THE PH DEPENDENCE OF NATURAL ORGANIC MATTER SORPTION TO NANOPARTICLES AND ITS ABILITY TO STABILIZENANOPARTICLES IN AQUEOUS SOLUTIONS

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Abstract

Several studies have demonstrated that natural organic matter (NOM) can reduce toxicity of most toxic chemicals through sorption /complexation processes. In the area of nanoecotoxicology, this has also been demonstrated. The sorption of NOM on to the nanoparticles (NPs) has further been lauded for particle stabilization and hence lessening the effect of particle aggregation. Comprehensive understanding of NOM – NPs interaction can help improve our predictive capability of fate and transport of nanomaterials in the aquatic environment. In this study, the particle stabilization of NOM on both sonicated and non-sonicated TiO_2NPs at different pH values was examined. The study further examined the sorption of NOM to TiO_2NPs at the same pH values. The unsorbed NOM was separated from the sorbed by both ultracentrifugation and 50 nm polycarbonate membrane filters (the results of both methods agreed to within 3%). The dynamic light scattering (DLS) technique was used to characterize the aggregates. The PALS Zeta potential analyzer was used to estimate surface charge. The total organic carbon was measured by the Total Organic Carbon Analyzer- Shimadzu (TOC-VCPH). The results indicated that the NPs stabilization by NOM was pH dependent and was more pronounced at higher pH, but lowest at pH values close to the point of zero charge (PZC) for the TiO_2NPs. The ability of NOM to stabilize non-sonicated NPs was found to be mild. As expected, the sorption results showed that the least amount of NOM was sorbed at higher pH, despite the observation that the highest stabilization occurred at higher pH.

Keywords: NOM, TiO_2 nanoparticles, stabilization, sorption

Introduction

Humic substances are a series of relatively high molecular substances that are ubiquitous in the environment (Koopal et al. 2005; Wang et al. 2010). The interaction of humic substances through sorption can affect fate and transport of various chemicals in the environment (Chen et al., 2003) including that of nanoparticles (NPs). Several studies have in fact shown that humic substances can form surface coatings or sorb to NPs surfaces in aqueous solutions (Amal et al., 1991; Baalousha et al., 2008; Yang et al., 2009; Keller et al., 2010). Such surface coating of NPs or particle encapsulation by NOM presumably affect aggregation behavior, resulting in reduced aggregation through a number of mechanisms such as anion exchange (electrostatic interaction), ligand exchange, hydrophobic interaction, entropic effect, hydrogen bonding, and cation bridging (Baalousha et al., 2008; Yang et al., 2009). However, other studies have also shown that any concentration of NOM in aqueous solution at or below the critical coagulation concentration (CCC) can enhance aggregation, presumably through charge neutralization and bridging mechanisms (Stumm and Morgan, 1981; Illes and Tombacz 2006; Keller et al., 2010). This interaction of NOM with NPs has interesting toxicological implications as it can influence particularly the chemistry (fate, transport and bioavailability) and physics (optical properties) of nanoparticles as both have influence on the NPs behavior and toxicity in aqueous environment (Stedmon et al., 2003). If the NOM-NPs interaction results in enhanced aggregation, sedimentation may occur (Scown et al., 2010; Keller et al., 2010). This would inevitably lead to reduced exposure and diminished effects on water column (pelagic) organisms, but potentially increasing adverse effects on the benthic organisms (Scown et al., 2010). However, when NOM-NPs interaction results in particle stability (Yang et al., 2009), there can be prolonged exposure of water column organisms and possibly increased transportation of the NPs over long distances (Baalousha et al., 2008; Scown et al., 2010). Whether this would result in increased negative effects or not, it may probably depend on the nature and strength of NOM-NPs complexation and on the environmental conditions (presence of adsorbates with higher adsorption affinity in guts of organisms).

