CHARACTERIZATION AND TRANSFORMATION OF ZNO NANOPARTICLES IN AQUEOUS SUSPENSION: INFLUENCE OF pH

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ABSTRACT

In recent years, zinc oxide nanoparticles (ZnO NPs) are widely used in industries and released into water sources that can result into exposure problem and human threat. In this study, aggregation and behavior of ZnO NPs in deionized water and tap water were investigated in order to obtain the stable phase of ZnO NPs in suspension. ZnO NPs were conducted in two types of water: deionized water and tap water from laboratory. ZnO NPs suspension were tested using dynamic light scattering technique to determine zeta potential and hydrodynamic size in a pH range (pH 3 to 12). ZnO NPs in deionized water was used as a control in order to study the behavior of ZnO NPs in tap water. The results for both suspensions were highly differ with each other as tap water contained ions other than ZnO NPs. The occurrence of aggregation of ZnO NPs for both suspensions were at different pH range due to the interference of ions existed in tap water. Based on the results obtained, it can be concluded that pH has strong influence on the behavior of ZnO NPs suspension in environment without considering existing ions in tap water.

Keywords: Aggregation, disaggregation, hydrodynamic size, zeta potential, zinc oxide nanoparticles.

INTRODUCTION

Nanoparticles are existed in different size that is from 1 nm to 100 nm. Due to the high usage of nanoparticles in commercial products, nanoparticles are inevitable to be discharged into the surrounding environment [1]. Currently, nanoparticles problem towards human and environment are created high attention [2, 3]. Metal oxide nanoparticles are one of the types of nanoparticles that widely used in products. The aggregation process of metal oxide nanoparticles has drawn attention from researchers towards their reaction [4, 5].

Zinc oxide nanoparticles (ZnO NPs) are highly applied in many fields such as electronics, optics and cosmetic products. This is due to the special properties in ZnO NPs as it can have properties such as electronic, piezoelectric and catalytic properties that are differ than other materials [6]. Diverse structure of ZnO that having high number of configurations cause it has wider application in sensors, nanogenerators and so on [6, 7]. However, ZnO NPs able to dissolve into the water and become toxic substance to algae in aquatic environment [8]. Besides, ZnO NPs are shown to be the highest toxic nanoparticle compared to other nanoparticles like CuO, Al_2O_3, La_2O_3, Fe_2O_3, SnO_2 and TiO_2 when conducting experiment on bacterium *E.coli* [9].

In previous research, characterization of ZnO NPs had been done using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and proton-induced X-ray emission (PIXE) analysis [10]. Zeta potential and size of ZnO NPs are another type of nanoparticles characterization in order to further understanding the chemistry and reaction of nanoparticles in aqueous suspension. The experiment is conducted using ZnO NPs as it is more likely to present in the water due to high usage in daily life and able bring harmful effect to humans in high concentration [11, 12]. The aim of this research is to investigate the behaviour of ZnO NPs as a function of pH (pH 3 to 12) through determination of zeta potential and hydrodynamic size in both deionized water and tap water. Zeta potential and aggregation rate are strongly related to each other and thus aggregation of ZnO NPs can be determined through zeta potential [13].

METHODOLOGY

Zinc oxide nanoparticles (ZnO NPs) suspension was prepared at 100 mg/L in deionized water. Ultrasonication process was required to be done for 30 minutes to avoid agglomeration occurred before conducting research. Initial pH of ZnO NPs was measured and recorded using pH meter. About 1 mL of sample was extracted to be tested using ZetaSizer Nano ZS (Malvern) and studied in term of zeta potential and hydrodynamic size from pH range of pH 3 to 12. pH of ZnO was adjusted with 0.25M HCl and 0.25M NaOH. The above steps were repeated to prepare 100 mg/L of ZnO NPs in tap water.

