

Sedimentation Process of TiO₂ Nanoparticles in Aqueous Solution

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Abstract

TiO₂ nanoparticles, a semiconductor photocatalyst is widely used in various applications especially for water treatment. The common problems for the application are separating the nanoparticles from the water body and recovering it to be reused. This research was conducted to investigate the aggregation and sedimentation properties of TiO₂ nanoparticles via chemical addition. The experiment was carried out for 5 hours by varying the pH, ionic strength, and the addition of organic matter such as rhodamine B, methylene orange, and humic acid. The results indicate that pH and ionic strength greatly affect the TiO₂ sedimentation process. Sedimentation can be formed properly when the solution is at pH 1 and 14, this happens because pH is close to the isoelectric point. Meanwhile, ionic strength with a concentration of 0.1 M gave the most optimal results in TiO₂ sedimentation. In the presence of ionic strength with the appropriate concentration, the thickness of the electrical double layer particles can be reduced so the attractive force increases and sedimentation occur. Meanwhile, in the presence of organic matter, rhodamine B, methylene orange, and humic acid did not significantly affect the formation of TiO₂ sedimentation.

Keywords: titanium dioxide, sedimentation, ionic strength, isoelectric point, water treatment

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INTRODUCTION

Due to its particular crystal structures, electronic, optical and thermal properties, TiO₂ nanoparticles are widely used in cosmetics, sunscreens, food preparation, drug delivery systems, and other products (Irshad et al., 2021). These nanoparticles are often combined with other compounds such as graphene (Sharma et al., 2018), aluminium (Giolando, 2013), silica (Azizi et al., 2020), or cellulose (Garusinghe et al., 2018) to produce a composite with desired properties for particular purposes. Its

remarkable performance in the photocatalysis process also derived a prospective application in water and wastewater treatment, especially for organic degradation (Tsang et al., 2019). By employing nano-sized particles of TiO₂, the optimum efficiency of the photocatalytic process can be achieved (Rodríguez-González et al., 2019). Apart from that, there are some industries that use TiO₂ nanoparticles in many purposes that are given in chart below:

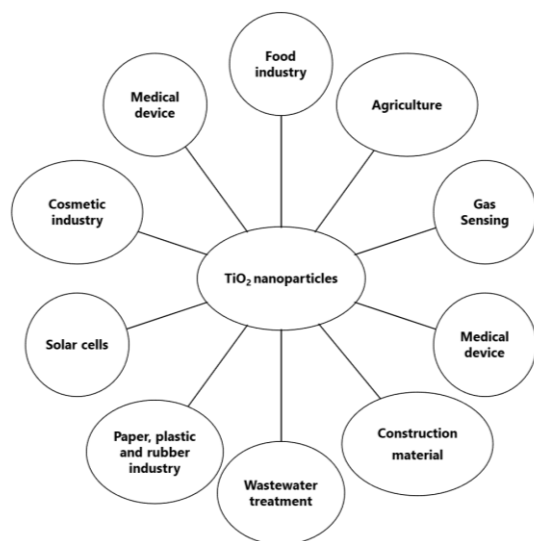


Figure 1. TiO₂ in industrial application

It is also undeniable that TiO₂ that is released to the environment in a particular way through ground or surface water can be toxic so it poses a risk to ecosystems and public health or affects the presence of other toxic pollutants (Wiesner et al., 2006). According to a Wastewater Treatment Plant (WWTP) report, untreated sewage included 100 to almost 3000 g Ti/l. TiO₂ particles between 4 and 30 nm in size were discovered in the treated effluent. After wastewater was treated, it was discovered that the amount of nano-TiO₂/l in the effluent ranged from less than 5 g to 15 g. TiO₂ nanoparticles have an impact on coastal ecosystems that support fishing and leisure activities as well as phytoplankton. In aquatic systems, algae are largely utilized as biological markers to investigate the toxicity of contaminants on living organisms. TiO₂ nanoparticles are reported to have algae growth inhibition by altering membrane structure because of elevated lipid peroxidation. Anatase TiO₂ nanoparticles exhibit more cellular toxicity as in the solution it can produce intracellular reactive oxygen species (ROS) that treats the living organism (Waghmode et.al, 2019). Thus, the recovery of TiO₂ nanoparticles is necessary.