The NOM is considered a flexible polyelectrolyte that has anionic functional groups with hydrophobic components (O’Melia, 1990). Structurally, its configuration can be affected by the pH and ionic strength of the aqueous solution in which it is dissolved (O’Melia, 1990; Stumm and Morgan, 1996). In fresh waters with moderate pH and relatively low ionic strength, its molecules assume extended shapes (structurally relaxation) as a result of intramolecular electrostatic repulsive interaction (O’Melia, 1990; Stumm and Morgan, 1996). However, in low pH environments the NOM molecules coil (aggregation), while in high pH environments, their molecules extends (relaxation) (Hudson et al., 2007), a situation likely to influence NOM-NPs interactions.When metal oxide NPs are introduced into the aqueous solution with dissolved NOM, surface ligand exchange (carboxylic or phenolic with surface hydroxyl groups) occurs augmented by hydrophobic interaction from hydrophobic components (Stumm and Morgan, 1996; Yang et al., 2009). This can result into the accumulation of negative charges on the surfaces of the metal oxide NPs causing electrostatic stabilization (Yang et al., 2009) and hence particle stability. However, if the NOM concentration is not high enough to cause complete charge reversal on the NP metal oxide surface, there would be particle aggregation (Stumm and Morgan, 1996; Illes and Tombacz, 2006). At low pH or high ionic strength where the NOM molecules are not well deprotonated, the interactions are mainly hydrophobic and the resultant particle stabilization could be due to steric effects. This means that the presence of macromolecular layer causes entropically unfavorable conditions at the close approach of particles (Stumm and Morgan, 1981; Illes and Tombacz, 2006). The of NOM-NPs interaction has been reported to be influenced by several environmental factors such as pH, ionic strength and divalent metal cations (McKnight et al., 2001; Chen et al., 2003; Swietlik and Sikorska, 2005). The high ionic strength conditions are presumed to cause charge screening and ultimately increase the hydrophobicity of the dissolved NOM in aqueous solutions (Chen et al., 2003).

Given the ubiquitous nature of dissolved NOM in aquatic systems on one hand and the increased release of NPs in aquatic systems on the other, it is critical to have comprehensive understanding of the NOM - NP interaction as this could help improve our predictive capability on the transport and fate of nanomaterials in the aquatic environment. In this study, the NOM-NPs interactions were investigated by examining the particle stability of NOM on both sonicated and non-sonicated TiO2 NPs at different pH values and further the sorption of NOM to TiO2 NPs at the same pH values was examined. The dynamic laser light scattering (DLS) technique was used to characterize the NPs stability (by measuring average aggregate sizes). The PALS Zeta potential analyzer was used to estimate surface charge. The separation of non-complexed/non-sorbed NOM from NOM sorbed to NPs was carried out using both filtration and ultracentrifugation and the comparison of the two separation techniques was performed. The total organic carbon was measured by the Total Organic Carbon Analyzer-Shimadzu (TOC-VCPH).

Materials and Methods

Materials

Titanium dioxide NPs used in this study were P25 (< 50 nm) purchased from Degussa Corporation. The Suwannee River Humic Acid (SRHA), reverse osmosis isolate (NOM-ROI) was purchased from International Humic Substances Society (IHSS). The following buffers were used as purchased without further purification: 2-(4-morpholino) ethanesulfonic acid monohydrate (MES); piperazine-N, N'- bis (2-ethanesulfonic acid) (PIPES); sodium acetate (NaAc); Tris-base. The pH measurements were carried out using a ThermoOrion pH meter and Ross combination glass electrode. The Autotitrator 836 titrando connected with pH meter - Ω metrohm was used for determining the point of zero charge (PZC) for TiO_2 NPs. The METLER TOLEDO balance, Xs 205 dual range; max 81/220 g capable of measuring weight down to 0.01 mg was used to weigh NPs. Surface Analyzer micromeritics 2010, was used to determine surface area using BET technique. High purity water, milli-Q water with resistivity >18 MΩ.cm was used throughout the experimental work. The degree of particle aggregation and hence determining stability were measured by dynamic laser light scattering (DLS) technique using both the Coulter N4 Plus and Brookhaven Instrument Corporation (BIC). The zeta potential was measured by the Zeta PALS of the BIC. The amber colored 125 mL bottles with Teflon lined caps were used for sorption study (preliminary experiments showed no significant adsorption of NOM to these bottles). The separation of non-sorbed NOM and NOM sorbed to NPs was carried out using both the 50 nm pore size polycarbonate filters and the Ultra centrifuge SORVALL EVOLUTION RC S/N 10300582. The TOC analysis was measured by Carbon Analyzer - Shimadzu (TOC –VCPH).

Methods

The NOM-NPs interactions at different pH values was carried out using TiO_2 NPs primarily because of its low dissolution over a wide range of pH. The first part involved determining the point of zero charge (PZC) for TiO_2 NPs. Then the ability of dissolved NOM to stabilize TiO_2 NPs at three different pH values was investigated. This was done at the PZC and two other pH values selected by taking two pH points below and above the PZC. This study was carried out using both sonicated and non-sonicated TiO_2 NPs at 5 mg/L particle loading and at three levels of dissolved NOM concentration (0.5, 2.5 and 5 mg C/L NOM). To maintain the pH at the specified values, buffer solutions were used. For the sorption study, the buffer solutions were not used because the analyte of interest, the total organic carbon is also contained in these buffers. The particle loading that was used in the sorption study was 300 mg/L.

