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Photocatalytic performance and dispersion stability of nanodispersed TiO₂ hydrosol in electrolyte solutions with different cations

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ABSTRACT

The existence of electrolytes in aquatic environment on the photocatalytic performance and coagulation of nanodispersed TiO₂ hydrosol and the corresponding photocatalytic alteration were investigated by studying cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, and Al³⁺). The photocatalysis reactions of nano TiO₂ with different dosages of electrolytes were measured by monitoring the degradation of Rhodamine B (RhB) under ultraviolet A (UV-A) irradiation over time. The results showed that the photocatalytic performance of TiO₂ was improved by the presence of Al³⁺, while the performance was impaired by the other tested cations. The negative influences of divalent ions on the photocatalytic performance of TiO₂ were more significant than monovalent ions. The TiO₂ sol dispersed stable at nano scale at low concentration of electrolyte (<0.01 mol/L) with slight change of pH, and coagulated into micro sizes at high concentration of electrolytes (>0.1 mol/L) with larger increase or decrease of pH. The positive effects of Al³⁺ on the photodegradation rate of RhB might relate to the strong hydrolytic action of Al³⁺ in aquatic solutions. The photocatalytic processes of TiO₂ in the presence of all ions followed the Langmuir-Hinshelwood model, and the reaction kinetic constant was increased with the decrease of pH caused by different cations. These work suggested a new perspective about the relationship between coagulation and photocatalytic performance of TiO₂ hydrosols in electrolyte with hydrolysable cations, which demonstrated that TiO₂ hydrosols may be suitable as photocatalysts in aquatic environments.

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Introduction

The photocatalytic reaction is one of the most widely studied topics in the fine chemical industry, building materials, water and air treatment, sanitation, environmental protection, automobile industry, etc. (Bahnmann, 2004; Chen and Poon, 2009;

Hashimoto et al., 2005; Dincer, 2000; Jing et al., 2010; Malato et al., 2009; Mills and Lee, 2002; Spasiano et al., 2013). Among the photocatalysts, titanium dioxide (TiO₂) particles have received the greatest attention. The multi-faceted functional properties of TiO₂, such as its chemical and thermal stability and strong mechanical properties have promoted its wide

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application in various fields like water treatment, air purification, etc. (Chong et al., 2010). Nanodispersed TiO_2 hydrosols are known to contain mainly anatase nano particles and are aggregation-stable even at high concentrations of dispersed phase and electrolytes mainly refer to strong acid solutions, which means the surface charge of nanodispersed TiO_2 hydrosol particles is normally positive (Abbas et al., 2011; Alphonse et al., 2010; Ghenne et al., 1998; Pavlova-Verevkin et al., 2003, 2005; Santacesaria et al., 1986). In the field of photocatalytic degradation of organic pollutants, hydrosol catalysts can be easily separated, collected and re-dispersed for continuous reuse because of its sensitivity to pH value and electrolyte strength of medium (Ghenne et al., 1998; Leroy et al., 2011; Pavlova-Verevkin et al., 2003, 2005, 2007; Santacesaria et al., 1986). Moreover, some research results show nanodispersed TiO_2 hydrosols exhibit high photochemical reactivity even superior to nano TiO_2 powders (Liu et al., 2008; Yu et al., 2010).

However, agglomeration and coagulation are the main physicochemical processes affecting the photocatalytic performance of nanodispersed TiO_2 hydrosols or nano powders (Brunelli et al., 2013). The cations like Fe^{3+} (Wang et al., 2008) would improve the efficiency of photocatalytic oxidation of TiO_2 hydrosols in solutions by influencing the complex hydroxyl groups bond between TiO_2 surface and Fe^{3+} . Volkova et al. (2012, 2010) had studied the coagulation properties and fractionation of TiO_2 hydrosol in haloid salts solutions, and the results supported that the sol stability was strongly affected by the coion (refers to cation) nature and valence.

Compared with nanodispersed TiO_2 hydrosols, the stability of nano TiO_2 powders influenced by inorganic cations in aquatic environments (Chen et al., 2012, 1997; Fu et al., 2005; Hotze et al., 2010; Terzian et al., 1991; Yang et al., 2010) has been studied relatively comprehensive. Common cations such as Na^+ (French et al., 2009), Ca^{2+} (French et al., 2009; Zhang et al., 2009) and Mg^{2+} (Loosli et al., 2015) were found to enhance agglomeration and sedimentation of nano TiO_2 particles by absorbing on the surface of particles surfaces, and the enhancement of divalent cations were greater because of the higher negative charge. For nano TiO_2 powders, aluminum salts, like $\text{Al}_2(\text{SO}_4)_3$, Al_2O_3 , were usually used as the coagulants to remove the particles during the primary water treatment (Honda et al., 2014; Xu et al., 2014). Some heavy cations, like Cu^{2+} (Đukić et al., 2015; Kanna et al., 2005), Pb^{2+} (Đukić et al., 2015; Islam et al., 2010; Kanna et al., 2005), Fe^{3+} (Kanna et al., 2005), Mn^{2+} (Đukić et al., 2015; Kanna et al., 2005) and Zn^{2+} (Đukić et al., 2015; Kanna et al., 2005), can absorb on the surface of nano TiO_2 powders in aquatic solutions, because of the deprotonated surface hydroxyls yield negatively-charged surface of nano TiO_2 powders. Due to the increasing application of TiO_2 catalyst for obtaining functional cement-based materials, the influences of Portland cement-like ionic environment on the surface chemical of nano TiO_2 powders had been studied in some researches (Folli et al., 2010; Yousefi et al., 2013).