Recovering the nanoparticle to be reused from the treated water is another challenge. Nanosized materials are difficult to be recovered and it needs study to compose the feasible and effective methods to do so. As according to Patchaiyappan et al., the effectiveness of re-using TiO₂ in photocatalytic degradation of rhodamine B is the same as using calcined and not calcined pristine TiO₂ particles (Patchaiyappan, et.al, 2016). The presence of the remaining organic pollutants in the treated wastewater can affect the recovery process of nanosized TiO₂. Furthermore, the interaction between the organic pollutants with TiO₂ chemically or physically can alter or interfering the recovery process. For example, rhodamine B as one of the organic pollutants that is widely used as a colorant in the manufacturing of textiles. It has been reported

that its present in the drinking water can trigger to subcutaneous tissue-borne sarcoma which is highly carcinogenic. Rhodamine B enters the body causing oxidative stress on cells and tissues and also leading to liver dysfunction or cancer (Sulistina and Martini, 2020). It categorized as cationic dyes that carries Cl⁻ in its chemical structures that could interfere the recovery process.

Many methods can be used to recover the TiO₂ nanoparticles. One of them is sedimentation that categorized as a mature technology as its significance implementation in the colloid systems and industrial applications. Many studies have been conducted in the TiO₂ recovery using sedimentation, however most of them are in micron size. TiO₂ nanoparticles aggregation is not much investigated. In addition, the supporting system such as acidity, ionic strength, and the presence of organic matter, which considered to be the important parameter in creating the stability of nanoparticle suspensions were ignored. Understanding nanoparticle sedimentation and aggregation behaviour are critical to predicting their transport and mobility in the aqueous environment. Therefore, it is essential to investigate the influence of pH, ionic strength, and the presence of organic compounds on the sedimentation process. This paper discussed the sedimentation behaviour of TiO₂ in an aqueous solution using pH, ionic strength, and the presence of organic matter (RhB, MO, Humic Acid) as parameters.

MATERIALS AND METHODS

Materials

For this research TiO₂ nanoparticle commercials were used with < 25 nm in size. NaOH and HCl were added for pH adjustment, while NaCl was utilized for ionic strength adjustment. Organic compounds used in this experiment were Rhodamine B purity ≥ 95%, Methyl orange 85%, and Humic acid 95%. All chemicals (purchased from Sigma Aldrich Co. LCC) were used without any purification.

Experimental Methods

TiO₂ were dispersed in distilled water (500 mL volume) and sonicated for 1 hour with different parameters. The first batch was to observe the sedimentation behavior at different pH value which was adjusted by the addition of NaOH or HCl. The second batch was used to investigate the influence of ionic strength to the sedimentation process. Ionic strength (mol/L), IS, is calculated by the total value all of ions concentration present in a solution. Thus, to examine the IS effect, the TiO₂ nanoparticles were dispersed in different molar concentrations of NaCl solution. The last batch was for sedimentation observation in the presence of other component such as organic matter by adding TiO₂ in the 5 ppm of organic solution as depicted in the Table 1.

Table 1. Experimental Design of TiO₂ sedimentation

Experimental code	Photocatalyst		pH	Ionic Strength	Organic presence (ppm)			Analysis	
	Name	Loading (g/L)			RhB	MO	Humic acid	Light absorption	pH
S101	TiO ₂	0.5	1					√	√
S102	TiO ₂	0.5	4					√	√
S103	TiO ₂	0.5	7					√	√
S104	TiO ₂	0.5	10					√	√
S105	TiO ₂	0.5	14					√	√
S201	TiO ₂	0.5		0.01				√	√
S202	TiO ₂	0.5		0.05				√	√
S203	TiO ₂	0.5		0.1				√	√
S204	TiO ₂	0.5		0.5				√	√
S301	TiO ₂	0.5			5			√	√
S302	TiO ₂	0.5				5		√	√
S303	TiO ₂	0.5					5	√	√

Glass container contained solution then put in a stable position and a sample was taken every 30 min for 5 hours of the experiment. Sample (3 mL) were taken from the supernatant carefully in the form of aliquots of the dispersions. It conducted with care, so the sampling procedure did not interfere the sedimentation process for further analysis.

Analysis

The sample taken from the sedimentation process then evaluated by calculating the concentration of TiO₂ in the sample solution. The calculation was based on absorbance value observed in a UV-Vis Spectrophotometer at 413 nm. The ratio of absorbance C measured at multiple intervals in comparison with the initial absorbance C₀ was calculated. At low ratio indicated high amount of TiO₂ had been accumulated, and this is proportional to the probability of sedimentation having occurred. While the pH of the solution was measured with a pH meter.