The Determination of the Point of Zero Charge for TiO2 NPs

The suspension of TiO_2 NPs at 4.0 g/L was prepared in 0.01 M $NaNO_3$ solution as a background electrolyte and introduced into the titration vessel. The suspension was purged with argon gas with constant stirring to drive out all the carbon dioxide (CO_2) gas. This was performed for about 45 to 50 minutes. The pH was then lowered to 3.85 using 0.1M HCl. Then the suspension was titrated with 0.1 M NaOH solution at 0.01 mL aliquot to a pH 10.5. The titration was done using two runs. During the first titration, subsequent addition of further aliquots of the titrant was continued only after the electrode stability reading was 0.5 mV/minute. In the second run, the titration was carried out slowly and the subsequent additions of the titrant was only done after the electrode stability reading was less 0.1 mV/minute.

Experimental Method for Particle Stability

The Sonicated TiO_2 Nanoparticles

The stock suspension of TiO_2 NPs at 100 mg/L in 0.01M solution of sodium nitrate (NaNO3) was prepared and sonicated for 60 minutes using the Branson® 5510 sonication bath. These metal oxides NPs suspensions were then stored at room temperature of 69-73 ^oF (20.55 – 22.77^oC) under quiescent conditions in the dark. Prior to preparation of the test suspensions, the stock suspension was sonicated using the Branson® 5510 sonication bath for 10 minutes to homogenize the suspension and as well as to break any aggregates that may have formed. The test suspensions were prepared by pipetting appropriate volumes of the stock suspension of TiO_2 NPs and 50 mg C/L NOM stock solution into 400 mL beakers and then diluting to 100 mL with each buffer to give the following concentrations: 5 mg/L particle loading at 0.5, 2.5 and 5.0 mg C/L NOM . The following buffers in 0.01M NaNO3 solution were used: 0.01M acetate, pH 4.50; 0.01M PIPES, pH 6.50; 0.01M Tris–base, pH 8.50. For each pH (buffer solution) there was a control suspension that comprised the matrix of each test suspensions except NOM. The purpose of the control suspensions was to check the influence of buffer solutions on particle stability or aggregation. Once prepared, the test suspensions were kept under quiescent conditions in the dark. The samples for the DLS and zeta potential measurements were taken every 24 h for 5 days (for 24, 48, 72, 96 and 120 h post preparation).

The Non-sonicated TiO_2Nanoparticles

The test suspensions were made by weighing 0.5 mg of TiO_2 NPs using a microbalance, the METLER TOLEDO, Xs 205 dual range 81/220 g that can weigh masses down to 0.01 mg. The weighed TiO_2 NPs were each introduced into 20 mL of 0.01M $NaNO_3$ solution in a 400 mL beaker. Each resulting suspension was allowed to stand for 24 h at room temperature of 69-73 ^oF (20.55 – 22.77^oC) under quiescent conditions in the dark. Then to each suspension was added an appropriate volume of 50 mg C/L NOM stock solution and then diluted to 100 mL with appropriate buffer solution to give the following: 5 mg/L particle loading at 0.5, 2.5 and 5.0 mg C/L NOM . The following buffers in 0.01M $NaNO_3$ solution were used: 0.01M acetate, pH 4.50; 0.01M PIPES, pH 6.50; 0.01M Tris–base, pH 8.50. For each pH (buffer solution) there was a control suspension that comprised the matrix of each test suspensions except NOM. The purpose of the control suspensions was to check the influence of buffer solutions on particle dispersion or aggregation. Once prepared, the test suspensions were kept at room temperature of 69-73^oF (20.55 – 22.77^oC) under quiescent conditions in the dark. The samples for the DLS and zeta potential measurements were taken every 24 h for 5 days (for 24, 48, 72, 96 and 120 h post preparation).

Experimental Method for NOM Sorption to TiO_2 NPs

This study was carried out at a constant room temperature of 24 ±1^oC (75.7 ^oF) in batch reactors (150 mL amber colored bottles). The study examined NOM sorption to TiO_2 NPs at 3 pH values of 4.50, 6.50 and 8.50 and at a constant ionic strength of 0.01M of $NaNO_3$ solution. A series of 7 sets of TiO_2 NPs of about 0.03 g each were weighed and each introduced into 20 mL of 0.01M $NaNO_3$ solution in a 400 mL beaker for each pH studied. Then each suspension was sonicated for 30 minutes and kept under quiescent conditions for overnight. Then appropriate volumes of NOM stock solution of 50 mg C/L (NOM dissolved in 0.01M $NaNO_3$) were pipetted and introduced into the suspensions and diluted to 100 mL using 0.01M $NaNO_3$ solution to yield a range of concentrations from about 2 mg C/L (5 mg/L NOM) to 32 mg C/L (80 mg/L NOM). The pH of interest was achieved by additions of appropriate volumes of HCl or NaOH (< 100µL) with stirring with a magnetic bar. During addition of HCL or NaOH care was taken to avoid inclusion of CO_2 by covering the beakers with parafilm. Once the desired pH was achieved and remained constant for over 24 h, the contents of each beaker were transferred into the 150 mL amber colored bottles and sealed with Teflon lined caps and were ready for tumbling.

