Transformation of zinc oxide nanoparticles under environmentally relevant conditions: influence of pH and ionic strength

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ABSTRACT: The demands from nanotechnology industry have been increasing every year. The number of usage of ZnO nanoparticles in the consumer products is also rapidly increasing. The release of nanoparticles to the environment may affect the environment itself and eventually on the human health. Water chemistry such as pH and ionic strength play important roles in the release of Zn ions. In this study, two commercially available zinc oxide (ZnO) nanoparticles of size < 50 nm and < 100 nm were purchased and were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) spectroscopy. XRD and TEM confirmed that the size of the particles was in the range stated at the labels. The dissolutions were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES). It was found that the dissolution is higher at pH 1 and decreased as the pH increased. In terms of ionic strength, small size nanoparticles are stable at lower pH while bigger size is ionic strength dependence.

KEYWORDS: Zinc oxide nanoparticle, Dissolution, Ionic strength, pH, Size

INTRODUCTION

Nanotechnology has become the most popular field ever since in the technology industry. The demand of the production of nanoparticles-based products has increased recently. Based on the definition of nanoparticles which has a size of less than 100 nm (Christian, Von der Kammer, Baalousha, & Hofmann, 2008), these nanoparticles have been chosen in many nanotechnology-based consumer products.

Nanoparticles were applied in various fields. Among these are medical field whereby nanoparticles have been used as pharmaceutical drugs (Mudunkotuwa, Rupasinghe, Wu, & Grassian, 2012). At smaller size, nanoparticles exhibit different or enhanced properties as compared to bulk materials due to an increased in surface area (Bondarenko et al., 2013), thus they exhibit excellent properties as antimicrobial, electric conductor, and biologically compatible (Mohd Omar, Abdul Aziz, & Stoll, 2014).

According to Akhil and Sudheer (2017) nanoparticles will change their physical and chemical properties in aqueous media. Aggregation, sedimentation and dissolution are some of the main physicochemical process that affect the fate of nanoparticles in water (Koetsem, Verstraete, Meeren, & Du, 2015). ZnO nanoparticles tend to aggregate when the ionic strength is increased

TRANSACTIONS ON SCIENCE AND TECHNOLOGY

(Han et al., 2014). According to Bian et al., (2011) increased in ionic strength will also increase the sedimentation of ZnO nanoparticles. In his experiment, it was found that the aggregation was pH-dependence. Omar et al., (2014) also concluded that the aggregation, disaggregation or stabilization of ZnO nanoparticles were dependent on the solution pH, concentration of humic acid and the physicochemicals properties of humic acid itself.

Extensive production of ZnO nanoparticles-based product may lead to environmental problems. Nanoparticles can enter the environment intentionally or accidentally during the production of nanoparticles, transportations and usage and treatment of nanoparticles (Akhil & Sudheer Khan, 2017). Environmental water chemistry such as pH, natural organic matter and ionic strength plays role in the behaviour of metal oxide. Till now, many researchers have done their research on other environmental conditions to study the fate and behaviour of metal oxides such as titanium dioxide, silver nanoparticles, iron oxide and cerium dioxide (Baalousha, 2008; Chinnapongse, MacCuspie, & Hackley, 2011; Koetsem et al., 2015; Romanello & Fidalgo de Cortalezzi, 2013) in aquatic environment. Some researchers combined the environmental factors and focussed on the stability and aggregation of metal oxides compound (Keller et al., 2010; D. Zhou & Keller, 2010). Therefore, limited study was found on the dissolution of ZnO nanoparticles influenced by pH and ionic strength. The objective of this study is thus to investigate the influence of pH and ionic strength towards the transformation of the commercial ZnO nanoparticles in two different sizes.

MATERIALS AND METHOD

Materials

Commercially manufactured zinc oxide (ZnO) nanoparticles were used in this study. Two different sizes, which are < 50 nm and < 100 nm, were obtained as dry powder and purchased from Sigma- Aldrich. To adjust the pH of solution, sodium hydroxide (NaOH; Amresco, Ohio) and hydrochloric acid (HNO₃; Fisher Chemicals), were used and measured using Martini Instruments (Model Mi 150) pH meter. Sodium chloride (NaCl; Duchefa Biochemie) was used to adjust the ionic strength of the solutions. All chemicals used were of analytical reagent grade and deionized water was used for the preparations of solutions.

Characterization of ZnO nanoparticles

The ZnO nanoparticles samples were characterized using transmission electron microscopy (TEM), X–ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy techniques. Briefly, 2 mg of ZnO nanoparticles powdered samples was weighed and diluted in 5 ml ethanol solution. For better dispersion, the solution was then sonicated for 30 minutes before mounted onto coated copper grids. The sample grids was left to dry before viewed under TEM (JEOL model JEM – 1230). Similar amount of ZnO nanoparticles sample powder was weighed and mixed with potassium bromide (KBr) in 1:5 ratios. The mixture was then finely crushed, compressed until it formed thin disc and analysed by FTIR in the range of 400 – 4000 cm^{-1} to obtain FTIR spectra (AbdElhady, 2012). Both samples were also sent for XRD analysis. X-ray measurements were performed using X-ray diffractometer (Panalytical XPert Pro MPD) operated using CuKα radiation at 40 kV and 30 mA.

