

Aggregation and Stability of Iron Oxide and Alumina Nanoparticles: Influences of pH and Humic Acid Concentration

(Pengagregatan dan Kestabilan Oksida Besi dan Zarah Nano Alumina: Pengaruh pH dan Kepekatan Asid Humik)

NUR SURAYA AHMAD*, SHAHIDAN RADIMAN & WAN ZUHAIRI WAN YAACOB

ABSTRACT

The scenario of released nanoparticles from consumer products into the environment especially natural waters has become a great concern nowadays. Assessing their aggregation and stability under environmental conditions is important in determining their fate and behavior in natural waters. The aggregation behavior of selected nanoparticles (iron oxide and alumina) was investigated at variable concentrations of humic acid (5, 10, 50 mg/L), and pH variation in solution. Dynamic light scattering was used to measure their z-average hydrodynamic diameter and zeta potential. Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was used to explain the thermodynamic interactions between two particles. Then, the stability was evaluated by assessing their aggregation. The increasing of humic acid concentrations enhanced aggregation of iron oxide and alumina nanoparticles, particularly at low pH levels. The maximum aggregation was found in pH below the point of zero charge (PZC) due to electrostatic destabilization and electrostatic stabilization that took place at pH above the point of zero charge. Meanwhile, at pH point of zero charge, nanoparticles were coated with negative humic acid charged. From this study, properties of nanoparticles (size, surface charge, Hamaker constant) and environmental condition (humic acid concentration, pH) have their specific roles to control the fate and behavior of nanoparticles in environmental media.

Keywords: Aggregation; DLVO; nanoparticles; stability

ABSTRAK

Pada masa ini, peningkatan senario pelepasan zarah nano daripada produk pengguna ke persekitaran terutamanya ke dalam air semula jadi amatlah membimbangkan. Penilaian agregasi dan kestabilan zarah nano adalah penting untuk menentukan keadaan dan tingkah lakunya di dalam kandungan air semula jadi. Kajian mengenai tingkah laku agregasi zarah nano (oksida besi dan alumina) pada pelbagai kepekatan asid humik (5,10,50 mg/L) dan pH yang berlainan dijalankan. Penyerakan cahaya dinamik digunakan untuk mengukur purata diameter hidrodinamik dan nilai keupayaan zeta. Teori Derjaguin-Landau-Verwey-Overbeek (DLVO) digunakan untuk menerangkan tindak balas termodinamik antara dua zarah. Kemudian, kestabilan dinilai berdasarkan tingkah laku agregasi. Peningkatan kepekatan asid humik telah menggalakkan/meningkatkan tingkah laku agregasi zarah nano oksida besi dan alumina pada pH yang rendah. Agregasi maksimum dijumpai pada pH di bawah caj titik sifar yang disebabkan oleh ketidakstabilan elektrostatik dan kestabilan elektrostatik dilihat berlaku pada pH di atas pH caj titik sifar. Manakala, pada caj titik sifar, zarah nano disaluti dengan caj asid humik yang bersifat negatif. Keputusan daripada kajian ini mendapati sifat zarah nano (saiz, caj permukaan, pemalar Hamaker) dan keadaan persekitaran (kepekatan asid humik dan pH) memainkan peranan yang penting dalam mengawal keadaan dan tingkah laku zarah nano pada medium sekitaran.

Kata kunci: Agregasi; DLVO; kestabilan; zarah nano

INTRODUCTION

The scenario of released manufactured or engineered nanoparticles (ENPs) into environment especially natural waters is heavily concerned nowadays. This scenario provokes questions regarding the fate and behavior of nanoparticles in environmental media. Nanoparticles are released into the environment during the production, transportation, consumer usage and/or disposal of the products (Hotze et al. 2010). Nanoparticles that have been released into the environment are as results of remediation, agricultural or water purification purposes (Wagner et al. 2014) while the unintentional releases are

such as atmospheric emissions, solid or liquid wastewater streams from production sites (Bhatt et al. 2011). This entire scenario create a huge dilemma when it comes to preservation of green environment.

