CHARACTERIZATION AND TRANSFORMATION OF SILICON DIOXIDE NANOPARTICLES IN AQUEOUS SUSPENSIONS: INFLUENCE OF pH IN DI WATER AND TAP WATER

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ABSTRACT

Silicon Dioxide (SiO_2) in nanoscale had been discharged as waste product into the river water for about two decades since the dawn of nanotechnology and it is proven to have adverse effects recently to human and animals' health, ecosystem and water treatment system. The removal of SiO_2 Nanoparticles (NPs) from water was still a challenge nowadays due to its small size and unknown interactions with the water body. In this study, dynamic light scattering (DLS) technique was applied to characterize SiO_2 in terms of surface charge and particle size as a function of pH within the range of 2.5 to 11 to find out the aggregation behavior and significance of the intermolacular interactions in deionized (DI) water and tap water. DLS analysis identified both pH of the point of zero charge (pH_{PZC}) of SiO_2 NPs in DI water and tap water at pH 3.2 and pH 2.8 respectively. The initial pH was discovered at 7.1 in tap water with the mean particle size of 346 nm and an average surface charge value of -27 mV compared to initial pH of DI water which was 5.4 with mean particle size of 295 nm and an average surface charge value of -33 mV. It was found that both in DI water and tap water, SiO_2 NPs were aggregated and increased in particle size but reduced in surface charge when pH is slowly decreasing towards their own pH_{PZC} from initial pH by adding 0.25M of hydrochloric acid. The mean particle size at pH_{PZC} in DI water is larger than tap water by around 1750 nm was found out and indicated that unknown substances in tap water interfered on aggregation. In conclusion, results suggested that pH will influence the surface charge of SiO_2 NPs and affect the aggregation behavior and the interaction with water.

Keywords: Dynamic Light Scattering, SiO_2, surface charge, particle size, pH.

INTRODUCTION

For the last two decades, nanotechnology industries had keep on increasing the production of nanomaterials, it is undeniable that there are by-products of these engineered nanoparticles (ENPs) had been unintentionally release as waste to river and sea water which some of them already reside in certain level in our drinking waters [4, 13]. These nanoparticles in industrial effluents able to build up into the human body through skin contact, inhalation of gas released from water, direct ingestion of water polluted with nanoparticles, or indirect exposure from eating vegetables and aquatic life such as fish, shrimps and octopus as food [4].

The investigation of hazards towards humans and animals brought by the risks of nanoparticles is still ongoing and remains as a challenge even though there are plentiful applications to be used [16]. However, there are properties of nanoparticles that might give negative effects to human body and animals. The very large surface area of these nanoparticles can generate harmful oxyradicals with other chemical substances; that can cause cytotoxicity. In addition, the nanoparticles have the ability to penetrate the body and cells thus provide potential ways for the delivery of nanoparticle-associated toxic pollutants to places where they would not go under usual condition [13]. As a result, nanoparticles can act as a vector for concentrated hazardous compounds [12].

In this study, the main focus of the nanoparticles to be investigated is silicon dioxide (SiO_2) in water. The main reason SiO_2 nanoparticles (NPs) is chosen because of the very large quantities of it is produced every year (10^2-10^3 ton/year) [11] compared to other categories and types of nanoparticles such as pure metallic nanoparticles, metallic oxides or oxy-hydroxides and carbonaceous nanoparticles. Although most of the contribution of SiO_2 NPs come from the discharged of semiconductor industries, SiO_2 NPs will be a major issue to environmental pollution and might give negative effects to our health because it have been widely used in our daily lives as well since the dawn of nanotechnology as nanomaterials in food products, paints, cosmetics, and biomedical applications such as drug delivery and multimodal imaging. Although there are still lack of toxicological data about the danger possessed by SiO_2 NPs in food and drinks, there are more and more researches shown that it might had the toxicity. For example, it showed the potential adverse impacts on human gut in one of the research [21]. Currently, the only regulation related to safety of using silica in food is only established by U.S. Food and Drug Administration (FDA) under 21 CFR, which the silica content should not be more than 2 % of food weight.