Dissolution measurement of ZnO nanoparticles

The preparation of ZnO nanoparticles stock solution was performed according to experimental method done by Bian et al (2011) and Zhou and Keller (2010). Briefly 0.8 g/L stock solution was prepared by dissolving ZnO nanoparticles powder in deionized water. For better dispersion of the nanoparticles, the solution was sonicated for 30 minutes in water bath sonicator (model). Prior to use, the stock solution were resonicated for 10 minutes to disperse the particles. The sonication time was found to be sufficient to break loose metal oxide nanoparticles agglomerates (Zhou & Keller, 2010). The stock was diluted to 100 mg/L before adjusting the solution pH. To study the effect of pH on the dissolution, four pH values was selected (pH1, pH6, pH7 and pH9) and the ionic strength was maintained at 0mM NaCl.

Same procedure was applied to study the effects of ionic strength. Two concentrations of ionic strengths were chosen (3 mM and 5 mM) and pH value was kept constant at pH7 which is similar to the fresh water pH value. Briefly, NaCl salt of known mass was dissolved in deionized water and diluted to 3 mM and 5 mM. The volume of NaCl added to ZnO sample solution was in ratio of 1:10. The NaCl solution was added before volumetric flask was filled to the final mark. Three aliquots (10 mL each) were drawn out at time intervals of 1 hour for the first 6 hours followed by 9 hours intervals for the next 3 samples and 15 hours interval for last sample with volumetric pipette, filtered with 0.45 µm filter paper to separate the solutions from ZnO nanoparticles and diluted. Sample was analysed using a Perkin Elmer Optima 8000 inductively coupled plasma optical emission spectrometer (ICP – OES) to quantify dissolved zinc. The average and standard deviation of triplicate measures are reported for all dissolution measurements. The calibration was conducted with 0.02, 1.00, 2.00, 3.00, 4.00, and 5.00 ppm Zn^{2+} standards prepared in deionized water.

RESULT AND DISCUSSION

Characterization of ZnO nanoparticles

Figure 1 shows the X-ray diffractograms obtained for the samples. Both exhibit single phase of ZnO nanoparticles with all detected peaks indexed to the space group $P6_3mc$ (186) of hexagonal wurtzite structure. The average crystallite size was determined from the full width at half maxima (FWHM) of a single Bragg peak profile using Scherrer Equation, after correction from Kα doublet effect and instrumental broadening. As this is order-independent, the highest diffraction peak (011) was chosen for the analysis of crystallite size. Scherrer's Equation is given by (Becheri, Durr, Lo Nostro, & Baglioni, 2008; Srivastava, Gusain, & Sharma, 2013)

$$size = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where K is the shape factor constant (0.9), λ is the X-ray wavelength (Cu Kα_1), β is the peak broadening in radian given by the FWHM of the diffraction peak after correction from instrumental broadening and Kα doublet effect, and θ is the Bragg diffraction angle. An instrumental broadening of 0.04° obtained from the instrumental functions measured using a Si wafer standard was used as the correction for the FWHM of the samples. The crystallite size of the samples was found to be 26 nm and 61 nm for ZnO nanoparticles of size less than 50 nm and less than 100 nm respectively. Based on XRD patterns, ZnO nanoparticles with size < 50 nm have a broader peak compared to ZnO

nanoparticles < 100 nm. According to Mudunkotuwa et al. (2012), the peaks were broaden with decreasing size and this happened due to introduction of non-uniform stress to the structure.
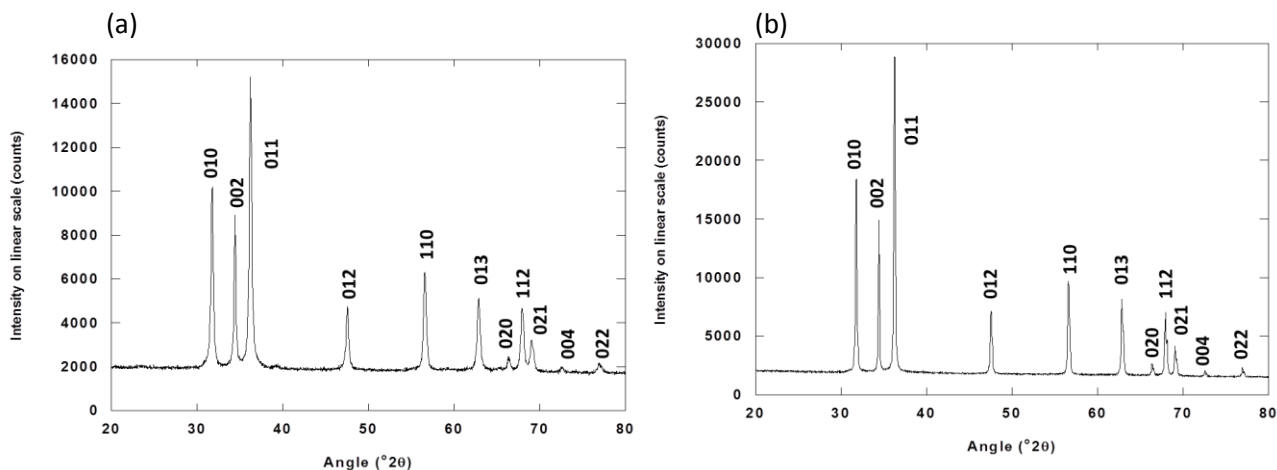