A critical review on the release of ENPs to the environment can be found in the recent literature (Gottschalk et al. 2013, 2011; Keller et al. 2013; Maurer-Jones et al. 2013). Silica, titania, alumina, iron and zinc oxide have been nanoparticles frequently been used in coating or pigments or paintings, electronics and optics, cosmetic, energy and environmental applications in 2010 (Keller et al. 2013). Approximate 63-91% of 260 000

- 309 000 metric tons of ENPs production ended up in landfills, 8-28% into soils, 0.4-7% in water bodies and 0.1-1.5% into the atmosphere (Keller et al. 2013). Iron oxide (Fe_2O_3) is one of the common nanoparticles, used in environmental remediation application including for contaminated land, soil and groundwater (Chekli et al. 2013a; Zhang et al. 2003). Aluminium oxide (Al_2O_3) is considered as significant due to its widespread use as catalyst, abrasive agent and insulator (Ghosh et al. 2010). Colloidal silica particles are widely exploited in many industrial applications, for example, polishing slurries, catalyst, composite coating, adsorbent, ceramics, chromatography and carrier in biomolecular transport (Barisiti et al. 2014; Kobayashi et al. 2005). The concentration of nanoparticles in surface water is predicted to increase over time with a greater use and disposal of products containing ENPs (Klaine et al. 2008).

Nanoparticles can naturally be founded in the environment but they often disappear from the environment by the natural process. Otherwise, the ENPs may undergo reactions with other materials lingering in the environment. The possible interactions that may occur when ENPs present in the environment are physical, chemical and biological transformations (Omar et al. 2014b). These interactions are expected to control the fate and behaviors of ENPs in the environment. Some ENPs may contain toxic components and have ability to significantly affect the environment. An aquatic environment that contains ENPs can result in adverse effects on cell and organs, accumulated by the organism and have a possibility to enter into human food chain or drinking water sources.

Because of increasing NPs concentrations in surface water, it is important to understand their interaction with natural water components such as natural colloids. Natural colloids can be defined as materials that are naturally produced by the process of weathering, microbial process and plant decomposition (Lead et al. 2006). Natural colloids are ubiquitous and exhibit high reactivity in the environment (Yang et al. 2009). They usually have at least one dimension in size in a range of 1 to 1000 nm (Lead et al. 2006). One of the major components of natural colloids is natural organic matter (NOM) (Buffle et al. 1998). NOM is a large organic compounds family that comprise of a wide range of molecules and macromolecules (Klaine et al. 2008; Wagner et al. 2014). Approximately 50-80% of the NOM in natural water are made up by humic substances (Buffle et al. 1998). Humic acid has a stabilizing effect on most nanoparticles (Fritz & Reinhard 2010) and adsorption of humic acid on NPs will enhance toxicity to aquatic life due to the dispersion of small particles in natural water (Hoecke et al. 2011).

Once adsorption of humic acid on NPs were formed, they will be able to undergo an aggregation due to the interaction with other natural NPs or larger particles (Nam & Lead 2008). It can facilitate the transportation of contaminants in the environment (Nam & Lead 2008).

Nanoparticles that are released into the environment has high impact on the transportation of low solubility contaminant due to aggregation and stabilization (Chekli et al. 2013a). Aggregation is the phenomenon that occurs when particles collide and stick to each other to form larger clusters and it can be determined by the total interaction energy between particles (Romanello et al. 2013; Therezein et al. 2014). Nanoparticles stability is achieved when the small particles have the ability to remain in suspensions (Hu et al. 2010) and stay separate with each other (Dickson et al. 2012). The stability controls the transportation, fates of NPs and low solubility contaminants in natural porous media (soils and groundwater aquifer) and natural water systems (lakes, rivers). Unstable suspensions will form large aggregate and settle down to the sediments.

Nanoparticles that are exposed to the environment may undergo surface modifications, depending on the nature, availability and concentration of NOM (Ghosh et al. 2010). The interaction between humic acid and nanoparticles in aqueous media is essentially influenced by several factors. Environmental conditions (pH value, ionic strength and NOM concentration) and properties of the nanoparticles (surface charge, size) have shown significant influences on the stability of particulate suspensions (Wagner et al. 2014). At high pH and low ionic strength, functional groups are fully ionized and the charges linked by organic structure tend to move as far as possible from each other (Tombacz et al. 2000).