Since the synthesis processes of nanodispersed TiO_2 hydrosols and nano TiO_2 powders are different, their phase, disperse composition and condition are totally different (Pavlova-Verevkin et al., 2003). For example, heat treatment is a requirement for synthesizing crystallized nano TiO_2 powders by sol-gel method, which causes the irreversible aggregation of particles. Namely, it is difficult to obtain nanodispersed systems

by re-dispersing nano TiO_2 powders because of the initial aggregation of particles. Moreover, the particles surfaces in nano dispersed TiO_2 hydrosols are normally positive, while the particle surfaces in nano TiO_2 powders aqueous suspensions are normally negative. Thus, the interaction mechanism between the cations and TiO_2 particles studied in literatures via nano TiO_2 powders can hardly explain the influence of cations to TiO_2 particles in nanodispersed hydrosol systems. In addition, few studies focus on the photochemical reactivity of nanodispersed TiO_2 hydrosols in aqueous solutions contaminated by cations with different valence. According to literature (Volkova et al., 2012, 2010; Zhang et al., 2018), the effect of certain cations on the coagulation of TiO_2 hydrosol particles is very pronounced, and the effect is closely related to the valence of cations and the pH of the aquatic systems.

The goal of this study was to investigate the probable relationship between photocatalytic property and stability of TiO_2 hydrosol with different kinds of inorganic cations. Ghenne et al. (1998) reported that in acidic media, the critical coagulation concentration of anions of NO_3^- and Cl^- was nearly 0.5 mol/L at pH = 2, and the critical coagulation concentration of anions decreased with the increase of pH values. Budarz et al. (2017) showed that the adverse impacts of NO_3^- on the photocatalytic property of nano TiO_2 are less than that of Cl^- in aqueous solutions. Therefore, in this work, the aqueous solutions of Na^+ , K^+ , Ca^{2+} , Mg^{2+} and Al^{3+} with a concentration of 0.005–0.5 mol/L were chosen as the tested cations, and NO_3^- was selected as the anion in this study. The photocatalytic activity of nanodispersed TiO_2 hydrosol was assessed by the photodegradation performance on Rhodamine B (RhB). The stability of particles in hydrosol over time was evaluated by the particle size and zeta potential values.

1. Materials and methods

1.1. Reagents and solutions

NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ and RhB were analytical pure commercial reagents and applied without further purification. Solutions of salts (0.005, 0.1, and 0.5 mol/L) were prepared with deionized (DI) water. A 30 mg/L RhB solution was prepared as the target pollutant in the test. The solid content of the commercial nano anatase TiO_2 was 10% in this hydrosol, the pH was 1.17 at 20°C and the mean particle size was 30.3 nm. In order to purify the TiO_2 hydrosol, the commercial TiO_2 hydrosol was filtrated by an ultrafiltration system for 10 cycles, and the 80 mm 100 kDa ultrafiltration membranes were used to remove the impurities. After purification, the pH of hydrosol was 2.32 at 20°C and the mean particle size was 37 nm. The detail method of TiO_2 purification can be find in supporting information.

1.2. Degradation experiments

The photocatalytic performance of TiO_2 was evaluated by examining the degradation of 50 mL solution with the initial RhB concentration of 30 mg/L under ultraviolet (UV) illumination. A 400 W ultraviolet metal halogen lamp (UV-400, Shanghai Libi Company of Vacuum Technique, China) was used

as the source of the UV irradiation light. The UV lamp was placed outside the reactor and the distance between the lamp and the reactor was 10 cm, the wavelength (λ) of the ultraviolet lamp ranges from 253.7 to 600 nm (centered at $\lambda = 365$ nm). The intensity of the UV light was 34.9 mW/cm^2 . The 2 g/L TiO_2 and 30 mg/L RhB solution were put into the reactor and mixed with a magnetic stirrer at 400 r/min during the test. The UV lamp was turned on after the 30 min adsorption–desorption equilibrium at dark. The UV light and the reactor were both inside the intelligent artificial climate box (PRX-350C, Saifu Experimental Apparatus Technology Company, China), by which the test temperature was controlled at $25 \pm 2^\circ\text{C}$. A 4.5 mL aliquot was sampled every 5 min ; it was centrifuged for 5 min at $10,000 \text{ r/min}$ and then filtered through a nylon syringe membrane filter with pore size of $0.45 \mu\text{m}$ (BS-QT-014, Biosharp, Japan) prior to analysis. Variations in the concentration of RhB in each degraded solution were monitored by UV–visible spectroscopy (UV–Vis) (UV-2600 spectrophotometer, Shimadzu, Japan). There are two different photodegradation processes of RhB, photobleaching and N-deethylation (Wu et al., 1998). With the increased radiation time, the N-deethylation of RhB causes the blue shift in the maximum absorption of the dye solution, and then absorption peak disappears rapidly after the N-deethylation (Qu et al., 1998). The photocatalytic oxidation rate of TiO_2 can be represented by the absorption of RhB at 554 nm , and can be calculated by the following formula (Kansal et al., 2007):