Figure 1. X-ray diffraction (XRD) patterns for ZnO nanoparticles of size (a) < 50 nm and (b) < 100 nm.
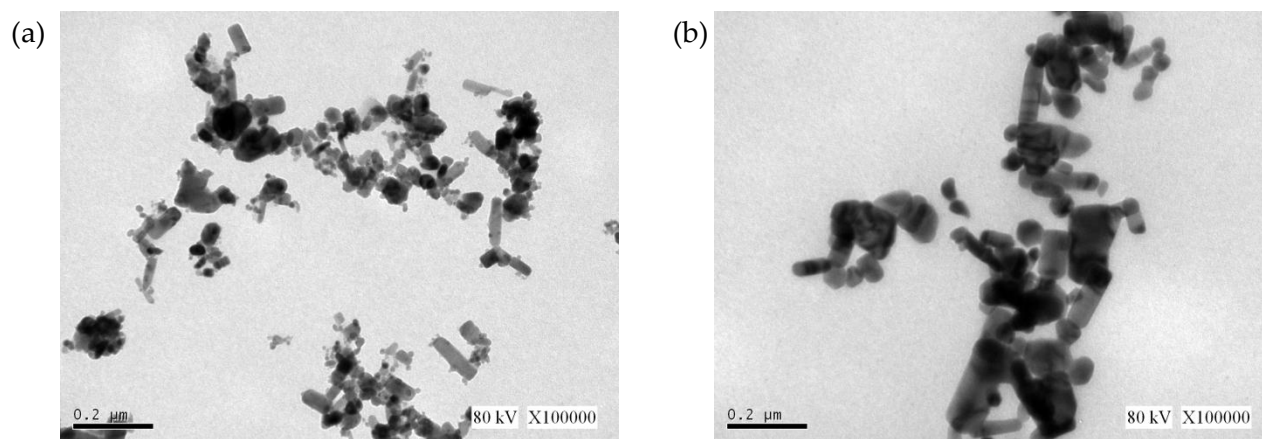

Figure 2. Transmission electron microscope (TEM) images of size (a) < 50 nm and (b) < 100 nm.

Table 1 compares the crystallite size of the particles obtained from the X-ray diffractograms with the diameters of the particles determined from the TEM micrographs in Figure 2 for the two samples. Over 100 particles were used to obtain the particle size distribution by Image J software. The particle size distribution of ZnO nanoparticles were shown in Figure 3 and Figure 4 below. It shows that the mean diameters for the ZnO nanoparticles of size less than 50 nm and 100 nm are 39 ± 16 nm and 71 ± 19 nm respectively. From Table 1, it can be seen that the crystallite size is almost approaching the particle size of the samples, which implies that the particles are of high lattice coherence.

Table 1. Comparison of the size of ZnO nanoparticles

ZnO NPs	Particle size (nm) (from TEM)	Crystallite size (nm) (from XRD)
< 50 nm	39 ± 16	26
< 100 nm	71 ± 28	61

Commercial manufactured ZnO nanoparticles of size < 50 nm shows that 76% particles are less than 50 nm with 27% nanoparticles are in the range of 21 nm to 30 nm followed by 24% nanoparticles with sizes in range of 31 to 40 nm. Meanwhile for ZnO nanoparticles < 100 nm, 99% of nanoparticles are less than 100 nm with highest percentage of 40% for size range from 61 to 80 nm.
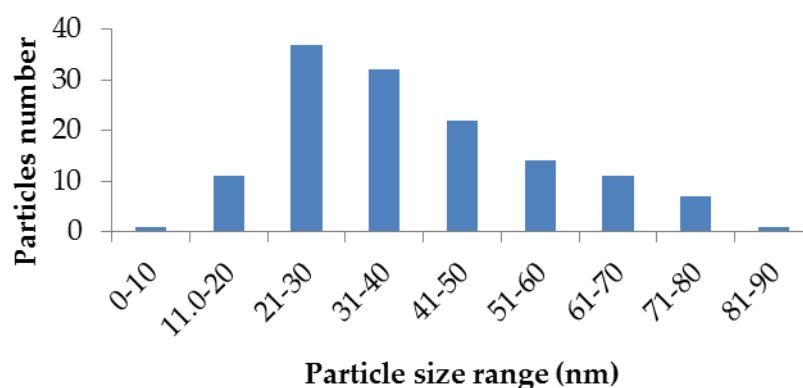
Figure 3. The particle size distribution of ZnO nanoparticles of size less than 50 nm.
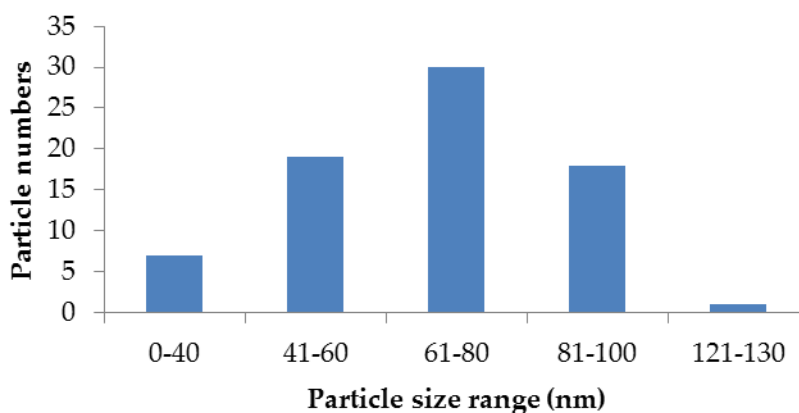
Figure 4. The particle size distribution of ZnO nanoparticles of size less than 100 nm.