Several reports on fate and behavior of TiO_2 (Almusallam et al. 2012; Erhayem & Sohn 2014; Loosli et al. 2013), Fe_2O_3 (Baalousha 2007; Chekli et al. 2013a, 2013b) and ZnO (Omar et al. 2014a, 2014b) NPs can be found in literature. Based on previous researches on Fe_2O_3 , factors that influenced the aggregation and stability were pH, NPs concentration and NOM concentration. Generally, there is a lack of knowledge about NPs behavior under environmentally relevant conditions of pH, ionic strength and natural organic matter concentration. Thus, the objective of our study was to investigate the aggregation and stability (physical transformation) of iron oxide (Fe_2O_3) and alumina (Al_2O_3) by considering humic acid concentration, nanoparticles concentration and a wide pH variation in solution. Unlike previous work, our experimental study used nanoparticles that readily available in powder forms that later on directly added into the humic acid solution.

MATERIALS AND METHODS

NANOPARTICLES

Two types of commercial nanoparticles (Fe_2O_3 , Al_2O_3) were purchased from Sigma-Aldrich (Malaysia) in the form of powder. The diameter sizes of two nanoparticles, given by supplier were < 50 nm for Fe_2O_3 (BET) and < 50 nm for Al_2O_3 (TEM). Humic acid was also purchased from Sigma-Aldrich (Malaysia).

HUMIC ACID CONCENTRATION

A stock solution with a concentration of 1 g/L was prepared by dissolving humic acid (HA) in deionized water for 24 h. The stock solution was then filtered through a 0.45 μm filter paper using vacuum suction and stored at 4°C prior to experimental use. HA solutions were freshly prepared by diluting the readymade stock solution with deionized water to obtain 5, 10, and 50 mg/L for each experimental use.

HUMIC ACID-NANOPARTICLES SUSPENSIONS

Five, ten, and fifty mg/L concentrations of HA were obtained by diluting the readymade stock solution with deionized water. Ionic strength of humic acid was adjusted to 0.01 M. The experiment was continued by adding 10 mg of Fe_2O_3 or in the humic acid solution. The solution was stirred for 24 h at a room temperature. A fresh aliquot of sample with different pH (pH3-9) was prepared. 0.1 M hydrochloric acid (HCl) or 0.1 M sodium hydroxide (NaOH) was added later on and adjusted until a required pH was obtained. As a precaution step, HCl or NaOH was added a drop at a time and there was no case in which both acid and base were added. To ensure the stability of sample, the suspensions solution was left 24 h and then centrifuged at 3000 rpm for 10 min before measurements were made.

CHARACTERIZATION OF NANOPARTICLE SUSPENSIONS Z-AVERAGE HYDRODYNAMIC DIAMETER AND ZETA POTENTIAL MEASUREMENTS

The z-average hydrodynamic diameter and zeta potential of solutions were measured by Dynamic Light Scattering (DLS) technique with Zetasizer nano ($\lambda = 633 \text{ nm}$, Malvern Instrument). DLS theory, physical principles and system have been described elsewhere (Chekli et al. 2013b; Omar et al. 2014a). To determine the z-average hydrodynamic diameter, an aliquot of 2 mL of suspension solutions was injected into 12 mm o.d square polystyrene cuvettes (DTS 0012) and conducted for 5 min at 25°C (room temperature). Three measurements for each suspension solution were performed. According to Smoluchowski's equation, zeta potential can be determined by electrophoretic mobility ($\mu\text{mcm/Vs}$). Zeta potential measurement was conducted with folded capillary zeta cell (DTS 1070). Triplicate measurements were performed for each suspension solution at 5 min at room temperature and an average of zeta potential was recorded.

DLVO CALCULATIONS

The Derjaguin-Landau-Verwey-Overbeek (DLVO) model is the most widely used model to describe the thermodynamic interaction between two particles in a suspension. In other words, DLVO theory is employed to explain the aggregation behavior and stability of nanoparticles in suspensions (Peters et al. 2012). This theory predicts the probability of two particles sticking together by the sum of van der Waals (V_{vdw}) force and electrostatic repulsive (V_{edl}) forces to get the total interaction energy (V_t). The sum of these two

forces determines if the net interaction between particles is repulsive or attractive. In short, if total interaction energy is negative, it represents the van der Waals that is more dominant than electrostatic repulsive force, hence it will be more net attractive and vice versa.