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where, R is the photo-degradation rate of RhB, $C_0 \text{ (g/L)}$ is the initial absorption of RhB at 554 nm before the illumination, and $C_t \text{ (g/L)}$ is the absorption of RhB at 554 nm at different illumination time.

1.3. Dispersion stability

Laser particle sizer (Microtrac S3500, Microtrac Inc., USA) was used to measure nano TiO_2 aggregate size. Time-resolved size measurements, reported in terms of median diameter (D50), were taken every 2 min for 30 min . To characterize the dispersion stability of nano TiO_2 , zeta potential of the Nanoparticles was measured by electroacoustic zeta potentiometer at each test time point (DT-310, Dispersion Technology Instrument, USA).

2. Results and discussion

2.1. Effect of cations on the photocatalytic degradation

Fig. 1 shows the photo-degradation rate of RhB in all the solutions over time. It can be seen that the degradation rate of pure TiO_2 hydrosol was 86.06% during the first 15 min , which was higher than that of TiO_2 in monovalent and bivalent cationic solutions. After 20 min illuminating, the photo-degradation rates of RhB in all electrolyte solutions were very close and the rate values were higher than 95% . The photo-degradation rate of RhB decreased with the increase of monovalent and bivalent cation contents. But in the $\text{Al}(\text{NO}_3)_3$ solutions, the photo-degradation rate showed different results.

Fig. 1 – Photodegradation rate of Rhodamine B (RhB) in solution within 30 min at (a) 0.005 mol/L , (b) 0.1 mol/L and (c) 0.5 mol/L cations.

The photo-degradation rate of RhB increased with the increase of $\text{Al}(\text{NO}_3)_3$ contents, and the rate values were higher than that in pure TiO_2 hydrosol after 10 min illumination.

2.2. Coagulation of TiO_2 particles

Due to TiO_2 hydrosol consisting of anatase nanoparticles are stable to disperse at high concentration and certain electrolytes and certain pH range, the stability of TiO_2 hydrosols caused by

Fig. 2 – Median diameter (D50) of TiO_2 particles in electrolytes over 30 min in the presence of NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, and $\text{Al}(\text{NO}_3)_3$.

electrolytes has been studied both experimentally and theoretically (Pavlova-Verevkin et al., 2007, 2003; Volkova et al., 2012, 2010). In most of studies, the optical density increment is chosen as the evaluation index for the stability of TiO_2 . Moreover, the photocatalytic oxidation process is related to the production and annihilation of electrons and holes, which are influenced by the particle size of TiO_2 in electrolyte solutions. To represent the stability of TiO_2 hydrosols in electrolytes intuitively, the particle sizes during coagulation process are measured in this work.

Fig. 2 shows D50 of the nano TiO_2 in different electrolytes over 30 min. In the presence of NaNO_3 and KNO_3 , the particle

size of nano TiO_2 was comparable with the initial nano TiO_2 size at 0.005 mol/L. The aggregated particle size increased to 2.0 and 7.0 μm at 0.1 and 0.5 mol/L, respectively. In the presence of $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$, the particle sizes of nano TiO_2 were also comparable with the initial nano TiO_2 size at 0.005 mol/L, then the particle sizes increased to around 5.0 and 11.0 μm at 0.1 and 0.5 mol/L, respectively. In the presence of $\text{Al}(\text{NO}_3)_3$, the particle size of nano TiO_2 was comparable with the initial Nano TiO_2 size at 0.005 mol/L, and the particle size increased and stayed around 0.5 and 3.0 μm at 0.1 and 0.5 mol/L, respectively. These results were consistent with the results in literature (Volkova et al., 2012) that the optical density of TiO_2 sols remains

unchanged at low concentration ($\leq 10^{-2}$ mol/L) of coagulants (haloids) and increase begins from the coagulants concentration of 0.03 mol/L. The ion-electrostatic repulsive forces between TiO_2 particles contributed to the stability of sols in the low concentrations.

Significantly, the aggregate sizes of sols in $\text{Al}(\text{NO}_3)_3$ solution were obviously smaller than that in $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ solutions at 0.1 and 0.5 mol/L. In addition, the aggregate sizes in 0.5 mol/L $\text{Al}(\text{NO}_3)_3$ solution were smaller than 4.0 μm , while the sizes in $\text{Ca}(\text{NO}_3)_2$ solution were between 4.0 and 11.0 μm and in $\text{Mg}(\text{NO}_3)_2$ solution were between 12.0 and 18.0 μm .