RESULTS AND DISCUSSION

A ZnO nanoparticles (ZnO NPs) suspension (100 mg/L) was used to study zeta potential and hydrodynamic size in the pH range of pH 3 to 12 in deionized water (Figure 1). ZnO NPs was one of the amphoteric oxide. In this experiment, point of zero charge of ZnO NPs in deionized water was at pH 9.3. This result was quite same as the result performed in other studies [13-15]. Initial pH of ZnO NPs was around pH 7 to 7.5. Zeta potential and hydrodynamic size of ZnO suspension were 34.2 mV and 705.6 d.nm respectively. The pH is one of the factors affecting the occurrence of aggregation in deionized water. ZnO NPs behaved differently from pH 3 to pH 12 through measurement of zeta potential and size. pH of solution is important because charge of ions can affect the effectiveness of ions to form aggregation. Aggregation occurred from pH 9.5 to pH 11 and partial dissolution was occurred between pH 6 to 7 in deionized water. Dissolution of ZnO NPs occur when it dissolves into Zn^{2+} and O^{2-} ions. Zn^{2+} ions are major component in this region that causing the increment of zeta potential (Figure 2). The chemical reaction that could occur in acidic and alkali region along the pH range are shown as following: [16-18]

$$ZnO\ (s) + 2\ H^+\ (aq) \leftrightarrow Zn^+\ (aq) + H_2O\ (l) \qquad \text{(Eqn. 1)}$$

$ZnO (s) + H^+ (aq) \leftrightarrow Zn(OH)^+ (aq)$ (Eqn. 2)

$ZnO (s) + OH^- (aq) + H_2O (l) \leftrightarrow Zn(OH)_3^- (aq)$ (Eqn. 3)

$ZnO (s) + 2 OH^- (aq) + H_2O (l) \leftrightarrow Zn(OH)_4^{2-} (aq)$ (Eqn. 4)

The reaction below is also may happen in water but in low solubility of product [18].

$ZnO (s) + H_2O (l) \leftrightarrow Zn(OH)_2 (aq)$ (Eqn. 5)

The point of zero charge (PZC) of suspension is the point at which the charge is neutral and highly unstable and thus more likely to form aggregation [19]. Based on Figure 1(b), the largest size form in the ZnO NPs suspension was 1408 d.nm at pH 10.2 and zeta potential of ZnO NPs was negatively charged. This phenomenon happened is because the charged of ZnO NPs was tend to stabilize around PZC and enable them to aggregate to form larger size.

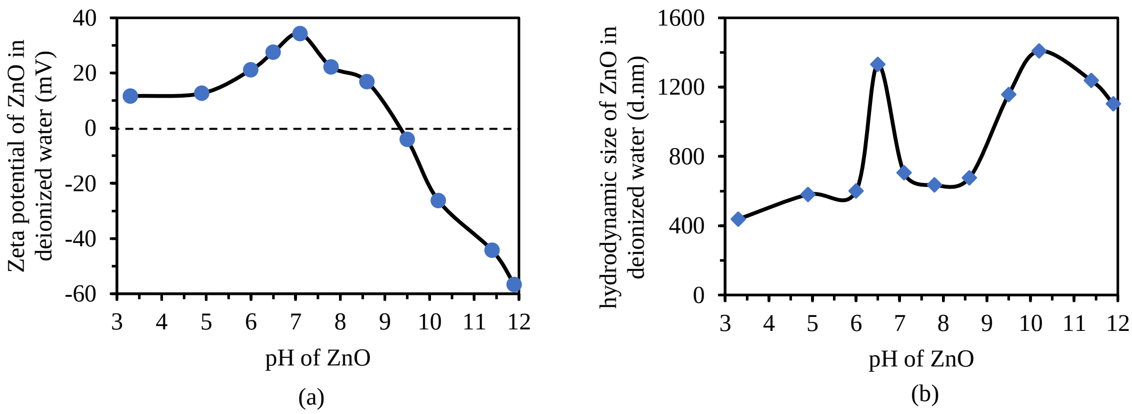

Figure 1. ZnO NPs profile of (a)zeta potential and (b) hydrodynamic size within pH 3 to 12 in deionized water

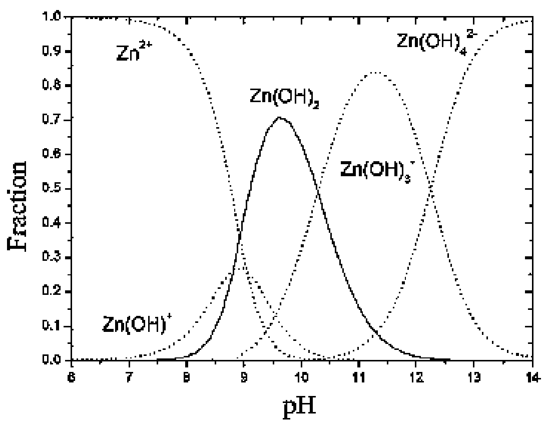

Figure 2. Speciation of Zn(II) species [20]