$$V_t = V_{\text{vdw}} + V_{\text{edl}} \quad (1)$$

DLVO calculations formula is expressed as the following according to Elimelech et al. (1995). The van der Waals attractive energy and electrical double layer repulsive energy is expressed as follows,

$$V_{\text{vdw}} = \frac{A_h r}{12s} \quad (2)$$

$$V_{\text{edl}} = 2\pi e r \gamma^2 e^{-ks} \quad (3)$$

In which A_h is the Hamaker constant. $2.5 \cdot 10^{-19}$ for Fe_2O_3 (De Mesquita et al. 2003) and $1.5 \cdot 10^{-19}$ for Al_2O_3 (Medout-Marere 2000); r (m), is the radius of particles; s (m), separation distance between the surfaces of interacting particles; e , elementary charge of an electron; k , Debye length; γ , zeta potential.

RESULTS AND DISCUSSION

IRON OXIDE NANOPARTICLES SUSPENSIONS

Figure 1 shows the z-average hydrodynamic diameter of Fe_2O_3 NPs suspension as a function of humic acid concentration at a variety of pH values in the range between pH3 and pH9. As pH increases in the suspensions, the z-average hydrodynamic diameter decreases for all concentrations of humic acid (HA). Significant aggregations of 5 and 10 mg/L of humic acid concentration were found between pH3 and pH4. This was due to charge neutralization between positive charges of Fe_2O_3 and negative charges of HA. Large humic acid was coated with Fe_2O_3 nanoparticles at pH3 and 50 mg/L concentration of humic acid that produced large and small aggregates. Large aggregate settled down as sediment and can be observed with naked eyes while small aggregate was observed in Figure 1, increasing humic acid concentration made z-average hydrodynamic diameter to become smaller due to stabilization process (pH5 - pH9). Fast sedimentation (within a few minutes) occurred in the low pH levels (3-4), whereas for high pH levels (5-9), an hour is necessary in order to see sedimentation.

Humic acid covered the surface of Fe_2O_3 NPs and adsorbed onto the particles thereby conferring negative surface charge across a wide range of pH values (Figure 2). Humic acid has a negative zeta potential at a whole pH while Fe_2O_3 has a positive zeta potential below PZC and negative charges above PZC with PZC at around pH7 (Chekli et al. 2013b). PZC is a pH at which particle surface is zero due to the absence of any positive and negative charges. The adsorption of HA to the surface of

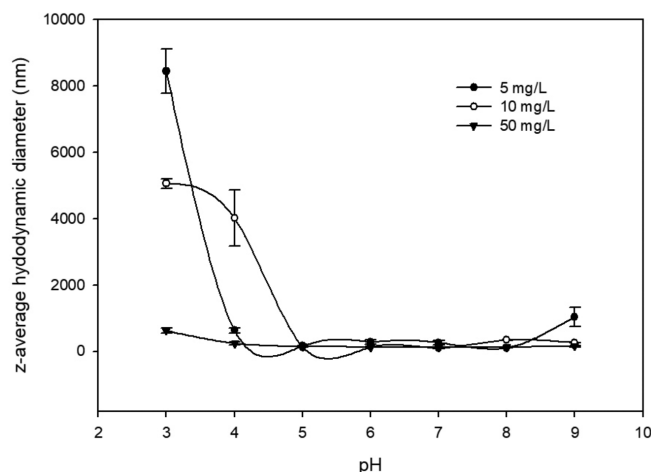


FIGURE 1. Z-average hydrodynamic diameter of Fe_2O_3 nanoparticles suspension solution as a function of pH. Heavy aggregation (unstable suspension) occurs at pH3 and pH4

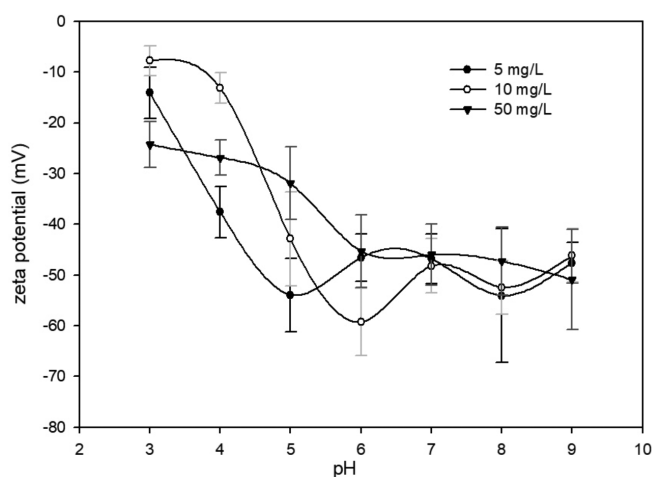


FIGURE 2. Reduction in the zeta potential of Fe_2O_3 nanoparticles suspension solution with an increase in pH due to humic acid adsorption