2.3. Zeta potential of TiO_2 and pH in solutions

Zeta potential is a physicochemical parameter of particular importance in describing the ion adsorption and electrostatic interactions between charged particles (Leroy et al., 2011), which reflect the dispersion-agglomeration properties of nanoparticles in aqueous media. Since the pH of solutions significantly affects the stability of TiO_2 hydrosols, monitoring the pH changing of solutions over time is helpful for evaluating the stability of sols.

The zeta potential of nano TiO_2 and the pH changes of electrolytes are shown in Fig. 3. It can be seen that the zeta potential of nano TiO_2 in the control group was about 60 mV, and the pH value was about 3.0. When the electrolytes content was 0.005 mol/L, the zeta potential of TiO_2 in NaNO_3 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ solutions decreased to around 30, 41, 27, 37 and 43 mV, respectively. When the salt content was 0.1 mol/L, the zeta potential of TiO_2 in NaNO_3 , KNO_3 , $\text{Mg}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$ and $\text{Al}(\text{NO}_3)_3$ solutions increased by 85.94%, 35.15%, 60.17%, 89.85% and 0.91% of the initial value, respectively. When the salt content was 0.5 mol/L, the zeta potentials of that were grown by 180.56%, 55.63%, 133.68%, 38.91%, and 4.91% of the initial value, respectively. These results revealed that in the presence of Al^{3+} , the zeta potential of TiO_2 did not change significantly over time that meant the interaction between nanoparticles was relatively limited.

It is clear that the pH values of solutions during the 30 min test were stable in each cation contents. As to $\text{Al}(\text{NO}_3)_3$ solutions, the pH of the solutions decreased with the contents of aluminum ion and the zeta potential of TiO_2 was relatively stable. In the presence of Na^+ and K^+ , when the electrolytes contents increased from 0 to 0.5 mol/L, Fig. 3a and b shows that the pH values of solutions increased from 3.0 to about 3.6.

Fig. 3 – Zeta potential of TiO_2 and the pH of solution over 30 min in the presence of (a) NaNO_3 , (b) KNO_3 , (c) $\text{Ca}(\text{NO}_3)_2$, (d) $\text{Mg}(\text{NO}_3)_2$, (e) $\text{Al}(\text{NO}_3)_3$.

Fig. 3c and d shows that in the presence of Ca^{2+} and Mg^{2+} , the pH values increased from 3.0 to about 3.6 when the metal ion contents increased from 0 to 0.1 mol/L, then the pH values decreased slightly when the metal ions content increased to 0.5 mol/L. As to Al^{3+} , Fig. 3e shows that the pH of solutions decreased obviously from about 3.0 to about 2.0, when the electrolyte contents increased from 0 to 0.5 mol/L.

It is worth mentioning that in the pH range of 2.0–4.0, according to the study of Ghenné et al. (1998), the critical coagulation concentration of NO_3^- affecting TiO_2 hydrosol is less than 0.5 mol/L. However, in the presence of 0.5 mol/L $\text{Al}(\text{NO}_3)_3$, the D50 of TiO_2 particles were not larger than those in other electrolyte solutions and the photo-degradation of RhB is the highest. As a result, the influence of Al^{3+} on the photocatalytic performance and stability in aquatic system needs further discussion.

2.4. Relationship between photocatalysis, coagulation of TiO_2 hydrosol and cations

2.4.1. Explanations in terms of photocatalytic kinetics

According to previous research (Chen and Ray, 1998; Galindo et al., 2001; Lee et al., 1999; Poullos and Aetopoulou, 1999; Poullos and Tsachpinis, 1999), the influence of the initial concentration of the solute on the photocatalytic degradation rate of most organic compounds is described by a pseudo-first-order kinetics, which is rationalized in terms of the Langmuir–Hinshelwood model (LH model), modified to accommodate reactions occurring at a solid–liquid interface (Sauer et al., 2002).

Fig. 4 shows the reaction rate kinetics in different cationic nitrate solutions. The slope values of the fitting equations were the k_{app} (the apparent first-order rate constant) that are shown in Table 1. From Fig. 4, the LH model fits the experimental data very well ($R^2 > 0.950$). The high R^2 values indicate that the LH model is appropriate for describing the RhB oxidation in cationic nitrate solutions, which meant the reaction rate was mainly controlled by the concentration of the reactants rather than the irradiation intensity or time. From Table 1, it can be seen that the k_{app} of the control group was 0.158 min^{-1} , and the k_{app} values decreased with the contents of cations except for the aluminum. The k_{app} values for sodium and potassium were similar, and the k_{app} values for magnesium at high contents (0.1 and 0.5 mol/L) were higher than that for calcium. Fig. 4e shows that the k_{app} values at 0.005, 0.1 and 0.5 mol/L were 0.178, 0.194 and 0.215 min^{-1} respectively, and indicated a greater reaction rate of the photo-degradation process.