For the determination of initial concentration of dissolved NOM in mg C/L, a parallel 7 sets of solutions were carefully prepared by pipetting appropriate volumes of NOM stock solution of 50 mg C/L dissolved in 0.01M $NaNO_3$ into 400 mL beakers and diluting to 100 mL to yield a range of concentrations from about 2 mg C/L (5 mg/L NOM) to 32 mg C/L (80 mg/L NOM) (same concentrations as the ones with NPs). The pH of interest was achieved by additions of appropriate volumes of HCL or NaOH solutions (< 100μL). Once the desired pH was achieved and was constant for over 24 h, a sample of 12 mL for each solution was taken for the measurement of total organic carbon. Then, the remainder of contents of each beaker were transferred into the 150 mL amber colored bottles and sealed with Teflon lined caps and were ready for tumbling. A blank solution for each pH was included which contained only 0.01M $NaNO_3$ solution. Then both the bottles containing TiO_2 NPs suspensions and the solutions were tumbled for 120 h (preliminary tests indicated that equilibrium is reached after 72 h). After tumbling, the pH of both the suspensions and the solutions were measured. Then the TiO_2 NPs suspensions of each sample (bottle) were divided into two portions, one portion was filtered through a 50 nm polycarbonate membrane filter and the other was centrifuged using Ultra centrifuge SORVALL EVOLUTION RC S/N 10300582 at 20500 rpm for 2 h and then both portions (filtrates and supernatants) were analyzed for the total organic carbon and the results were compared for agreement. Prior to the filtration of the samples, the 50 nm pore size polycarbonate filter membrane was thoroughly washed with Milli-Q water and then about 3 mL of the suspension was passed through the membrane to ensure that any possible sorbing surfaces were saturated. Once this was done, a well washed and dried vacuum flask was used for the filtration and collection of the filtrate.

The solution of each sample (samples without particles) was divided into 3 portions. The first portion was filtered just as described for the suspension. The second portion was centrifuged just as described above, while the third portion was used directly and all these portions were analyzed for total organic carbon and the results were compared for agreement.

Statistics

The one way ANOVA with Tukey’s pair wise comparisons of means from Origin Pro 8.6 software was used to identify the significant differences between means. The means (each calculated from three replicates) at each pH for three levels of NOM and the means (each calculated from three replicates) at each NOM at three levels of pH were examined for thesignificant difference using this software both stability and sorption studies.

Results and discussion

Point of Zero Charge for TiO_2NPs

The results for the point of zero charge (PZC) for the TiO_2NPs in this study was found as 6.50 (Figure 1). This value is consistent with the literature values that range from 4.20 to 7.5 (Fernandez-Nieves et al., 1998; Kosmulsiki, 2009). However, it is important to note that the PZC for the metal oxide NPs can vary widely depending on several factors such as chemical modification, surface modification, particle size and particle transformation (Hotze et al., 2010, Lin et al., 2010). In this study as indicated under the materials section, the P25 TiO_2 NPs of 50 nm particle size were used and this material (NPs) were manufactured about two years earlier before being used in this investigation. Therefore, a very specific value of PZC for these NPs was needed as an input in the next part of this study. The analysis as described under the methods section was carried out using two runs. The first run was quick and was meant to be a guide for the second run whose value was used for the next part of our study.