Characterization of surface functional group for these samples was determined from FTIR spectroscopy. The spectra are given in Figure 5. The spectrum obtained shows that the adsorption band of Zn – O was 461 cm^{-1} and 417 cm^{-1} for < 50 nm and < 100 nm respectively. Characterisation of manufactured and synthesised of ZnO nanoparticles was shown in the region 400 and 600 cm^{-1} (Bagabas, Alshammari, Aboud, & Kosslick, 2013; Bhuyan, Mishra, Khanuja, Prasad, & Varma, 2015;

Lavand & Malghe, 2015). Based on Bagabas et al.'s spectrum (2013), asymmetric and symmetric stretching O – H vibration bands was observed between 3600 and 3200 cm^{-1} while O – H bending bands can be observed between 1630 and 1600 cm^{-1}. For samples of ZnO nanoparticles < 50 nm, the peaks at 1614 cm^{-1} was belong to hydroxyl group and peaks 1624 cm^{-1} for ZnO nanoparticles < 100 nm.
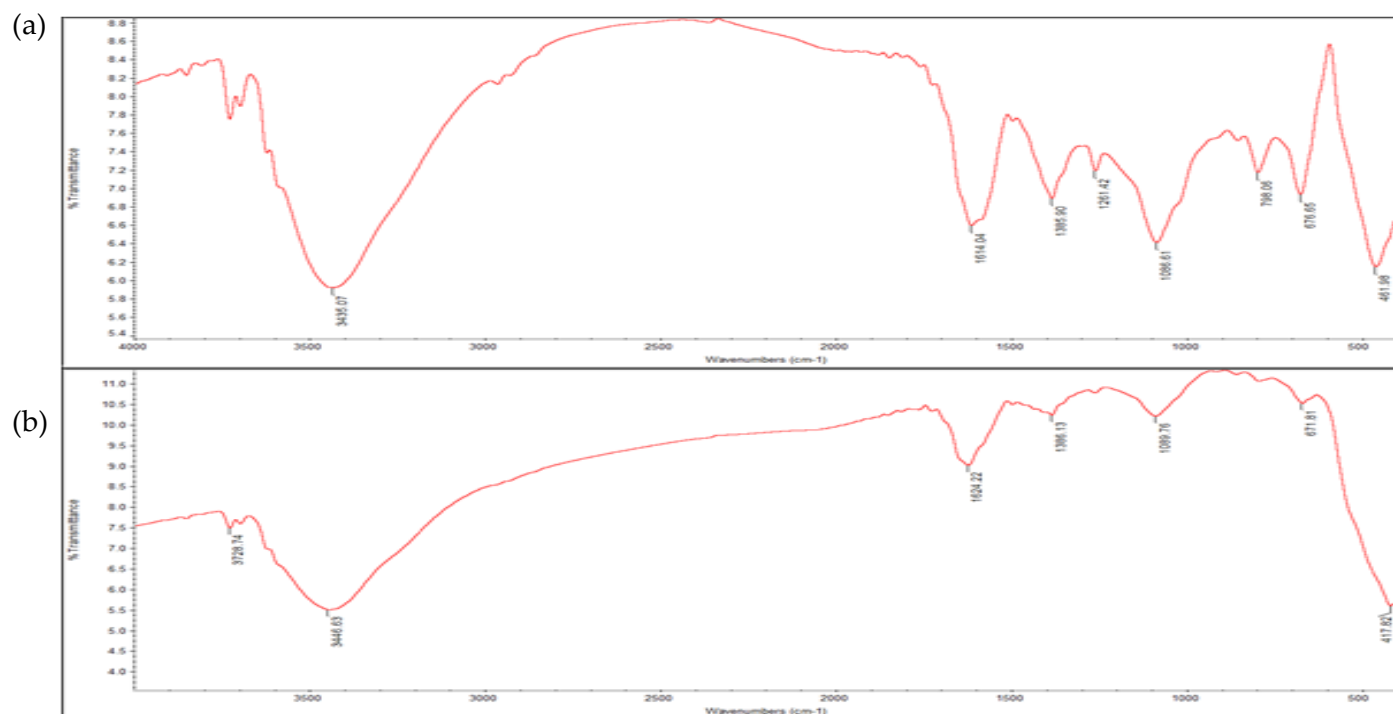
(a)

(b)

Figure 5. FTIR spectra of ZnO nanoparticles of size (a) < 50 nm and (b) < 100 nm.

Dissolution of ZnO nanoparticles
    i.   Effect of pH

As shown in Figure 6, pH value has a significant influence on both sizes of ZnO nanoparticles dissolution. At pH = 1, the ZnO nanoparticles was dissolved approximately 40% from total of 100 mg/L sample solution prepared. The percentage dissolved Zn ions dropped significantly as pH was increased to pH 6, indicating the negative effect of weaker acidity (J. Han, Qiu, & Gao, 2010). As pH increased there was a slight increase of total dissolved ions at pH 7 and dropped again as the pH further increased to pH 9.
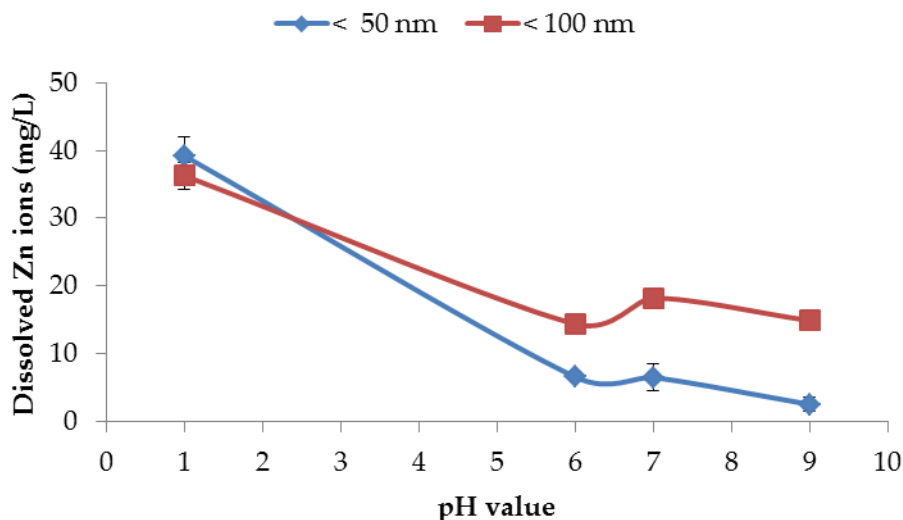
Figure 6. Dissolution of ZnO nanoparticles at different pH value after 24 h