Recently, SiO_2 NPs in water not only found out to be dangerous to human health, but also had brought negative effects towards ecology system, animal health as well as water treatment process. It was discovered that SiO_2 NPs affects the health and behavior of Zebrafish Embryos and Larvae [7] and causes renal and kidney disease to buffalo [18]. Because of their small size, SiO_2 NPs surpasses conventional water treatment processes thus make them hard to be removed from water. This is also due to nanoparticles have specific properties because of their surface area over volume ratio make them mix with other substances in water. It clogs water pipes [2] and cause low separation efficiency [12]. It is also one of the most common foulant for membrane fouling [22].

Therefore, the development of specific treatments (e.g. coagulation, flotation or filtration) and suitable additives for water consisting nanoparticles is necessary. In 2007, the treatment of CMP effluents contain silica nanoparticles by chemical coagulation with polyaluminium chloride (PAC) has been studied [3] but it causes a bulky sludge. In 2012, investigation of the coagulation and flocculation of nanosilica by some organic polymers had been carried out but the efficiency does not meet expected results [1]. In the same year as 2012, $AlCl_3$ was used as cationic surfactant but a lot of coagulants required to remove silica from water [11]. In 2013, aggregation by cationic surfactant cetyltrimethylammonium bromide (CTAB) had been investigated and appeared to have a better removal but nano-size smaller than 30 nm had found out to be difficult to remove [12]. Meanwhile, other researches had been done to remove SiO_2 from water such as coagulation process, reverse osmosis process, micro-buble flotation technology, electrocoagulation technology, suppression technique with chemical scale inhibitor and ion exchange technology but all the results remain to be less efficiency or uneconomically [24].

Summarily, due to the separation of SiO_2 NPs from water is difficult and have major adverse impacts to environment and health, it is important to study the fundamental of nanoparticles life cycle in water before efficiently removing them from the water. However, the fate of nanoparticles in actual aquatic environmental system is complex and hard to predict because of many factors. According to Zhang et al. [23], the transformation of ENPs in water is determined by three main root causes: (1) aqueous solubility; (2) possible chemical reaction of the nanoparticles with the aquatic system; and (3) their interaction with biological system in the environment. The three factors establish that the significant of the environment conditions ENPs had to react such as pH, ionic composition, ionic strength, salinity, natural organic matter content, liquid motion and other properties that may alter the characteristics of ENPs. However, the types and behaviour of ENPs are important to change the fate of ENPs as well [14]. Nanoparticle behaviour is based on its unique particle properties such as its dimensions, structure, chemical composition and zeta potential as well as state of particle whether it is free or matrix incorporated while discharge into the aquatic system [14]. After knowing the properties and behaviour of ENPs in different environmental conditions, the interactions of particles with itself or aggregate with environmental surface will be discovered and only then their fate in the environment can be anticipated [15]. In this study, solution pH had been selected among all those factors as the manipulated variable in order to identify the basic characteristic of SiO_2 NPs in deionized (DI) water and tap water by measuring the surface charge and particle size distribution.

METHODOLOGY

Sample Preparation

Silicon dioxide was purchased from R&M Chemicals, United Kingdom in the form of nanopowder with 99.0% purity and below 1000 nm diameter size. SiO_2 nanoparticle powder was added to a background solution (deionized water at >18.2 MΩ, Purelab Option-Q, ELGA) for DI water sample and (Tap water collected at Civil Engineering School of Universiti Sains Malaysia) for tap water sample to make a 100 mg/L solution for each experiment. Ultrasonication was then done using an ultrasonicator (Elmasonic E Ultrasonic Bath E30H) for 30 min to break up the dry NP aggregates in the solution. Analytical grade NaCl, NaOH and HCl were purchased from Sigma-Aldrich. The nanoparticle suspensions were titrated with diluted HCl and NaOH solutions and the pH was monitored using a pH meter (BP3001, TRANS INSTRUMENTS). An aliquot of the sample was taken out at specific pH values and the surface charge and particle size were determined with a ZetaSizer Nano ZS (Malvern) at 25 °C. Freshly made suspensions were prepared before each experimental run. Experiments were done in pentaplicates and the mean surface charge and particle size were determined.