In this experiment, 100 mg/L of ZnO NPs was used to study the behaviour and reaction of ZnO NPs in tap water. ZnO NPs suspension was positively charged from pH 3 to 5 while negatively charged from pH 5 to 12. At initial pH 7.7, zeta potential and hydrodynamic sized of ZnO NPs suspension in tap water were -22.9 mV and 1882 d.nm respectively. The point of zero charge of ZnO NPs suspension was at pH 5. The changes of pH along the solution caused the occurrence of aggregation. Aggregation of particles occurred from pH 5 to 6.2 as hydrodynamic size of particles increased significantly and disaggregation of particles happened from pH 6.2 to 8.2. The increment of pH from pH 3 to pH 12 caused the decreasing of zeta potential of solution. This is because pH of suspension plays important rules in aggregation and disaggregation process. Repulsion of nanoparticles occurred when same charged of nanoparticles existed in suspension and thus caused in disaggregation. Different charged of nanoparticles caused the attraction of nanoparticles and thus helped in formation of aggregation.

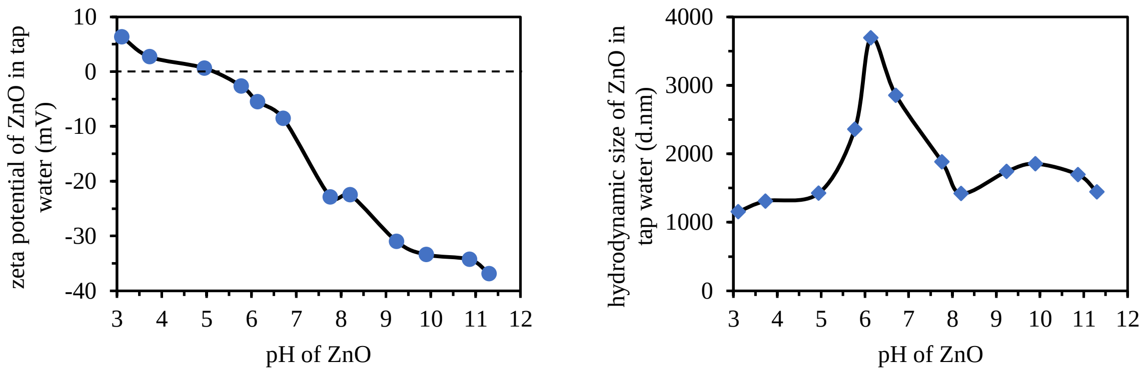

Figure 3: ZnO NPs profile of (a) zeta potential and (b) hydrodynamic size within pH 3 to 12 in tap water

ZnO NPs showed different characteristics and properties in deionized water and tap water. The initial pH for both ZnO NPs suspensions were approximately the same but the zeta potential of suspensions were highly different. [Figure 1(a) and Figure 3(a)]. The differ of both suspension is positive charge of ZnO NPs in deionized water while negatively charge of ZnO NPs in tap water around pH 7.5. The result shows that high amounts of anions exist in tap water that contribute to negatively charged by using deionized water as control. In addition, the hydrodynamic size of ZnO NPs suspension in tap water (1882 d.nm) is differ than ZnO NPs suspension in deionized water (705.6 d.nm). This is because other elements such as calcium, magnesium, selenium, molybdenum exist in tap water that react with ZnO NPs to form larger size. Partial dissolution of ZnO NPs only occurs in deionized water as less interference from other charges exist in tap water. Besides that, aggregation occurred at alkaline region for deionized water while at acidic region for tap water. This is because the existence of other ions and molecule in the tap water affect the behaviour of ZnO NPs to have aggregation at acidic region.

CONCLUSION

The stability of ZnO NPs in deionized water and tap water were studied as a function of pH 3 to 12 through monitoring the zeta potential and hydrodynamic size to evaluate the fate of ZnO NPs in suspension. For ZnO NPs in deionized water, dissolution occurs in acidic region and aggregation occurs in alkali region. For ZnO NPs in tap water, aggregation occurs at slightly acidic region (pH 5 to 8). By studying zeta potential and hydrodynamic diameter of ZnO NPs, these results can serve a better understanding on the behavior of ZnO NPs at a function of pH. pH is proved to be one of the factors that highly influence the state of ZnO NPs in environment.

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