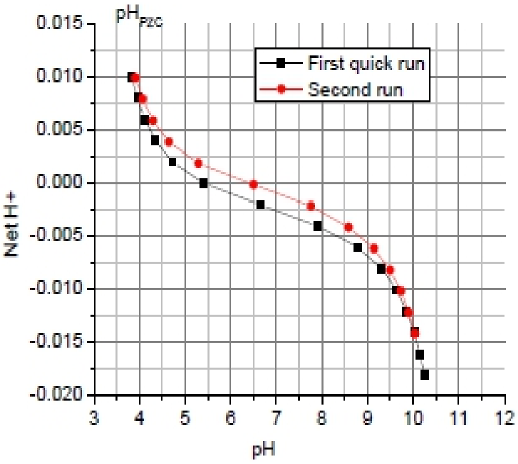


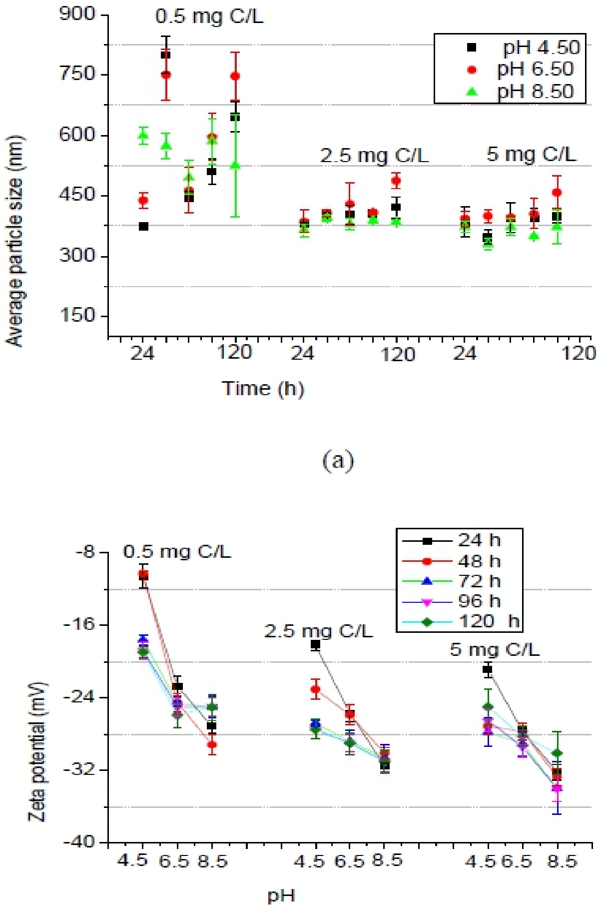
Figure 1: The pH of point of zero charge for TiO_2 nanoparticles

NOM Stability of both sonicated and non-sonicated TiO_2 NPs at different pH values

Based on the PZC for TiO_2 NPs (found as 6.50), three pH values of 4.50, 6.50 and 8.50 were selected (as described under methods section) and used to investigate the ability of dissolved NOM to stabilize TiO_2 NPs at three levels of NOM (0.5, 2.5 and 5.0 mg C/L) for both sonicated and non-sonicated NPs. These results indicated that NOM indeed caused the stability of TiO_2NPs as evidenced by the differences in the average aggregate sizes between the controls and those with NOM (Figures 2 to 5). For the controls, the average aggregate particle sizes were significantly larger than ($p < 0.05$) those treated with NOM and their average aggregate sizes were outside the measuring range (2 nm to 3000 nm). The data also indicated that there were NOM concentration dependent differences in the average aggregate particle sizes. For example, for the sonicated TiO_2 NPs (Figures 2 and 4) at 0.5 mg C/L NOM, the average aggregate particle sizes were significantly larger ($p < 0.05$) than the average aggregate particle sizes at 2.5mg C/L and 5.0 mg C/L NOM for all the three pH values. However, the differences in the average aggregate sizes at 2.5 mg C/L and 5.0 mg C/L NOM for all the pH values (except for pH 6.50 at 120 h at both 2.5 and 5.0 mg C/L NOM) were not significantly different ($p> 0.05$). These results therefore seem to suggest that there is a maximum NOM concentration above which there could be no differences in the TiO_2 NPs stability. Furthermore, at the NOM concentration of 2.5 mg C/L and 5.0 mg C/L, the data suggest that there is pH dependence in the stability of the TiO_2 NPs, although the differences were not statistically significant ($p>0.05$.

For the non-sonicated TiO_2 NPs, the results revealed an interesting and probably most environmentally relevant trend. For example, at 0.5 mg C/L NOM the average aggregate particle sizes (for non-sonicated) were outside the measuring range (2 nm to 300 nm), indicating that this concentration of NOM was unable to stabilize the TiO_2 NPs. However, at the NOM concentrations of 2.5 mg C/L and 5.0 mg C/L, the data showed that NPs stability was achieved and the average aggregate particle sizes for the two concentrations of NOM (Figures 3 and 5) were not statistically different ($p>0.05$). The comparison of the average aggregate particle sizes for the non-sonicated NPs and sonicated NPs showed that the average aggregate particle sizes for the non-sonicated TiO_2 NPs were much larger than the sonicated TiO_2 NPs. These results suggest that in the absence of sonication (like in actual environments), the ability of NOM to stabilize NPs is quite mild and would require large concentrations of NOM to stabilize the NPs. The values of the zeta potential (ZP) for both the sonicated and the non-sonicated TiO_2 NPs were, as expected observed to be getting more negative with increases in NOM and pH (Figures 2b, 3b,4b and 5b). The data also revealed higher variability in the ZP of the non-sonicated NPs than the sonicated NPs. The ZP of the controls (results not shown) was also getting more negative as the pH increased. However, it was particularly interesting to observe that pH dependent ZP had small effect on suspension stability (based on the surface charge of controls), whereas NOM-pH dependent ZP had large effect on suspension stability. The NOM dependent increase in the stability of NPs suspensions could be attributed to NOM sorption to NPs and the higher the NOM concentration the greater the sorption and hence the greater the increase in the stability either by steric repulsion or electrostatic repulsion depending on the pH of the suspensions.