individual Fe_2O_3 NPs can enhance their surface charge and stability. Hence, it will shift the isoelectric point and maximum aggregation will occur at lower pH values (Illes & Tombacz 2006). At pH below PZC, Fe_2O_3 NPs are positive. Then, the adsorption of HA will neutralize the positive charges and induce electrostatic destabilization. In short, electrostatically destabilization happens when particles are initially having positive charges. At PZC, the adsorption of HA imparts more negative surface charges onto Fe_2O_3 due to intrinsic negative charges of HA. While at pH above PZC, electrostatic stabilization occurs because Fe_2O_3 are negatively charged and as showed by a low of zeta potential value. Magnetic forces between particles also occur when pH of the solution approaches PZC (Labille & Brant 2010), which influences the aggregation behavior of the Fe_2O_3 nanoparticles.

From zeta potential graph (Figure 2), pH5 and above have a zeta potential less than -30 mV for all humic acid concentrations. As a rule, zeta potential values below -30 mV will provide sufficient force to keep NPs in a

suspension and stabilization. As a proof, it can be observed in z-average hydrodynamic diameter result (Figure 1).

Plotted in Figure 3 are the DLVO interaction energy profiles for Fe_2O_3 NP-NP interaction as a function of pH and humic acid concentration. The DLVO theory-explains the stability of nanoparticles dispersion in humic acid conditions. High attraction forces dominated at pH3 (5 and 10 mg/L of humic acid concentration), resulting in the formation of large aggregate and have a low negative value of zeta potential. This can be explained according to DLVO theory as the significant decreases in surface charges and NP aggregates in diffusion-limited aggregation mode, which implies that each collision between primary and/or aggregates leads to particles sticking. Interaction energy decreases and approaches zero with increasing pH and humic acid concentration. Starting at pH5, the particles become highly negatively charged (Figure 2) and decreases van der Waals forces between the particles. Although the negative interaction energy exists, however, it is too low to enhance the aggregation of nanoparticles

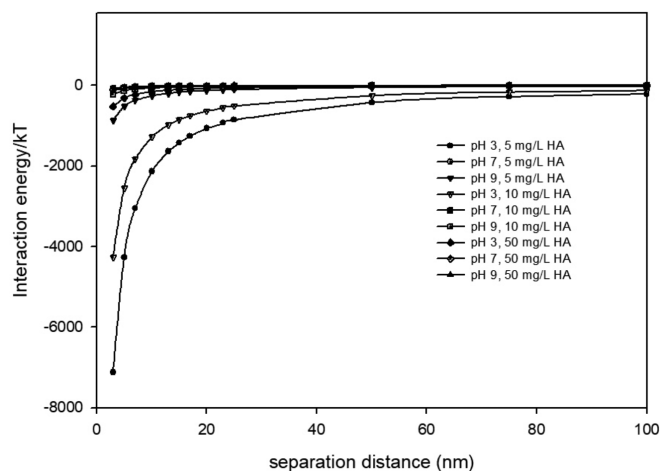


FIGURE 3. Interaction energy between Fe_2O_3 nanoparticles as a function of pH and humic acid concentration

that have enough energy to prevent their aggregation. From profiles of z-average hydrodynamic diameter, zeta potential and interaction energy, at low pH, nanoparticles will be aggregated and there is a tendency to settle down as sediment high. While at high pH levels which is in natural water pH range, nanoparticles are stable and mobile.