As seen from Table 2, the k_{app} reported in literatures showed that the k_{app} for nano TiO_2 powders degradation of RhB was lower than 0.1 min^{-1} , even for some surface modified nano TiO_2 powders. In this study, the k_{app} of TiO_2 hydrosol (10 wt.%) without cations was 0.158 min^{-1} , which was more than 10 times higher than the results in literatures mentioned in Table 2. The re-dispersion of nano TiO_2 powders in aqueous solution is still a thorny problem. There is no doubt that the nano TiO_2 particles were agglomerated irreversibly during the drying process of producing nano TiO_2 powders. This instinctive agglomeration is one of the main reasons for the low photocatalytic performance of nano TiO_2 powders in aquatic

environments. According to Fig. 2, the D50 of TiO_2 in control group was nearly 35 nm during the irradiation in 30 min, the better dispersity in aqueous solution of TiO_2 hydrosol tested in this study could explain the higher k_{app} and shorter half period of RhB degradation.

According to the test results about D50 of TiO_2 particles and degradation of RhB in this study, these explanations can partly interpret the inhibition of Na^+ , K^+ , Ca^{2+} and Mg^{2+} . Due to the aggregation of TiO_2 particles in the presence of these cations, the photocatalytic activity of TiO_2 was hindered and the degradation of RhB was decreased. However, these explanations cannot explain the acceleration effect of Al^{3+} on the degradation of RhB, because the agglomeration is also measured when the content of Al^{3+} is higher than 0.1 mol/L.

2.4.2. Explanations in terms of spectroscopy

As reported in the literature (Ortelli et al., 2014), the degradation mechanism of RhB caused by nano TiO_2 is proposed as two ways, one way is de-ethylation process that has been reported in other studies (Qu et al., 1998; Wu et al., 1998), another way is the degradation process of the chromophore structure. The changing trend of UV–Vis spectra of RhB in five kinds of electrolyte was similar in the test, to reduce the space, the groups in $\text{Al}(\text{NO}_3)_3$ solutions were taken as the analysis example. Other spectra images can be found in Appendix A. Supplementary data.

The UV–Vis absorption spectra of nano TiO_2 powder degrading RhB have been studied in several reports (Lei et al., 2012; Wahyuningsih et al., 2014; Wang and Zhang, 2011; Wang et al., 2009; Zhao et al., 1998; Zhu et al., 2014). In these literatures, the absorbing peak values at the range of 230–270 nm in the spectra of nano TiO_2 powder degrading RhB were smaller than the peak values at 554 nm, and there was only one peak at the range of 200–350 nm. While, in this study, Fig. 5 shows the UV–Vis spectra of RhB collected during 30 min of irradiation at $\text{Al}(\text{NO}_3)_3$ solutions. De-ethylation of RhB causes a blue shift of the main absorption band at visible light range, as can be seen in Fig. 5, the main absorption spectra of RhB decreased rapidly with the blue shift over irradiation time. The main absorption band at 554 nm is due to the chromophore structure, like $\text{C}=\text{N}$ and $\text{C}=\text{O}$, of RhB, and the wide and strong absorption band in 230–270 nm is due to the benzene rings of RhB. The results showed that in the relatively low concentration ($\leq 0.01 \text{ mol/L}$) of electrolyte, the absorption peak of RhB was wide in ultraviolet range indicating the typical benzene rings absorption peak in polar solvent for example water. When the concentration of electrolyte was high ($\geq 0.01 \text{ mol/L}$), beside the sharply decrease of absorption at 554 nm and the blue shift, the absorption peak of RhB in ultraviolet range was divided into two peaks near 230 and 290 nm that were the typical absorption peaks of pyrocatechol salts (Tyson and Martell, 1968). These phenomenon means the chromophore structure in RhB had been destroyed in electrolyte with high concentration.

The presence of cations and the positive surface of TiO_2 particles might lead to the obvious different results between this study and literatures mentioned before. As shown in Fig. 5, there were still absorbing peaks near 290 nm

Fig. 4 – Reaction rate kinetics at different contents in the presence of (a) NaNO_3 , (b) KNO_3 , (c) $\text{Ca}(\text{NO}_3)_2$, (d) $\text{Mg}(\text{NO}_3)_2$, and (e) $\text{Al}(\text{NO}_3)_3$. R^2 : the coefficients of determination; C_0 (g/L): the initial absorption of RhB at 554 nm before the illumination; C_t (g/L): the absorption of RhB at 554 nm at different illumination time.

when the UV light was turned off with high content (>0.01 mol/L) of the Al^{3+} . RhB is a typical ionic dye (Das and Bhattacharyya, 2014), in aqueous solution, RhB molecule has both anionic group COO^- , cationic $\text{N}(\text{C}_2\text{H}_5)_2^+$, and Cl^- (one RhB molecule contains one Cl^-). Without the disturbance of impurity cations, RhB molecule may absorb on the surface of TiO_2 particles in hydrosol by COO^- and Cl^- via Coulomb force. However, in the presence of electrolytes

with high content (>0.01 mol/L), the cations may partly break the structure of RhB molecule by combining with COO^- , which lead to the increase of the absorption peak of benzene rings. In the presence of Al^{3+} , the absorption peak of benzene rings is higher than that of other cations because of the greater Coulomb force between Al^{3+} and COO^- . Besides, it is easily understood that there may be competitive absorption between RhB molecules and anion

Table 1 – Apparent-first-order reaction rate constants (k_{app} (min⁻¹)) of different cations.