The highest increase in the NPs stability was observed at pH8.50 (trend wise) for all NOM concentrations used and this could be attributed to the electrostatic repulsion of highly ionized NOM adsorbed on the NPs (Yang et al., 2009). The next higher NPs stability was observed at pH 4.50 (trend wise), where the NOM molecules were assumed not ionized in comparison to that at pH 8.50. The NOM-NPs interactions at the pH 4.50 were predominantly hydrophobic and therefore the stabilization was attributed to steric hindrance (Illes and Tombacz, 2006). The least stability was observed at pH 6.50 (the PZC). This was expected since the lowest stability of particles is always around the PZC (Stumm and Morgan, 1981; Illes and Tombacz, 2006). The observed higher variability in the zeta potential of the non-sonicated NPs could be attributed to the greater heterogeneity (non-uniformity) in surface site energies of the NPs (Amal et al., 1990), which could be expected to be higher in the non-sonicated NPs. The use of controls in this study demonstrated that the buffer solutions used in this investigation had no influence on the observed stability of TiO_2 NPs.



(a)

(b)

Figure 2: Effect of pH at constant NOM on particle dispersion (a) and the corresponding zeta potential (b) for sonicated TiO_2 NPs. The error bars indicate the standard deviation of the three replicates (n = 3)

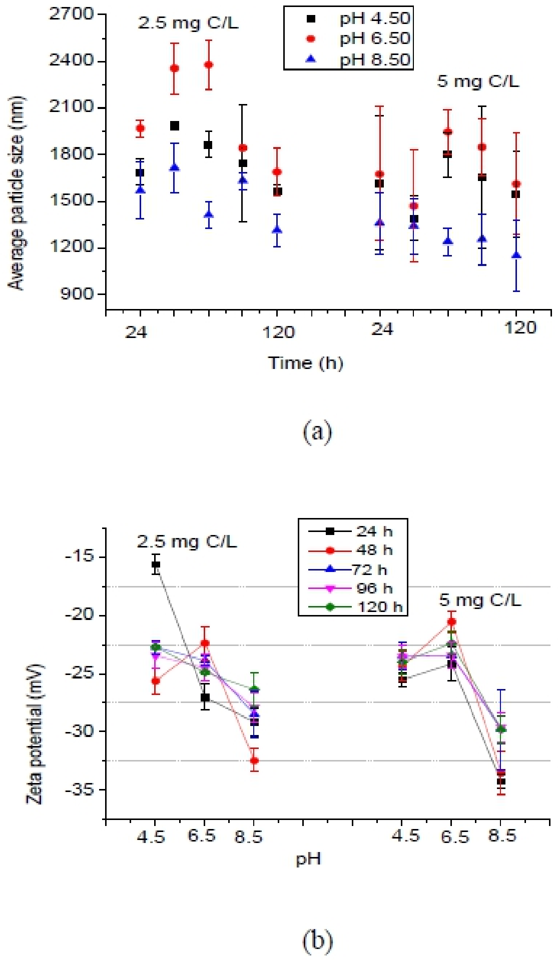
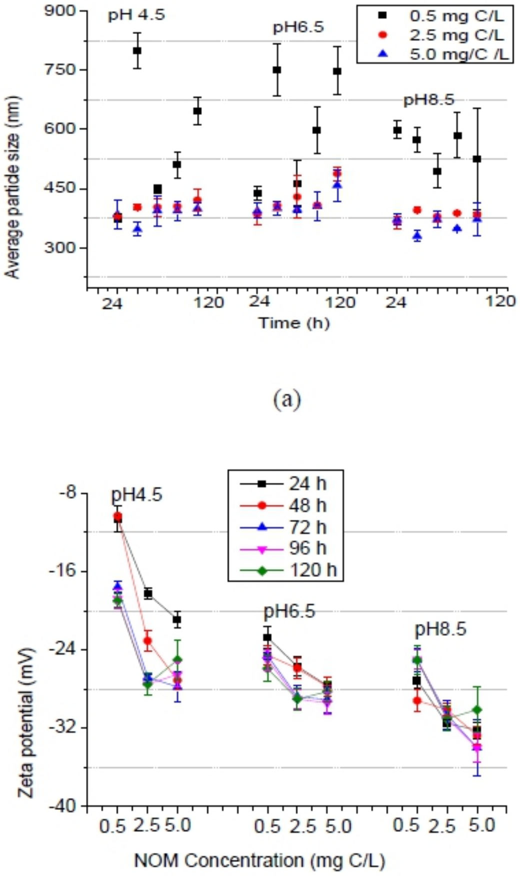