ALUMINA NANOPARTICLES SUSPENSION

Figure 4 demonstrates that coagulation occurs in pH3 - pH5 at high concentrations of humic acid (10 and 50 mg/L). Coagulation is a process in which colloidal particles come together irreversibly to form larger masses, thus, destabilize the colloids. Destabilization occurs when the charge is neutral and the coating of aluminium by humic substances happen at a high concentration of humic acid. The adsorption of humic acid on positively charged Al_2O_3 occur at acidic pH and the addition of a small quantity of

humic acid at a very low ionic strength may also destabilize Al_2O_3 NPs (Ghosh et al. 2010). As the pH increases, the z-average hydrodynamic diameter becomes smaller and it will be stabilized in the suspensions.

Adsorption of negative humic acid charges took place on positively charged of Al_2O_3 below pH point of zero charged (PZC). Figure 5 shows that when the pH is below than pH5, the zeta potential value is above than -30 mV for all concentration of humic acid. This is due to the dominant neutral charge and electrostatic attractive force of nanoparticles itself that induce the aggregation. That interaction has encouraged the coagulation process to take place and destabilize the nanoparticles. This result is consistent with a z-average hydrodynamic diameter in Figure 4. Above pH point of zero charges, Al_2O_3 NPs have been negatively charged. Humic acid will coat NPs and enhance colloidal stability at the point of zero charges (pH6 - pH9) (Philippe et al. 2014) and above through

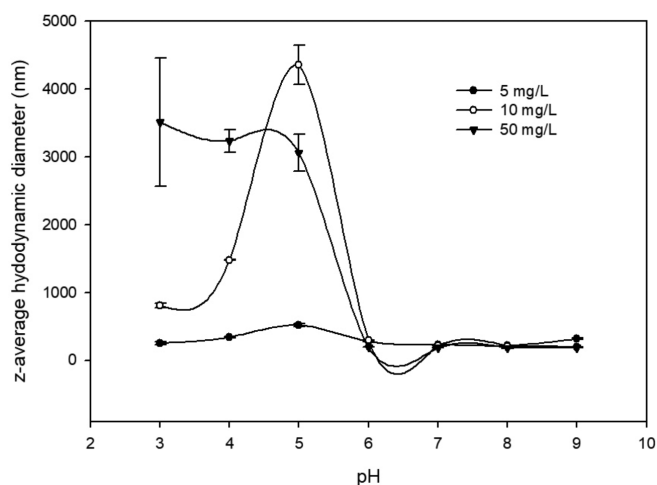


FIGURE 4. Z-average hydrodynamic diameter of Al_2O_3 nanoparticles suspension solution as a function of pH. Maximum aggregation (unstable) occurs at pH4 and pH5 (10 and 50 mg/L) and decrease with increasing pH

electrostatic repulsive forces and/or steric repulsion. Based on z-average hydrodynamic diameter and zeta potential value result for suspensions at pH6 and above, the size of particles is small (< 315 nm) and zeta potential value is below -30 mV. The size and zeta potential confirm that the particle has an ability to remain in suspensions, stay separated from each other and it will be stabilized in the suspensions.

According to DLVO theory, when high attraction forces are dominated, then the formation of aggregate occurs. From DLVO model in Figure 6, aggregation between Al₂O₃ nanoparticles occurs at pH3, at 5 mg/L and 10 mg/L concentration of humic acid. The interaction energy decreases and approaches zero with increasing of pH and concentration of humic acid. Although interaction energy exists, however, it is too weak to enhance the aggregation process, thus, not enough to form aggregate and make Al₂O₃ stable in the solution. Based on z-average hydrodynamic diameter (Figure 4), zeta potential (Figure 5)

and interaction energy profiles (Figure 6), the researchers conclude that nanoparticles will be aggregated and settle down as sediment at low pH levels (pH3-pH5). While at high pH which is pH range for natural water, nanoparticles are stable, mobile and transported.

CONCLUSION

There are two factors that influence the physical transformation of nanoparticles: Humic acid concentration and pH of the suspension. It is the fact that, the typical environmental concentration of humic acid and low ionic strength (0.01 M) of natural water are sufficient to stabilize the nanoparticles. Generally, pH levels of natural waters are in the ranges of 5.5 - 8.5 (Almusallam et al. 2012). At pH lower than natural waters, the researchers found Fe₂O₃ and Al₂O₃ nanoparticle has similar behaviors. They rapidly aggregate, unstable and finally settle down as sediment.