RESULTS AND DISCUSSION

The influence of ionic strength in the sedimentation of TiO₂

In this study, the effect of ionic strength on the TiO₂ sedimentation was observed at several ionic strength values made from a different concentration of NaCl, 0.01 M; 0.05 M; 0.1 M; and 0.5 M. Result depicted in Figure 2 shows that the ionic strength affects the TiO₂ sedimentation. The concentration of TiO₂ in the solution decreased with increasing time. It occurred because most TiO₂ particles underwent a sedimentation process (Markus et al., 2015). The best results are shown in ionic strength 0.5 M, where at the 300 minutes almost all TiO₂ particles have settled down, followed by the presence of ionic strength in 0.1 M NaCl, in which capacity wise over a period of time has the most concentration reduction, means more TiO₂ sediment was formed compared to lower ionic strength.

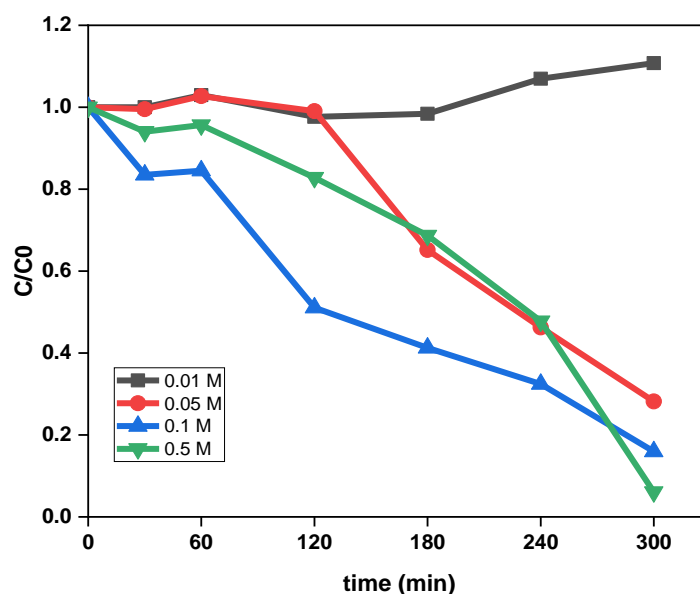


Figure 2. Decrease in TiO₂ concentration due to sedimentation process with variable ionic strength

The stability of particles during sedimentation is determined by the summary of the attractive and repulsive forces between individual particles which can be described in Figure 3. The attraction between particles is driven by the van der Waals force. Further, the interaction of the electrical double layer surrounding each particle that commonly called as an electrostatic repulsive force, has two important properties which are the zeta potential and the thickness of the electrical double layer (Hotze et al., 2010).

The higher the zeta potential and the thicker the electrical double layer, the electrostatic repulsive interaction will increase. Meanwhile, the thickness of the electrical double layer is a function of ionic strength of the supporting solution. With the increase of ionic strength, the thickness of the double layer will decrease.

In general, nanoparticles have functional groups on their surface, with the addition of ions, the charge on the surface of particles will get a pair so it reduces the

thickness of the electrical double layer and the repulsion force. This condition will certainly make attractive force between particles dominant over the repulsive force, resulting in highly aggregated dispersion. The energy barrier to prevent aggregation decreased with increasing solution ionic strength.

The zeta potential is the potential gap between the bulk and the slipping plane located at some distance from the surface of the particle (dependent on the electrical double layer thickness) (Jiang et al., 2009). Ionic strength addition leads to the compression of the electrical double layer. Therefore, although the particle surface charge does not change in the present of sodium and chlorine, as they do not interact with the TiO₂ particle surface (due to its chemical stability), the zeta potential decreases with increasing ionic strength. The effect of ionic strength on TiO₂ sedimentation can be illustrated in Figure 4.