Surface Charge and Particle Size measurements

Surface charge of SiO_2 NPs in DI water and tap water was determined according to the Smoluchowski equation while the nanoparticle size was measured using the dynamic light scattering (DLS) method with the Zetasizer Nano ZS (Malvern). While measuring, the particle suspension had been passed through by a 633-nm He–Ne laser beam and the scattered light is detected and collected by a photo-detector at a fixed scattering angle of 173°. The correlator then collect the light signal and carry out a light scattering intensity autocorrelation function. The diffusion coefficients of the particles that undergo Brownian motion are defined by the fluctuation of the autocorrelation function over decay time. The particle size of SiO_2 is determined from the diffusion coefficients in terms of the Stoke–Einstein equation. The range of particles size that can be measured is limited in the range from 2 nm to 6 μm. Nanoparticle suspensions were injected into polystyrene vials using a syringe for DLS measurements. All vials were used only once and were rinsed with DI water before being filled with suspensions. Measurements were carried out for 5 min at room temperature (25 °C) to obtain the mean particle size.

RESULTS AND DISCUSSION

Characterization of SiO_2 nanoparticle in DI water

In order to have a better understanding of the pH effect on SiO_2 surface charge and aggregation, a SiO_2 suspension (100 mg/L) was titrated with acid (hydrochloric acid) and base (sodium hydroxide) within the pH range of pH 2.5 to pH 11 in DI water (Figure 1a). When silica chemically reacted with water below pH 9, small amounts of silica dissolve and enter the aqueous phase and formed SiO_2 with a partial of surface consists of $Si(OH)_4$ which is silanol groups (Si-OH) as shown in equation below [19]:

$$(SiO_2)_n + 2H_2O = (SiO_2)_{n-1} + Si(OH)_4 \qquad (1)$$

When the pH is higher than 9, it will start to form $(HO)_3SiO^-$ and $(HO)_2SiO_2^{2-}$ [9] as shown in equation below:

$$Si(OH)_4 = (HO)_3SiO^- + H^+ \qquad (2)$$

$$Si(OH)_4 = (HO)_2SiO_2^{2-} + 2H^+ \qquad (3)$$

The initial pH of the SiO_2 suspension was determined at 5.4 with a surface charge between -31 mv and -35 mv and a mean particle size of 296 nm. When the pH was decreased, the surface charge was found to decrease rapidly from 5.4 to 4, then slowly to the point of zero charge (pH_{PZC}) which was measured at pH 3.2. This is important as other study have reported that pH 3 is close to the point of zero charge for SiO_2 NPs [14]. As the pH was continue decreased from pH_{PZC} towards 2.5, the surface charge remain slightly positive in charge (< +5mv). Meanwhile, by increasing the pH above pH 5.4 and towards pH 11, the surface charge was affected and decreased slowly between -31 mv and -35 mv towards -59 mv and -61 mv.

The particle size of SiO_2 aggregates is plotted as a function of pH in Figure 1b. At an initial pH of 5.4, the mean particle size of SiO_2 measures at 296 nm. When the pH was decreased, the particle size was found to increase rapidly from 5.4 to 3.2, with the highest particle size around 5000 nm. It is proven that aggregation occurred during pH 5.4 to pH 3.2. As the pH was decreased from 3.2 to 2.5, the particle size decreases rapidly to 1000 nm. When the pH was increased from 5.4 to 11, the particles size remains below 500 nm. SiO_2 was in dissolution region when pH was higher was supported by the results obtained.