Content (mol/L)	NaNO ₃	KNO ₃	Ca (NO ₃) ₂	Mg (NO ₃) ₂	Al (NO ₃) ₃
0	0.158	0.158	0.158	0.158	0.158
0.005	0.142	0.119	0.150	0.150	0.178
0.1	0.116	0.109	0.118	0.133	0.194
0.5	0.107	0.101	0.102	0.125	0.215

(NO₃) on the positive surface of TiO₂ particles of hydrosol, which may inhibit the degradation rate of RhB. Unfortunately, these explanations seem not to be able to explain the enhance effect of Al³⁺ on the process of TiO₂ hydrosol degrading RhB. Therefore, the role of Al³⁺ on the photocatalytic activity of TiO₂ hydrosol needs further discussion, which is presented in Section 2.4.4.

2.4.3. Explanations in terms of pH and the dispersion stability of TiO₂

The pH and dissolved ionic solutes play crucial roles on dispersion stability of nano TiO₂ in engineered and natural systems. These parameters can be controlled in laboratory settings but they may vary spatially and temporally in practice. Spatial heterogeneity of minerals in the subsurface alters the concentration of ionic species present in different systems (e.g., groundwater versus surface water). Variation in aquatic environment pH stems from the same phenomenon (Mao et al., 1991). In some specific environment, like concrete pore solution, the high contents of some inorganic ions and high pH may affect the dispersion stability of TiO₂ if adding the nano TiO₂ in the concrete by mixing water. Thus, a better understanding of how pH and dissolved ionic solutes affect the photocatalytic behavior of TiO₂ in the aqueous environment is needed.

In most of studies on the dispersion stability of nano TiO₂ powders in aqueous system, due to the pH of tested solutions was controlled by added extra acid and alkaline solution, the influence of inorganic cations on the change of pH was

ignored. In this study, the change of pH in the tested solutions was mainly caused by adding different amount of the studied cations. From the results shown in Fig. 4 and Table 1, the relationship between the pH and the k_{app} was derived. In addition, the results were shown in Fig. 6, it could be seen that the k_{app} was linear with the pH of the solution, and R² was 0.954, indicating the very good relativity. The photo-degradation rate decreased with the increase of pH of the solution. Yu et al. (2012) had studied photo-degradation rate of Methylene Blue by TiO₂ hydrosol with different solution pH (adjusted by HNO₃ solution) under sunlight irradiation, and the results showed that hydrosol with pH ranging from 1 to 4 all had high photocatalytic activity toward Methylene Blue, and the photo-degradation rate was higher with lower pH. Although the dispersion stability of nano TiO₂ particles was directly related to the pH of system, the causes of the change of pH need further study, for example the presence of inorganic cations studied in this work.

From Figs. 2 and 3, it can be seen that the variation trend of the zeta potentials of TiO₂ affected by the cations was intuitively similar to the particle size. TiO₂ particles agglomerated significantly over time and the zeta potential also obviously increased with time, which indicated that the nano TiO₂ particles showed dynamic instability with the presence of cations like Na⁺, K⁺, Ca²⁺ and Mg²⁺ at higher contents (0.1 and 0.5 mol/L). Moreover, TiO₂ particles showed much stable zeta potentials in the presence of Al³⁺ with the same contents, and the TiO₂ particles increased much slower than that in other groups. These results suggested that TiO₂ particles presented better dispersion stability in solutions with the presence of high content of Al³⁺. According to the literature data (Holmberg et al., 2013; Leroy et al., 2011), the isoelectric point of TiO₂ nano particles without extra electrolytes are in a pH range of 5.6–6.0. When at a pH near 5.6–6.0, the TiO₂ sols undergo coagulation that results in a relatively low ion-electrostatic repulsion barrier, which cannot terminate particles agglomeration (Volkova et al., 2012). According to Volkova et al. (2012, 2010), mental ions (Na⁺, K⁺, Ba²⁺ and La³⁺) caused the point of zero charge (PZC) shift to the acidic region, and

Table 2 – k_{app} for nano TiO₂ powders degradation of RhB in literature.