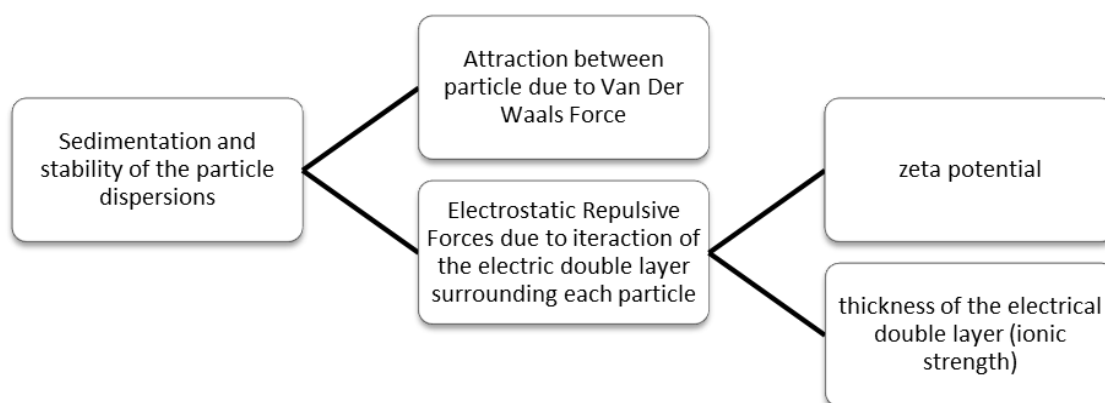


Figure 3. Factors affecting particle dispersion

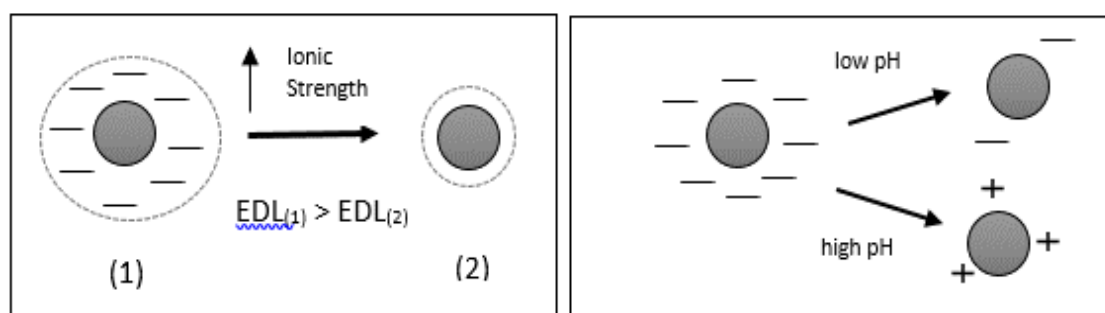


Figure 4. Illustration of the effect of ionic strength and pH on TiO₂ sedimentation. Modified from Hotze et al.: Nanoparticle Aggregation: Environmental Transport and Reactivity (Hotze et al., 2010)

The influence of pH in the sedimentation of TiO₂

Based on the experimental results shown in Figure 5, the extreme TiO₂ concentration reduction, which indicates optimal sedimentation, occurs at pH 1 and pH 14. It turns out that pH affects surface particle charge. In general, at low pH value, the particles normally have positive surface charge in reverse, at high pH value, the particles will have negative surface charge (Hotze et al., 2010). The isoelectric point is where the particle has zero net surface charge or at the

intermediate pH value. When pH value is far distance from the isoelectric point, the absolute value of zeta potential becomes higher. The electrostatic repulsive force is then dominant over the van der Waals force, so sedimentation is difficult to form. When pH approaches the isoelectric point, the repulsive force is weakened due to the low surface charge. Under these conditions, sediment is formed which is visible clearly in the solution as depicted in Figure 6.

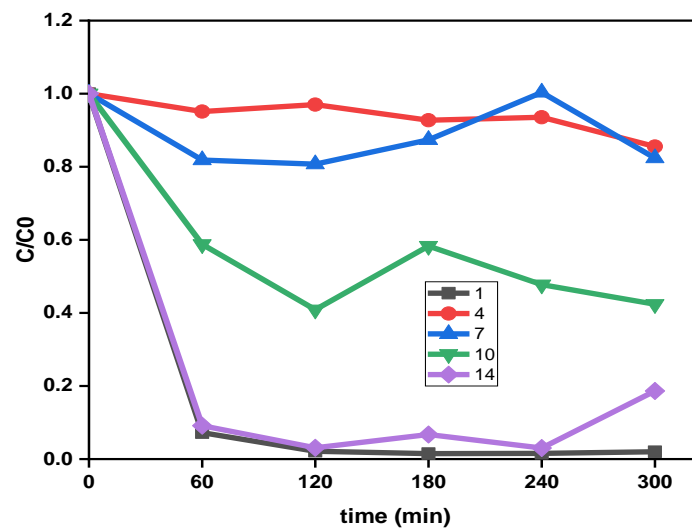


Figure 5. Decrease in TiO₂ concentration due to sedimentation process with variable pH



Figure 6. Stages of sedimentation due to the influence of pH

In this experiment, sedimentation occurs when the solution is at pH 1 and pH 14. This indicates that both pH values are close to the isoelectric point. When pH increased, OH⁻ in solutions would compete for more active sites and bond with H⁺ on the surface of the nanomaterials, resulting in a low surface charge (W. Liu et al., 2013). Due to this condition, the absolute value of the zeta potential decreases and it triggers an increase in the attractive force between particles because of the van der Waals force so as promoting TiO₂ sedimentation.