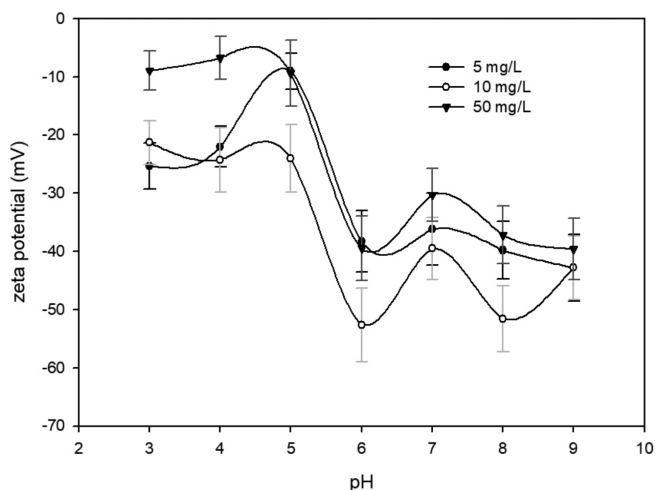


FIGURE 5. At pH6 and above, Al₂O₃ are highly negative charge and nanoparticles will be stable in the suspension

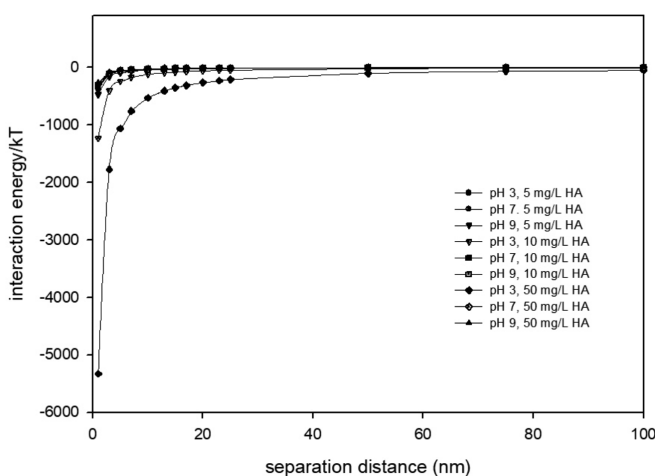


FIGURE 6. Interaction energy profiles for Al₂O₃ as a function of pH and humic acid concentration according to DLVO theory

Humic acid consists of the abundance of carboxylic and phenolic functional groups. It exists as negative charge. The small amount of humic acid are sufficient to interact with nanoparticles. At low pH levels (pH3-5), the interaction between nanoparticles that have a positive charge is controlled/governed by attractive forces which are van der Waals interaction and reduced electrostatic repulsive forces. Fe₂O₃ and Al₂O₃ have a negative charge in most environmentally relevant pH (i.e. pH6-pH8) conditions and electrostatic repulsive forces take place.

The stability of nanoparticles in water is related to its Hamaker constant (Zhang et al. 2008). At the same solution and surface chemistry, particles with low Hamaker constant have lower aggregation tendency, compared with particles with a high Hamaker constant (Hotze & Lowry 2010). Iron oxide (2.5 10⁻¹⁹) has a high Hamaker Constant, compared with alumina (1.5 10⁻¹⁹). Nanoparticles properties (type, surface charge, size particles) need to be carefully considered before releasing nanoparticles in the environment. Typical conditions of environmental (i.e. humic acid concentration (Baalousha 2007; Omar et al. 2014a)), low ionic strength (Philippe et al. 2014), pH range 6-8 (Baalousha 2007; Chekli et al. 2013a) help the stabilization of nanoparticles.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support received from Universiti Kebangsaan Malaysia (UKM) under grant UKM-AP-2015-006 and Center for Research and Instrumentation (CRIM) for the support given.

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Nur Suraya Ahmad* & Shahidan Radiman
 School of Applied Physics
 Faculty of Science and Technology
 43600 UKM Bangi, Selangor Darul Ehsan
 Malaysia

Wan Zuhairi Wan Yaacob
 School of Environmental and Natural Sources Sciences
 Faculty of Science and Technology
 43600 UKM Bangi, Selangor Darul Ehsan
 Malaysia

*Corresponding author; email: nursoraya_ahmad@siswa.ukm.edu.my

Received: 2 May 2018

Accepted: 19 October 2018