Catalyst	Solid content (g/L)	Light intensity (W/m ²)	k_{app} (min ⁻¹)	Half period of RhB degradation (min)	Reference
Nano TiO ₂ powder suspension	10	450	0.0658	10.53	Asilturk et al. (2006)
Nano TiO ₂ powder	2	Not mentioned	0.00793	87.41	Pang and Abdullah (2012)
TiO ₂ nanotubes	2	Not mentioned	0.03271	21.19	Pang and Abdullah (2012)
TiO ₂ nanotubes + ultrasonic	2	Not mentioned	0.005	138.63	Pang et al. (2011)
Nano TiO ₂ powder	2	Not mentioned	0.005	138.63	Song et al. (2012)
Nano TiO ₂ powder	1	3.6 × 10 ⁵	0.0165	42.01	Priya and Madras (2006)
P25	1	3.6 × 10 ⁵	0.0114	60.80	Priya and Madras (2006)
Nano TiO ₂ coated activated carbon	2.5	1.8 × 10 ⁴	0.0207	33.49	Zhang et al. (2011)
TiO ₂ nanodispersed hydrosol	0.02	349	0.158	4.39	This study
TiO ₂ nanodispersed hydrosol + 0.5 mol/L Al ³⁺	0.02	349	0.215	3.22	This study

P25: a commercial nano TiO₂ powder produced by Degussa (Evonik) Company.

Fig. 5 – Absorption spectra of RhB with TiO₂ hydrosol under ultraviolet (UV) light irradiation without cations (Control groups) and in the presence of 0.005, 0.1, and 0.5 mol/L Al³⁺.

the single charge anions (Cl[−], Br[−] and I[−]) did not affect the surface charge of anatase TiO₂ and the position in solutions of 1:1 background electrolytes. These may additionally explain the agglomeration of TiO₂ particles in large dosage of nitrates with Na⁺, K⁺, Ca²⁺, Mg²⁺ and Al³⁺. In addition, in literature

(Volkova et al., 2012, 2010), compared with other low valance cations the higher valence of La³⁺ caused the worst agglomeration of TiO₂ sol and the greatest PZC shifting at the presence of 0.1 mol/L La³⁺. However, in this study, Al³⁺, which was also a cation with high valence, caused little coagulation of TiO₂ hydrosol and enhanced the photocatalytic performance of TiO₂.

According to the above analysis in this section, the negative influence of Na⁺, K⁺, Ca²⁺, Mg²⁺ on the photocatalytic performance might be explained by exacerbating the competitive absorption among RhB molecule and anions on the surface of TiO₂. The competitive absorption led to the unstable surface charge of the TiO₂ surface and resulted in the agglomeration and lower photodegradation of RhB. However, the acceleration of Al³⁺ on the photocatalytic performance of TiO₂ cannot be explained by these explanations. In the following section, we were trying to explain the role of Al³⁺ on the photocatalytic activity of TiO₂ hydrosol in degrading RhB.

Fig. 6 – Relationship between k_{app} and the pH of solutions.

2.4.4. Role of Al³⁺ on the photocatalytic activity of TiO₂ hydrosol
The UV-light induced TiO₂ photocatalytic reaction mechanism was well studied by many researchers (Hoffmann et al., 1995; Kamat, 1993; Ma et al., 2019, 2018; Wang et al., 2018). Based on the previous analysis, Fig. 7 shows the probable

Fig. 7 – Photocatalytic reactions of TiO₂ for degrading RhB. h⁺: holes; e⁻: electrons.

degradation process of RhB in the studied system of this study. It is clear that H⁺ plays a significant role in the photo-oxidation process. The higher concentration of H⁺ is favored for accelerating the reduction reaction and hindering the recombination of holes (h⁺) and electrons (e⁻) of TiO₂ surface inspired by UV light.

In general, the transformations and distributions of Al³⁺ are very complicated in aqueous solution because of the hydrolytic action. The hydrolytic form of Al³⁺ in water can be divided into three types, the monomeric hydroxyl group, the polymeric hydroxyl group, the colloidal polymerization form or amorphous aluminum hydroxide sol. Al³⁺ also show amphoteric characteristics in aquatic systems. In addition, the species distribution of aluminum hydrolysates varies with the pH value of solutions. The hydroxy aluminum complex ions in water tend to polymerize strongly to form dimer, oligomer, and hyper-polymer (Hiradate et al., 1998; Phillips et al., 2000). In the aquatic environment, aluminum is colloidal poly-aluminum hydroxide under the normal pH. The aluminum can convert into soluble hydroxyl polymerized aluminum with the decrease of pH value:

where, p ($1 \leq p \leq 24$) and q ($1 \leq q \leq 60$) are stoichiometric numbers (Akitt and Elders, 1988). The hydrolytic polymerization forms of aluminum are a series of metastable states (poly (hydroxo) species) from Al³⁺ to Al_m(OH)_{3m}. However, these forms can hardly coexist in the same solution, and the dominant form will vary with the conditions (Akitt and Elders, 1988).

To distinguish the effects of Al³⁺ and H⁺ on the photocatalytic process of TiO₂ hydrosol, the influences of H⁺ at different pH values induced by acid were also studied (the detail information can be found in Appendix A Fig. S8 and Table 3). It can be seen from Table 3 that the apparent first-order rate constant k_{app} values in two groups increased with the decrease of pH value. The k_{app} of TiO₂ hydrosol in the group of pH induced by HNO₃ was smaller than that of pH induced by Al(NO₃)₃.