The presence of organic matter in the sedimentation of TiO₂

The presence of organic matter was less influential in the process of TiO₂ sedimentation as shown in figure 7. This can be seen from the results of the study where a small amount of organic matter was added to the solution and showed no sign of TiO₂ sedimentation. Organic matter attaches to the surface of the particles in various ways. Stabilization or destabilization of the attachment is also influenced by various factors such as the type of organic matter, its concentration, and solution chemistry.

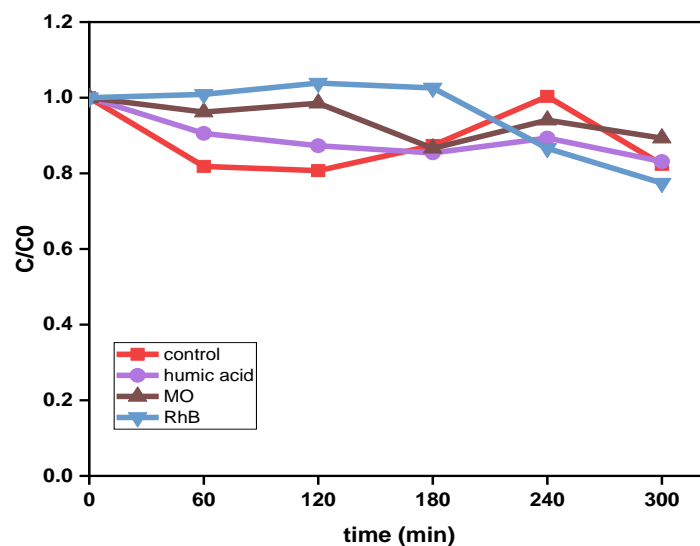


Figure 7. Decrease in TiO₂ concentration due to sedimentation process with variable organic matter

Change of material chemical composition influence surface charge, and play a dominant role in the sedimentation and aggregation of TiO₂ nanoparticle suspensions (X. Liu et al., 2011). Stabilization usually occurs when organic matter forms a stable charge layer on the outer surface of the particle.

Organic matter is adsorbed on the surface of TiO₂ through electrostatic interaction, hydrophobic interaction, and complexation-ligand exchange (Zhao et al., 2019). When a lot of organic matter is adsorbed on the surface of TiO₂, it would be dominant and its impact becomes stronger. Organic matter adsorbed on the surface of the TiO₂, which formed an electrostatic double layer (EDL) on the surface of the particles to significantly increase the repulsive energy between the particle (Li et al., 2015). Stability or instability depends on each attachment characteristic that occurs. From these experiments, it is proven that the presence of organic matter causes a steric hindrance force and increases the energy barrier for the formation of sedimentation. These results are in accordance with research conducted by He et.al about the sedimentation behavior of n-TiO₂ based on sedimentation efficiency (SE) at a quasi-stable state used fulvic acid (FA). In this study, FA were analyzed in terms of n-TiO₂ sedimentation efficiency after 4 h of process at the quasi-stable state. FA was known to have a high molecular weight (approximately 500–1500 Da). The pH of the suspension was adjusted to 7.0 (±0.1) to eliminate the effect of high H⁺ concentration. Consequently, as the n-TiO₂ settled with FA and if FA remained coated on the surface, the aggregation between n-TiO₂ particles was hindered because of great steric repulsion (He et al., 2015).

CONCLUSIONS

Ionic strength influences dispersion stability by changing the electrical double layer thickness, by reducing its thickness, attractive or van der Waals forces between particles increasing and resulting sedimentation. While pH can change the dispersion state by altering the zeta potential (surface charge). The smaller the zeta potential and the value of pH is close to the isoelectric point; the greater sedimentation occurs. The electrostatic repulsive force caused by the thickness of the electrical double layer or a large zeta potential value can inhibit the attractive forces between particles so sedimentation is hard to happen. The presence of organic matter not only increases the density of surface charge but also the energy barrier between particles by steric hindrance. The tendency of TiO₂ sedimentation can be done in the presence of ionic strength and the condition of pH solution. Sedimentation can already occur with a minimum concentration of 0.05 M ionic strength, while a solution

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