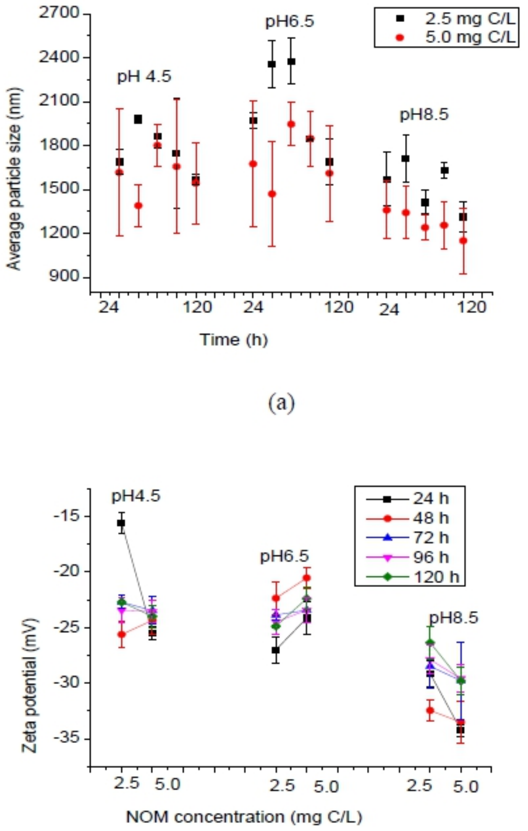
Figure 3: Effect of pH and NOM on particle dispersion (a) and the corresponding zeta potential (b) for non sonicated TiO_2 NPs. The error bars indicate the standard deviation of the three replicates (n = 3)



(a)

(b)

Figure 4: Effect of NOM at constant pH on particle dispersion (a) for sonicated TiO_2 NPs (b) and corresponding zeta potential. The error bars indicate the standard deviation of the three replicates (n = 3)



(a)

(b)

Figure 5: Effect of NOM at constant pH on particle dispersion (a) for non sonicated TiO_2 NPs (b) and corresponding zeta potential. The error bars indicate the standard deviation of the three replicates (n = 3)

Sorption of TiO_2 NPs to NOM at different pH values

Arising from the results of the stability study that indicated that NOM promotes NPs stabilization and that this stabilization is influenced by the pH of the suspension, a study was therefore designed to explain the observed stability in terms of sorption. This was carried out at the three different pH values (same as considered in the stability study). Our hypothesis was that NOM would sorb to NPs more at lower pH than at higher pH values.

The amount of the NOM sorbed to TiO_2 NPs were determined from the difference between the concentration of the initial NOM measured as total organic carbon (TOC) before sorption and the final concentration of NOM when at equilibrium during sorption. The results of the TOC measurements between the filtered and centrifuged suspensions agreed with in a precision of about 2%. The TOC results for the solution of the filtered, centrifuged and the directly measured indicated an agreement within 3% precision. With the agreements of the filtration and centrifugation results being within less than 5% precision, the results were used without any corrections.

The results of this study consistent with our hypothesis, demonstrated that the highest amount of NOM was sorbed to TiO_2 NPs at pH 4.50, followed by sorption at pH 6.50 and the least sorbed was at pH 8.50 (Figure 6). The sorption of the largest amount NOM at low pH can be attributed to the fact that the NOM molecules at low pH were less ionized and the interaction was predominantly hydrophobic with increased van der Waals forces of attraction (O’Melia, 1990). This meant that once some NOM molecules were sorbed further molecules could still be sorbed due to attractive van derWaals forces. At higher pH, the NOM molecules were highly ionized and after initial sorption of NOM to NPs, less sorption could further take place due to electrostatic repulsion and hence the observed low sorption at pH 8.50. At the intermediate pH 6.50, NOM molecules were not completely ionized. There were still some hydrophobic influences and hence some van der Waals forces of attraction, but at the same time some electrostatic repulsive forces were exerting their influence and hence the observed relatively low sorbed NOM compared to pH 8.50.