Dissolution at pH 1 showed that the total dissolved Zn ions for ZnO nanoparticles of size less than 50 nm is 39 mg/L compared to 100 nm which is 36 mg/L. According to Bian et al. (2011), the dissolution rate was proportional to the particle surface area. Therefore, small nanoparticles should dissolve faster than the bigger particles due to high surface area. As pH value was increased further, the total dissolved Zn ions were in vice versa where the dissolution of < 100 nm was higher than < 50 nm.
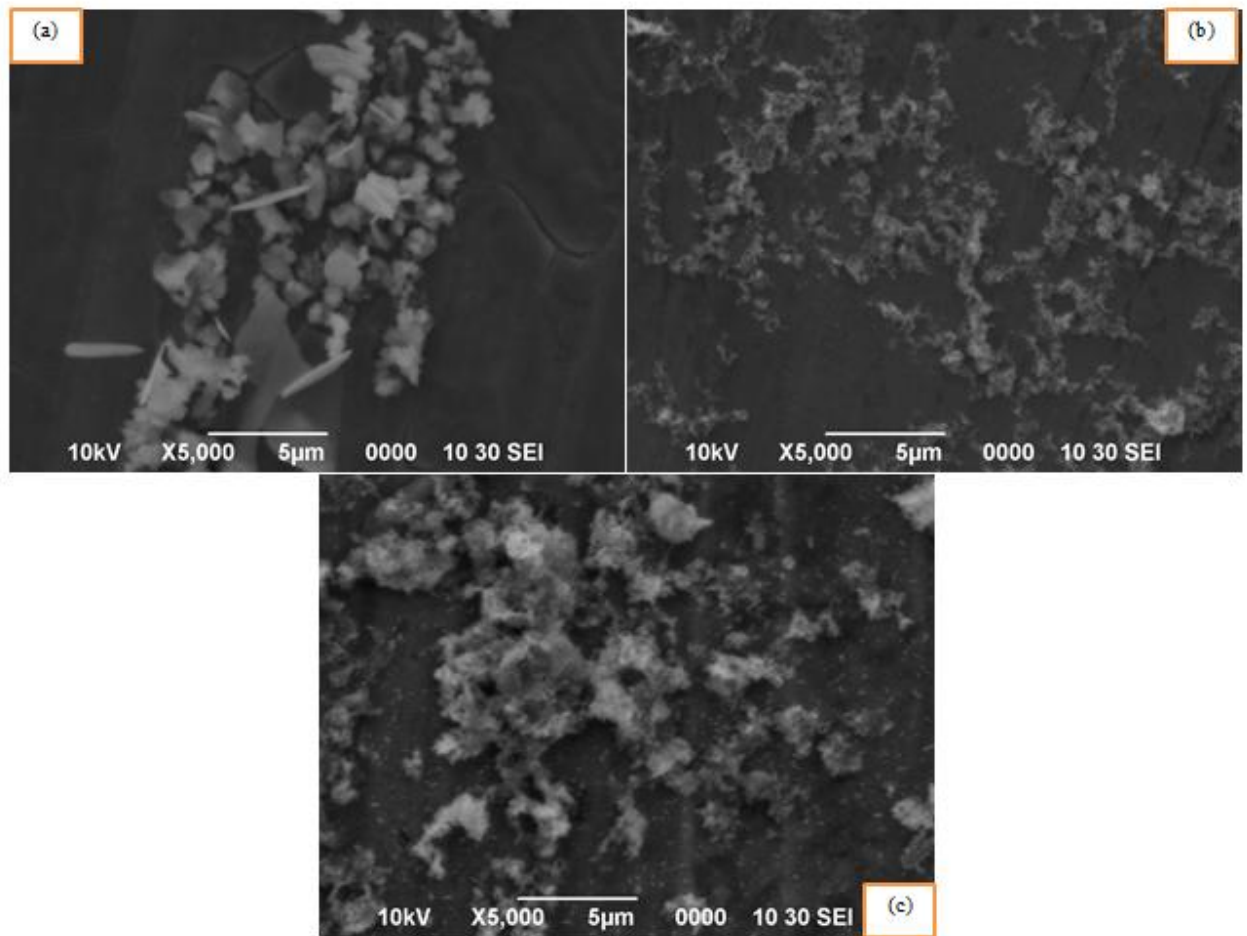
Figure 7. SEM images of < 50 nm ZnO nanoparticles at different pH conditions; (a) pH 1 (b) pH 7 (c) pH 9