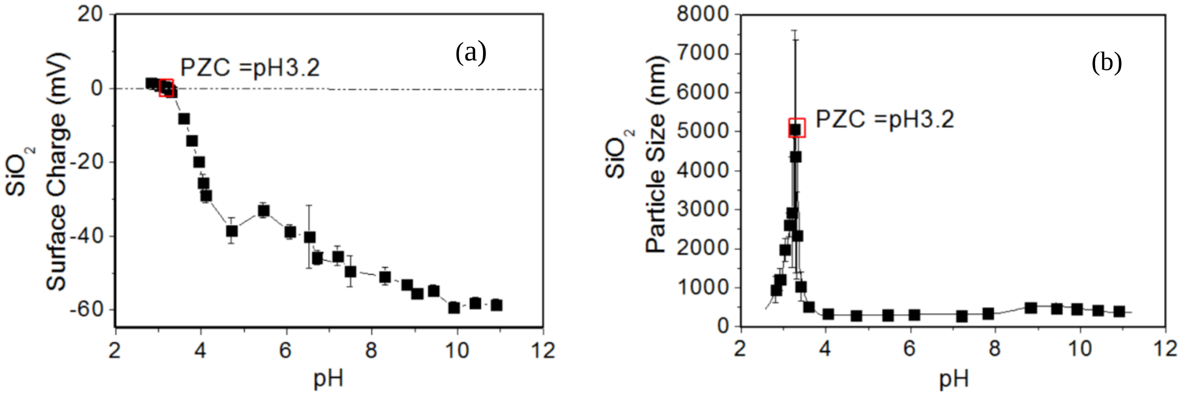

Figure 1. (a) Surface charge of SiO_2 in DI water as a function of pH at a range of pH 2.5 to 11. The initial pH was found at 5.4 with a surface charge of -33 ±2 mv. The pH of point of zero charge (PZC) was identified at 3.2. (b) Particle size measurement of SiO_2 in DI water as a function of pH at a range of pH 2.5 to 11. The initial pH was found at 5.4 with a particle size of 296 ±19 nm. The pH of point of zero charge (PZC) was identified at 3.2.

The particle size measurements in Figure 1b are concurrent with the surface charge values presented in Figure 1a. The mean particle size was shown to be the highest when in the range of $pH_{PZC.}$ Furthermore, the particle sizes were also found out to be smaller when the surface charge was further from the point of zero charge. At PZC, the silanol groups (Si-OH) were stabilize due to the same amount of negative and positive charges of silanol groups created on the surface of the silica particles. The "hairy layer" in Figure 2 which consists of polysilicilic acid on the silica particle surface was created at low pH with high ionic strength [11]. The "hairy layer" might be caused by water molecules diffusing into and becoming larger with the silica.

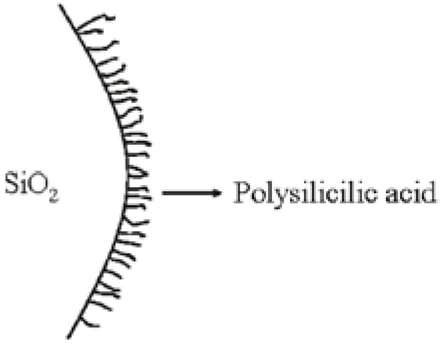

Figure 2. The schematic of the "hairy layer" on the silica particle surface [11].

As the pH value increases from 3.2 to 11, the number of negative charges increased on the particle surface. Due to more negative charges will produce higher surface energy and shift the equilibrium of the SiOH/SiO− acid/base dissociation into producing more SiO− species, the silanol group on the silica particle surface will break down to SiO− species. The condensation of silanol groups (Si-OH) will be catalyzed by Louis base as indicated in the following equations [8]:

$$SiOH + OH^{-} = SiO^{-} + H_2O \tag{4}$$

$$SiO^{-} + Si\text{-}OH = Si\text{-}O\text{-}Si + OH^{-} \tag{5}$$

Characterization of SiO_2 nanoparticle in tap water

In order to have a better understanding of the pH effect on SiO_2 surface charge and aggregation, a SiO_2 suspension (100 mg/L) was titrated with acid (hydrochloric acid) and base (sodium hydroxide) within the pH range of pH 2.5 to pH 11 in tap water (Figure 3a). The initial pH of the SiO_2 suspension was determined at 7.1 with a surface charge between -25 mv and -29 mv and a mean particle size of 346 nm. When the pH was decreased, the surface charge was found to decrease gradually from 7.1 to 4, then rapidly to the point of zero charge (pH_{PZC}) which was measured at pH 2.8. This is important as other study have reported that pH 3 is close to the point of zero charge for SiO2 NPs [14]. As the pH was continue decreased from pH_{PZC} towards 2.5, the surface charge remain slightly positive in charge (< +5mv). Meanwhile, by increasing the pH above pH 7.1 and towards pH 11, the surface charge was affected and decreased slowly between -25 mv and -29 mv towards -35 mv and -39 mv.