The relationship between the surface charge (ZP) and the amount of the NOM sorbed at the three pH values considered in this study was further examined. As expected the results indicated that the surface charge (zeta potential) was more negative at pH 8.50 and corresponded to the least amount of NOM sorbed (Figure 7). The surface charge at pH 4.50 was the least negative and corresponded to the highest amount of NOM that was sorbed. Therefore the stability of NPs was due to NOM sorption and when taken together, the stability and the sorption results suggest that stabilization of the TiO_2 NPs suspension is more effective with NOM electrostatic repulsion than with the NOM steric hindrance.

The sorption data was fitted to the nonlinear Langmuir model. The model described the experimental data at all pH values fairly well as shown in Figure 8. However, the fundamentals or the basic concepts of the Langmuir cannot be said to have been met at all the three pH values. However, based on the sorption data, it can probably be argued that the basic concepts of the Langmuir adsorption isotherm were fulfilled (fixed adsorption sites, equal surface energies and no interaction between sorbed molecules) at pH 8.50 where the sorption was assumed predominantly electrostatic. But at pH 4.50 and pH 6.50 the Langmuir adsorption isotherm was probably not met as the interaction could have involved hydrophobic moieties of NOM through van der Waals attraction. The model was used to estimate the values of the total amount of sorbate that could be sorbed at equilibrium (Q_{max}) and the Langmuir constants (K_L) for each pH studied. At pH 4.50, the Q_{max} and the K_L were found as 14.8 mg NPOC/g TiO_2NPs and 0.36 respectively. While at pH 6.50, the Q_{max} and the KL were found to be 10.4 mg NP OC/g TiO_2 NPs and 0.22 respectively, and at pH 8.50, the Q_{max} and the K_L were found as 2.4 mg NP OC/g TiO_2 NPs and 0.15 respectively. These values were consistent with the observed experimental results which showed higher sorption for lower pH and lower sorption for higher pH.

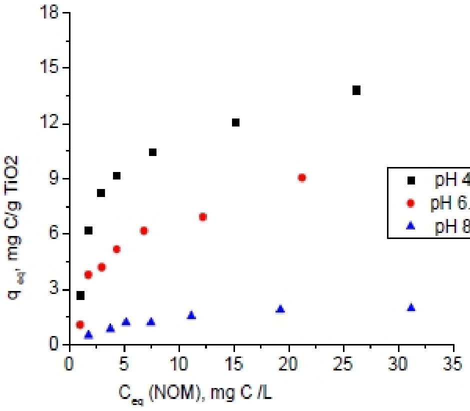


Figure 6: Sorption of NOM to TiO_2 nanoparticles at different pH values

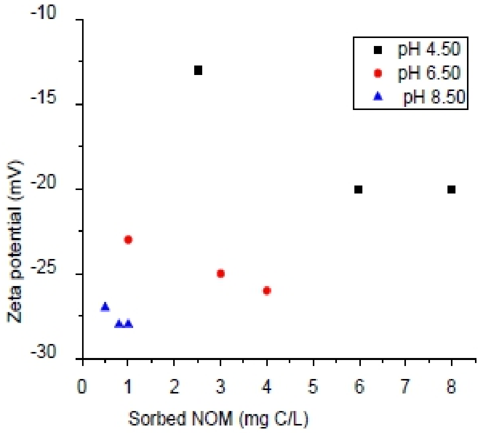


Figure 7: Relationship of zeta potential and adsorbed amount of NOM at given pH

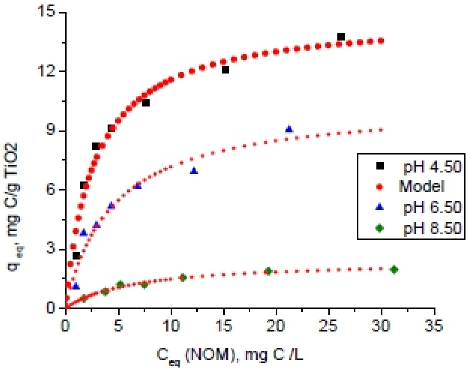


Figure 8: Fit of sorption experimental data to nonlinear Langmuir adsorption isotherm

Conclusion

The NOM-NPs interaction in aqueous medium can result in several outcomes. For instance, it can lead to enhanced stability of NPs and hence increased residence time and increased transportation within the aqueous environment. The results of this study have demonstrated that the stability of TiO_2 NPs upon interaction with NOM was due to the sorption of NOM. The data also demonstrated that the NOM concentration was critical in promoting NP stability. The results further suggest that the stability is pH dependent and that it is much higher at higher pH than at lower pH values. According to the sorption study, the amount of NOM sorbed was however, demonstrated to be higher at the lower pH than at higher pH values. With non-sonicated TiO_2 NPs, barely stabilized, this study would also suggest that when NPs are aggregated whilst in powdered form, breaking them apart required much more energy than could possibly be supplied by NOM.

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