In fact, this phenomenon was due to the solubility of the nanoparticles itself. The solubility of ZnO nanoparticles was reduced as pH was further increased. Low solubility was due to the aggregation of nanoparticles. The bigger the aggregation, the lower the solubility thus resulting in a decrease of total dissolved ion released (Bian, Mudunkotuwa, Rupasinghe, & Grassian, 2011). This was confirmed in Figure 7 and Figure 8. At lower pH, pH 1, the nanoparticles were most likely to disperse compared to pH 7 and pH 9. At pH 7 the particles were loosely attached and at pH 9, the particles were aggregated.
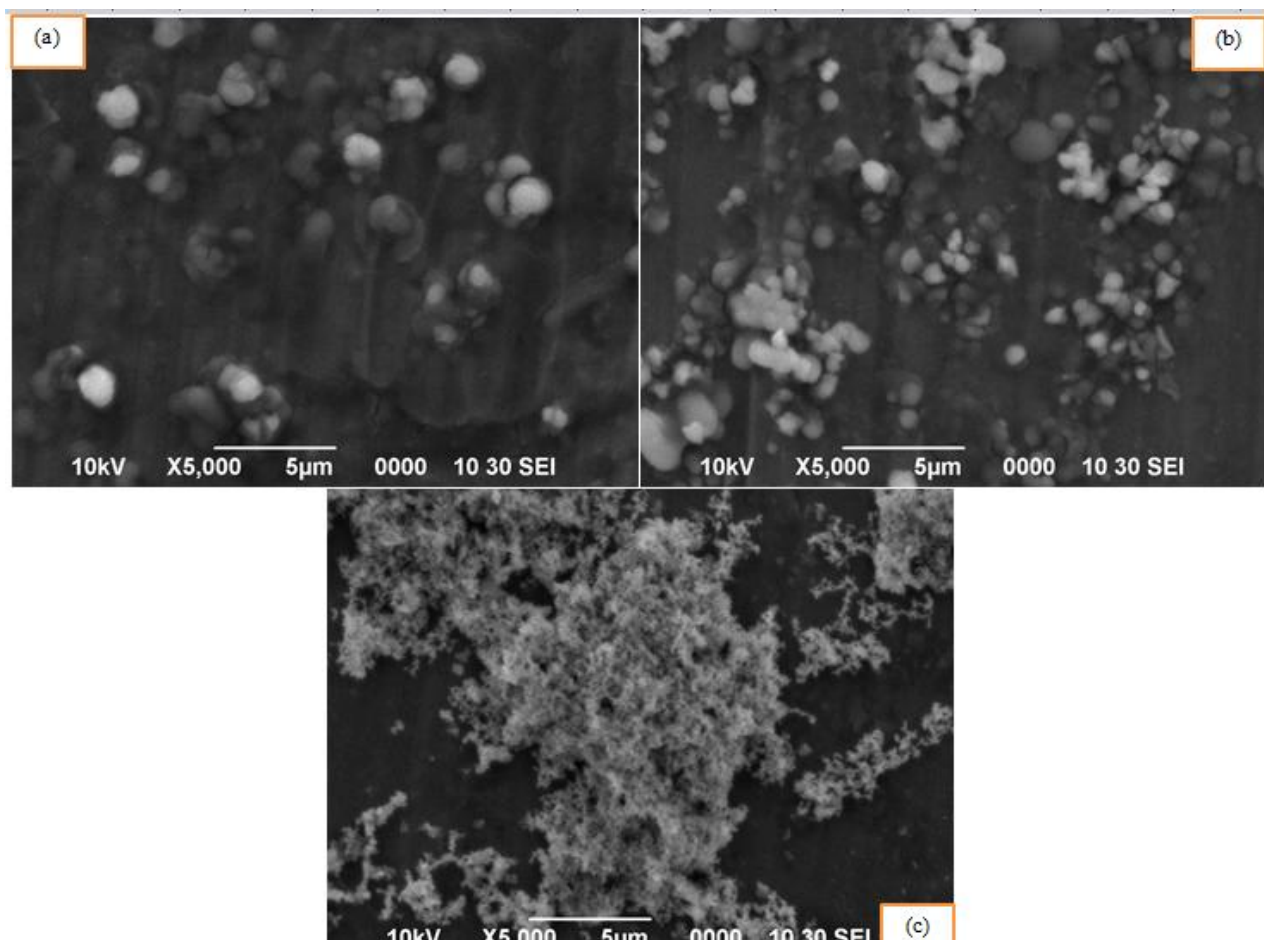
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Figure 8. SEM images of ZnO nanoparticles of size < 100 nm at different pH conditions; (a) pH 1 (b) pH 7 (c) pH 9.