The particle size of SiO_2 aggregates is plotted as a function of pH in Figure 3b. At an initial pH of 7.1, the mean particle size of SiO_2 measures at 346 nm. When the pH was decreased, the particle size was found to increase rapidly from 4.0 to 2.8, with the highest mean particle size around 3250 nm. It is proven that aggregation occurred during pH 4.0 to pH 2.8. As the pH was decreased from 2.8 to 2.5, the particle size decreases rapidly to below 1500 nm. When the pH was increased from 7.1 to 11, the particles size remains below 500 nm. SiO_2 was in dissolution region when pH was higher was supported by the results obtained.

The particle size measurements in Figure 3b are concurrent with the surface charge values presented in Figure 3a. The mean particle size was shown to be the highest when in the range of $pH_{PZC.}$ Furthermore, the particle sizes were also found out to be smaller when the surface charge was further from the point of zero charge. At PZC, the silanol groups (Si-OH) were stabilize due to the same amount of negative and positive charges of silanol groups created on the surface of the silica particles. The “hairy layer” in Figure 2 which consists of polysilicilic acid on the silica particle surface was also created in tap water at low pH with high ionic strength [11].

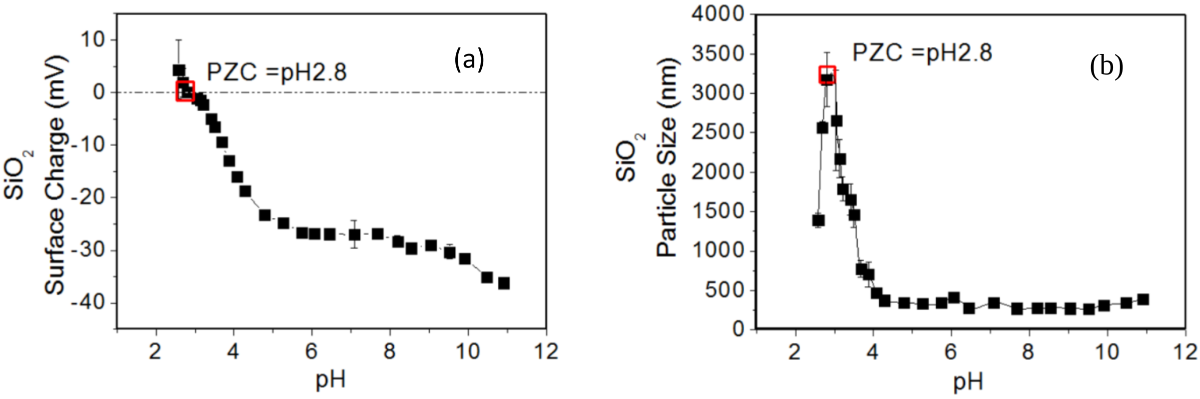

Figure 3. (a) Surface charge of SiO_2 in tap water as a function of pH at a range of pH 2.5 to 11. The initial pH was found at 7.1 with a zeta potential of -27 ±2 mv. The pH of point of zero charge (PZC) was identified at 2.8. (b) Particle size measurement of SiO_2 in tap water as a function of pH at a range of pH 2.5 to 11. The initial pH was found at 7.1 with a particle size of 346 ±24 nm. The pH of point of zero charge (PZC) was identified at 2.8.

Comparison of Characterization of SiO_2 nanoparticle in DI water and tap water

The first different of SiO_2 nanoparticle in DI water and tap water is the initial pH of tap water is neutral (7.1) and DI water is slightly acidic (5.4). It shows that tap water has other chemical ions which able to neutralize the pH since DI water are just consist of OH- and H+ ions besides consisting of SiO_2 nanoparticle. The second different of SiO_2 nanoparticle in DI water and tap water is tap water has lower pH_{PZC} than DI water and the third different of SiO_2 nanoparticle in DI water and tap water is the mean particle size at pH_{PZC} in DI water is larger than tap water by around 1750 nm. Both second and third difference between SiO_2 nanoparticle in DI water and tap water indicated that unknown substances in tap water interfered on aggregation. In order to further understand the interruption caused by the other present ions in tap water, testing is required to run to identify the ions in tap water. According to Table 1, these are the four most common anions (Cl^{-}, SO_4^{2-}, NO_3^{-} and F^{-}) and four most common cations (K^{+}, Ca^{2+}, Na^{+} and Mg^{2+}) that can be found in tap water of Malaysia. For cations (K^{+} and Na^{+}) of the tap water, the most possible situation that will occur inside the tap water will be silanol groups act as cation exchanging groups and form chemical equation as followed [10]:

$$SiOH + Me^{+} + OH^{-} = SiO^{-}Me^{+} + H_2O \tag{6}$$

As for divalent cations Ca^{2+} and Mg^{2+}, both alkaline earth metals act as catalyst on silicic acid polycondensation [5].