Because of the flocculation effect of the hydrolysates of aluminum, they have a strong adsorption effect on impurities

in water (Van Benschoten and Edzwald, 1990; Cao et al., 2016; Tang et al., 2015). The solution pH plays an important role on the hydrolysis process of aluminum (Zhao et al., 2009), i.e. the at lower pH (<6), the amount of monomer aluminum and oligomeric state aluminum increase with the decrease of pH, and the amounts of middle and high polymer state aluminums are revised. The monomer aluminum and oligomeric state aluminum could produce cohesive force in sludge flocculation (Cao et al., 2016), and the formed flocs is larger and looser so the sludge flocs can re-grow more easily after shearing. In solutions, the attractive force between the impurity particles are reduced by compressing the diffusion layer and reducing the surface potential, the adsorbed positively charged complex ions (e.g., RhB⁺ of RhB) are interconnected and agglomerated when the attractive force gains the upper hand. These flocculation of aluminum probably enhances the surface contact between TiO₂ particles and RhB molecules in solution, which leads to the higher degradation rate and larger k_{app} .

In brief, the existence of TiO₂ hydrosol successfully creates the low pH system in solution. Moreover, according to Eq. (2), the hydrolytic action of Al³⁺ produces more H⁺ into the solution that lead to a lower pH system, and the agglomeration of TiO₂ hydrosol is relived because of the looser and easy-to-shear floc structures caused by monomer aluminum and oligomeric state aluminum. As mentioned before (Asilturk et al., 2006), the high content (1 wt.%) of nano TiO₂ suspension decreased the photodegradation rate of RhB because of the agglomeration and sedimentation of the TiO₂ particles caused by the collision between excited state molecules and ground state molecules. Compared with results in this study, the H⁺ produced by Al³⁺ hydrolytic action promotes the photocatalytic actions of nanodispersed TiO₂ hydrosol notably, which may buffer the collision between TiO₂ molecules in different

Table 3 – k_{app} (min⁻¹) at different pH induced by HNO₃ and Al(NO₃)₃.

pH	3.1	2.9	2.1
Induced by HNO ₃	0.154	0.172	0.196
Induced by Al(NO ₃) ₃	0.178	0.194	0.215

states. Moreover, the hydroxy aluminum groups have a higher valence that can break the RhB molecule by absorbing COO^- . Hence, the photo-induced degradation rate of RhB increased in the presence of Al^{3+} in TiO_2 dispersed hydrosol.

3. Conclusions

The effect of five inorganic electrolytes in the concentration range of 0.005 to 0.5 mol/L on the photocatalytic degradation rate RhB solution by TiO_2 hydrosol was investigated. The relationship between photocatalysis, coagulation of TiO_2 hydrosol and cations was evaluated. Firstly, the effects of cations on the photocatalytic activity of TiO_2 hydrosol were discussed from the angle of the change of photocatalytic reaction kinetics. Secondly, the influences of cations on the UV–Vis absorption spectra of RhB were discussed from the view of the interaction between ions. Thirdly, the relationships between TiO_2 dispersion stability and pH of solution caused by cation contents and types were discussed. The enhancement mechanism of Al^{3+} on the photocatalytic performance of TiO_2 hydrosol was studied specially.

The presence of monovalent and bivalent, like Na^+ , K^+ , Ca^{2+} and Mg^{2+} , inhibited RhB degradation and the inhibition effect increased with the increased concentration of cations because of exacerbating the competitive absorption among RhB molecule and anions on the surface of TiO_2 . Due to the higher valence, the negative effects of Ca^{2+} and Mg^{2+} were greater than that of monovalent. The reaction kinetic constants of the pseudo-first-order reaction kinetics model were linearly inversely proportional to the pH value of solutions with cations, revealing the photocatalytic performance of TiO_2 hydrosols would be enhanced when containing hydrolysable cations like aluminum. Due to the hydrolytic effect of Al^{3+} in electrolytes, the risk of agglomeration of TiO_2 particles in hydrosol was reduced; the photochemical reactivity of TiO_2 hydrosol was improved, resulting in enhanced reaction rate. In the presence of 0.5 mol/L Al^{3+} , the apparent first-order rate constant was 0.215 min^{-1} , and the half period of RhB degradation (the time of degrading 50% RhB) was 3.22 min. The results in this study revealed different mechanism about the coagulation of TiO_2 hydrosols in electrolyte with hydrolysable metal ions. The acidic shift of point of zero charge caused by electrolytes could be partially offset by the hydrolytic action of Al^{3+} in the examined systems. Therefore, the coagulation of TiO_2 particles could be hammered and the stability of TiO_2 sols was consequently improved. These results supported that the nanodispersed TiO_2 hydrosol was suitable to be used as photocatalyst in the environment containing Al^{3+} , like urban sewage and Portland cement-like ionic environment.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jes.2019.07.013>.

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