At pH 1, the smaller the size of nanoparticles, the higher the total number of dissolved Zn ions. This can be observed from Figure 9. For ZnO nanoparticles of size < 50 nm, the dissolution after 1 hour reaction time was almost complete with total dissolved ions of 76 mg/L. Total dissolved Zn ions remained constant at 40 mg/L for the rest of 48 hours reaction time. Differs to ZnO nanoparticles of size < 100 nm, total dissolved Zn ions after 1 hour reaction was 13 mg/L and kept increasing to 49 mg/L at 6 hours reaction time. The total of dissolved ions dropped to 24 mg/L at 15 hours of reaction time and then increased again to 52 mg/L until experiments were completed.
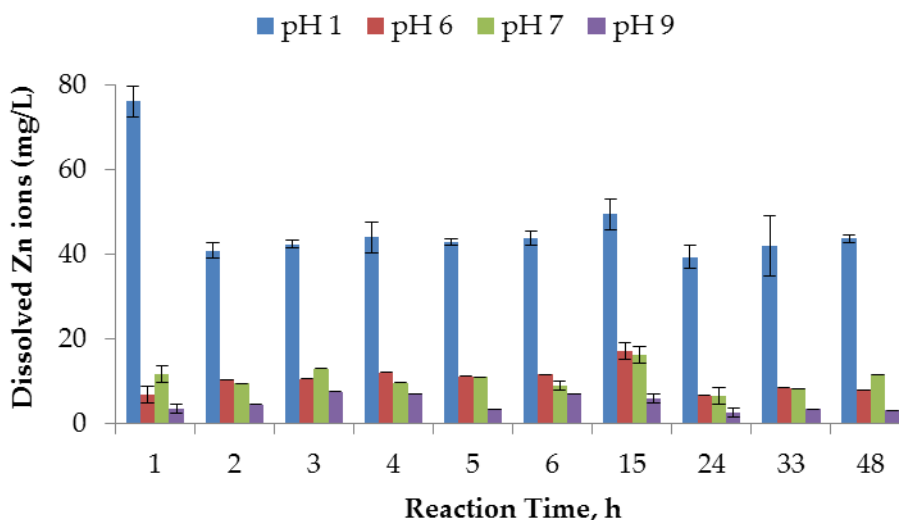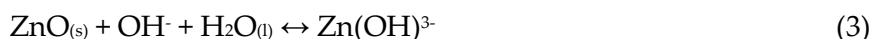
Figure 9. Dissolution of ZnO nanoparticles of size < 50 nm at different pH conditions

The dissociation of ZnO nanoparticles in water can be explained through the equations below:

$$ZnO_{(s)} + 2H^+ \leftrightarrow Zn^{2+} + H_2O_{(l)} \tag{2}$$

$$ZnO_{(s)} + OH^- + H_2O_{(l)} \leftrightarrow Zn(OH)^{3-} \tag{3}$$

Equation 2 showed the reactions of metal oxide in water when the pH value is low thus encourage the solubility of heavy metals. As the level of hydrogen ions increases, metal cation such as zinc is released into water instead of being absorbed. Meanwhile Equation 3 shows the reaction of metal oxide in higher pH and its product as hydroxyl complexes.

The dissociation of Zn ions can be explained further through Equation 2 as suggested by J. Han et al. (2010) and Bian et al. (2011) where free hydrogen ions (H+), known as proton, will react directly onto ZnO nanoparticles surfaces thus facilitated the release of Zn ion. At the same time the dissolved Zn ions will remain in the form of Zn^{2+} and $Zn(OH)^+$ as shown by Equation 4 below;

$$ZnO_{(s)} + H^+ \leftrightarrow Zn(OH)^+ \tag{4}$$

Therefore, lower pH of the solution corresponds to faster ZnO nanoparticles dissolution and more zinc ions released.
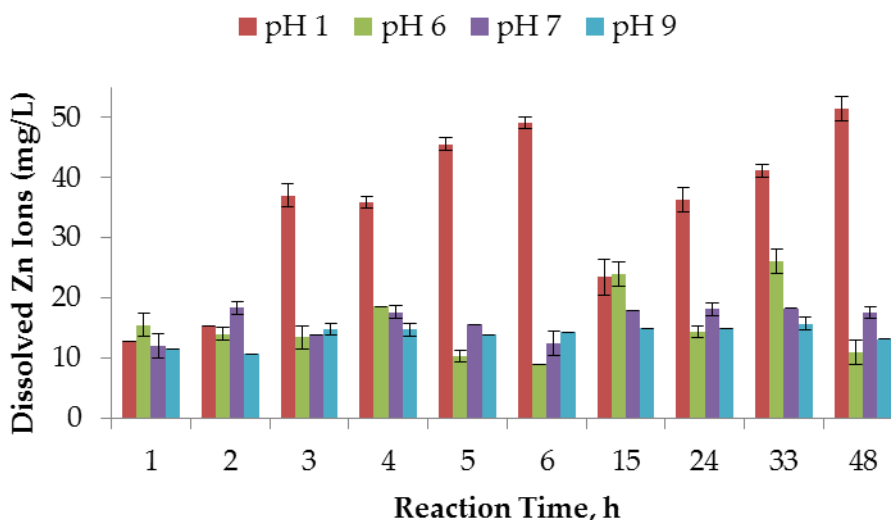
Figure 10. Dissolution of ZnO nanoparticles of size < 100 nm at different pH conditions