However, the present of other anions group in tap water could reduce the chemical reaction happen in equation 6 by 'stealing' the common cation groups in tap water and positive charge silanol groups which end up decreasing the size of particles formed and results in required lower pH to reached PZC. As for anions of the tap water, the silanol group react with chloride ion might form as equation below [1]:

$$\mathrm{SiOH} + \mathrm{H}^+ = \mathrm{SiOH_2}^+ \qquad (7)$$

$$\mathrm{SiOH_2}^+ + \mathrm{Cl}^- = \mathrm{SiOH_2}^+ \ldots \mathrm{Cl}^- \qquad (8)$$

For F^-, the silanol group might form as equation below [9]:

$$\mathrm{SiOH} + \mathrm{F}^- = \mathrm{SiF} + \mathrm{OH}^- \qquad (9)$$

Meanwhile, it is proposed that anions such as Cl^-, SO_4^2 will affect aggregation formed by metal ions and silica, but not NO_3^- [6]. As a result, it not only reduced other present cations in tap water to react with silica, but also decreased silica self-aggregated.

Table 1. Concentration profiles of the common anions and cations in Tap water sample in Penang, Malaysia [17].

Concentration (mg litre^{-1}) of mineral								
Water sample	Anion				Cation			
	Cl^-	SO_4^{2-}	NO_3^-	F^-	K^+	Ca^{2+}	Na^+	Mg^{2+}
Tap water								
Day 1	5.2	8.0	1.3	1.9	2.5	8.2	3.3	3.7
Day 2	5.4	8.2	1.7	2.1	2.5	9.1	3.1	3.7
Day 3	5.5	8.4	1.7	2.2	2.6	8.5	3.2	3.8
Day 4	5.6	8.5	1.7	2.4	2.6	8.8	3.2	3.7
Day 5	5.5	8.4	1.7	2.4	2.6	8.7	3.2	3.7
Day 6	5.7	8.3	1.7	2.4	2.7	7.7	3.2	3.4
Day 7	5.8	8.0	1.8	2.4	2.5	8.1	3.2	3.5

CONCLUSION

Particle size and surface charge measurements were used to simultaneously investigate the interactive processes and stability of suspensions containing SiO_2 NPs in DI water and tap water. Our results clearly show that aggregation or disaggregation SiO_2 NPs is dependent on the changing of pH. Our study also indicates that SiO_2 NPs in tap water is much harder to treat than DI water by finding out the aggregation of SiO_2 NPs in tap water is 1750 nm smaller than DI water when both in the range of pH_{PZC}, which is the aggregation domain. Meanwhile, the potential interaction of SiO_2 NPs with DI water and tap water also had been studied. By having a better understanding of the characteristics of SiO_2 NPs, the performance of water treatment system can be improved by using more suitable coagulant which can be analysed using dynamic light scattering (DLS) method as well, thus benefit industry area in achieving economic and environmental sustainability. DLS method provides a lot of advantages in the field of water treatment. By using DLS method from zetasizer, the preliminary study on characterization of certain pollutants and/or coagulant will be more efficient instead of using conventional method which is the jar test. The destabilization of colloid can be identified through zeta potential shown by using zetasizer, which help to narrow down the range of suitable pH to achieve optimum coagulant dosage. Moreover, zeta potential measurement from zetasizer can help saving cost on chemical usage and sludge disposal. This is because desired results obtained by using zetasizer only required small amount of chemical when comparing to jar test. The zetasizer testing can also save a lot of time because the analysis only takes minutes and the result is quite accurate and convincing. Thus, it is highly recommended to apply this technique for water treatment system.

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