TiO_2 NPs decreased at higher KNO_3 concentrations due to compression of the EDL and lowering of the energy barrier between the particles. The Cd(II) could reduce the stability of HA-TiO_2 NPs even at low KNO_3 concentrations, as was evidenced by the decrease in the scattered light intensity and the decreased CCC in the presence of Cd(II). The significant reduction of HA-TiO_2 stability by Cd(II) implied that Cd(II) could alter the environmental behavior of HA-TiO_2 NPs. Meanwhile, the bioavailability and toxicity of heavy metals might also be affected in real aqueous systems with both HA and nano-TiO_2. Further research should focus on the bioavailability and toxicity of toxic pollutants to aqueous organisms with the coexistence of HA and NPs.

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