ii.   Effect of ionic strength

The effect of ionic strength was studied by using 3 mM NaCl and 5 mM NaCl. The pH used during this experiment was kept constant at pH 7. Figure 11 shows that, the total dissolved Zn ions with smaller size are lower at 0 mM NaCl concentration and increase as the ionic strength increased to 3 mM and 5 mM NaCl. This trend is reversal when the ZnO nanoparticles sizes are bigger (< 100 nm).
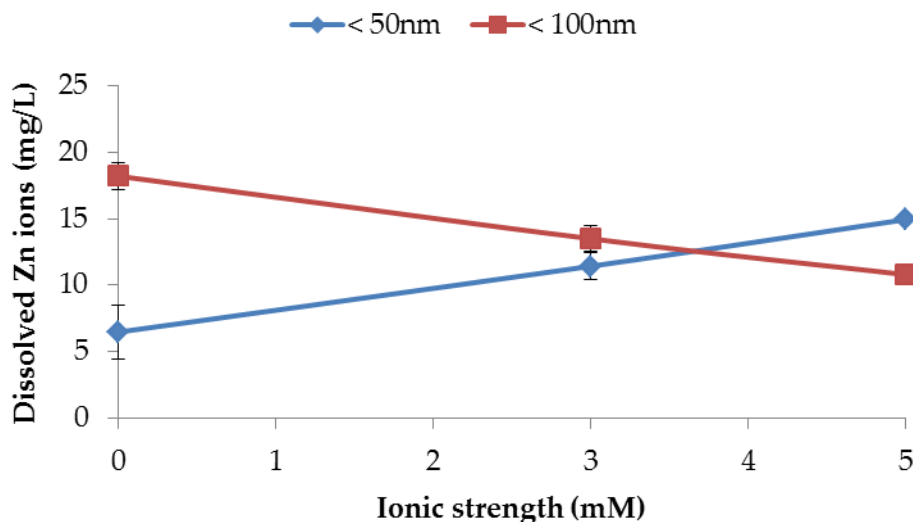

Figure 11. Effects of ionic strength towards the ZnO dissolution

From Figure 12 and Figure 13, ZnO less than 50 nm show that the particles are more stable at lower ionic strength concentration. The total dissolved Zn ions are constant in range of 8 mg/L until 16 mg/L when the ionic strength is 3 mM NaCl. When increased the ionic

strength from 3 mM to 5 mM NaCl, the total dissolved Zn ions keeps fluctuating for the first six hours and the concentrations are ranging from 10 mg/L to 18 mg/L.
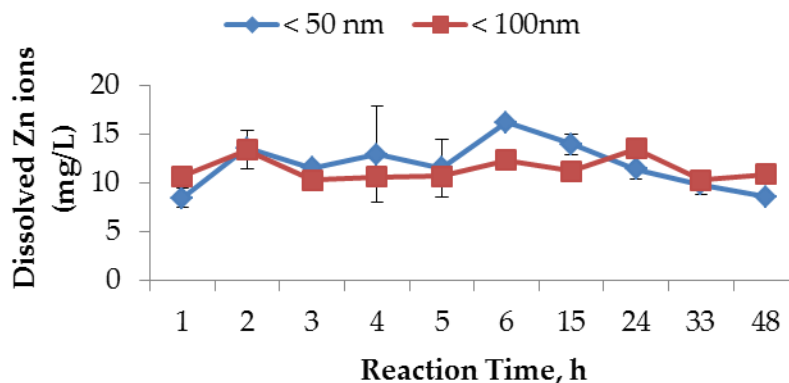

Figure 12. Dissolution of ZnO nanoparticles; Ionic strength = 3 mM NaCl, pH = 7

According to D. Zhou & Keller, (2010) the presence of ionic strength will also influence the particle surface charge by reducing the electrostatic repulsion resulting in aggregation and reducing the dissolution of heavy metal. Contrary to ZnO nanoparticles sizes < 100 nm, the total dissolved Zn ions are constant during the reaction time which indicates that ZnO with larger sizes are stable at any concentration of ionic strength.
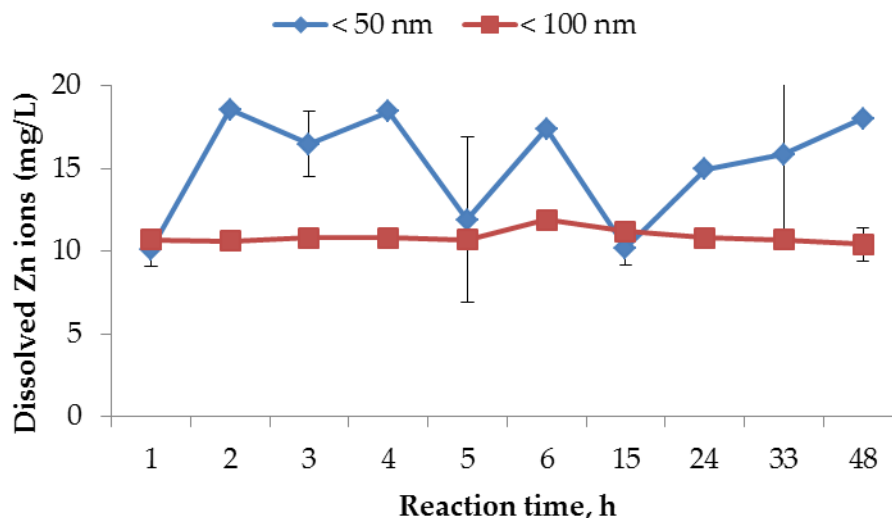

Figure 13. Dissolution of ZnO nanoparticles; Ionic strength = 5 mM NaCl, pH = 7

CONCLUSION

In the current study, the effect of pH and ionic strength on the dissolution of two different sizes of ZnO was investigated. Based on the nanoparticles dissolution, size of particles also plays a significant role in the dissolution. In the case of smaller size, increased ionic strength would result in an increasing concentration of ion released while larger particles are most likely tend to be stable.

Dissolution of ZnO nanoparticles also shows pH dependence whereby for both sizes, the dissolution increased when pH decreased. The present study demonstrated the effects of pH and ionic strength on the behaviour of ZnO nanoparticles and these effects may influence the fate and transport of Zn ions in the aquatic environment.

ACKNOWLEDGEMENTS

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