Understanding effect of solution chemistry on heteroaggregation of zinc oxide and copper oxide nanoparticles

Tanushree Parsai, Arun Kumar[*]

Department of Civil Engineering, Indian Institute of Technology, New Delhi, India

HIGHLIGHTS

- Study of effects of pH, ionic strength, nanoparticle concentration on heteroaggregation rate constant.
- Development of aggregation rate constant - and settling rate constant - predicting equations.
- Change in settling of CuO nanoparticles when present in mixture with ZnO nanoparticles.
- Dominance of van der Waals forces of attraction on aggregation.

GRAPHICAL ABSTRACT
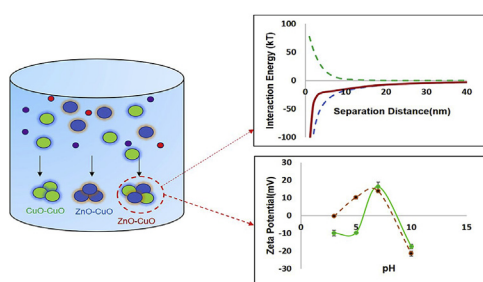
ARTICLE INFO

ABSTRACT

The reported presence of mixture of nanoparticles in environmental water warrants developing understanding on their aggregation and fate. This study tried to address this question and focused on understanding effects of pH (3,7 and 10), background electrolyte concentration (1 mM and 10 mM as NaCl) and nanoparticle (NP) concentration (1 and 10 mg/L) on stability of suspension containing mixture of two commonly-found metal oxide-based NP (i.e., ZnO and CuO NPs) in a 6-h study (output variables: aggregation rate constant, settling rate constant, difference in zeta potential, change of metal content in suspension and on aggregates). Two iso-electric point values were obtained: pH 3.08 and 8.33 for mixture suspension in DI (De-ionized) water and pH 5.69 and 8.65 for mixture suspension with 10 mM electrolyte concentration. Settling rate constant and aggregation rate constant values of suspension containing mixture of NPs varied between 0.02 and 0.23 NTU/(NTU-hour) and 0.0002 and 0.03 nm/s, respectively. At natural pH condition, settling rate constant and aggregation rate constant values were obtained to be 0.05 NTU/(NTU- hour) and 0.012 nm/s. The Derjaguin—Landau—Verway—Overbeek (DLVO) analyses indicated that aggregation of mixture of NPs might be happening due to combined effects of ionic layer compression, charge neutralization and van der Waals attraction. Dissolution of nanoparticles was found to be significantly affected by change in pH of suspension. Stability of mixture of nanoparticles was observed to decrease with increasing pH, ionic strength and nanoparticle concentration values. For ZnO and CuO nanoparticles, model equations were developed for predicting their (i) aggregation rate constant, (ii) settling rate constant, (iii) difference in zeta potential, (iv) percentage change of metal in suspension and (v) solid Zn fractions of mixture of nanoparticles as a function of pH, ionic strength and NP concentration. These information are useful in understanding fate of mixture of NPs in suspension as well as in settled solids in natural water bodies and in water treatment systems.

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* Corresponding author.
E-mail addresses: tanushreeparsai@gmail.com (T. Parsai), arunku@civil.iitd.ac.in (A. Kumar).

1. Introduction

The widespread use of nanomaterials (example: CNT, Ag NPs, ZnO, and TiO$_2$) in different products has increased the chances of entering of engineered nanoparticles (NPs) to environment (Dumont et al., 2015). The reported usages of more than one type of NPs have increased chances of their co-occurrence in environmental systems as well. They end up in aquatic systems and have toxic effects on aquatic life due to various transformational changes and bioaccumulation (Chupani et al., 2018).

Nanoparticles released to river water undergo various transformational processes, such as aggregation, dissolution, sedimentation, adsorption, etc. depending on aquatic systems chemistry (Peng et al., 2017). Studies have focused on understanding effects of factors, such as natural organic matter, natural colloids, cations, ionic strength and pH on aggregation and settling of NPs (Fang et al., 2017; Keller et al., 2010; Praetorius et al., 2014; Quik et al., 2010; Smith et al., 2015, Sygouni and Chrysikopoulos, 2015) (Table S1, Supporting Information). The development of understanding of aggregation of nanoparticles with other nanoparticles and/or natural colloids is of importance as it affects fate of NPs in suspension and in settled solids. For example, aggregation study between CeO$_2$ and TiO$_2$ at different ratios reported an increase in stability with increase in nanoparticles concentration ratio (Luo et al., 2017). Similarly, another study observed homoaggregation among ZnO NPs (or TiO$_2$ NPs) and heteroaggregation between ZnO and TiO$_2$ NPs (or between NPs and colloids) and attributed it to be the main mechanism for the observed sedimentation (Fang et al., 2017). Overall, there have been heteroaggregation studies focusing on interaction between nanoparticles and clay (Quik et al., 2010; Labille et al., 2015). Some studies have focused on aggregation of mixture of different nanoparticles (example: between zinc sulphide and CNT (Sarpong et al., 2017); Gold nanoparticles and CNT (Afrooz et al., 2013), Hematite nanoparticle and CNT (Huynh et al., 2012)) to understand: 1) aggregation of single nanoparticles in presence of natural colloids or carbon nanotubes, and 2) effect of solution chemistry on aggregation. However, the questions related to interaction of two types of engineered nanoparticles are poorly understood till date. In this direction, there have been some studies which focused on interaction between two types of metal oxide nanoparticles, like CeO$_2$ and TiO$_2$ (Luo et al., 2017), ZnO and TiO$_2$ (Fang et al., 2017), ZnO and TiO$_2$ (Tong et al., 2014) and studied effect of ratio of nanoparticles (Fang et al., 2017) and NP concentration (different TiO$_2$ concentration; Tong et al., 2014) on aggregation. Findings of these studies still do not provide some information to understand effect of water chemistry on nanoparticle stability.

The objective of this study was to understand effect of water quality constituents (pH, ionic strength, nanoparticle concentration and nanoparticle chemistry type (hereafter referred as nanoparticle type) on aggregation behaviour of mixture of ZnO and CuO NPs using a 2$^{4-1}$ factorial approach (measurement variables: turbidity, hydrodynamic diameter (HDD), zeta potential (ZP), metal content describing dissolution over 6-h duration). ZnO and CuO nanoparticles were chosen in this study as these NPs along with Cu and Zn ions have similar toxicological profiles (Chang et al., 2012). These NPs have good electrical, optical and magnetic properties (Das and Srivastava, 2018) and have been used in antimicrobial industry (Bondarenko et al., 2013), electronics industry and personal care products-making industry, etc. (Jeon et al., 2016) and thus can be detected together in wastewater and in stream water. It becomes important to understand their dissolution and aggregation characteristics in water under different conditions. The factorial

approach was used to (1) relate effects of main factors (i.e., pH, ionic strength, NP concentration and NP mixture) and interaction among these factors on output variables (i.e., settling rate constant, aggregation rate constant, difference in zeta potential) and (2) obtain equations for predicting settling rate constant and aggregation rate constant for suspension containing mixture of ZnO and CuO NPs. Behaviour of these NPs in water was also studied at natural water condition (near neutral pH and low ionic strength) for obtaining information on aggregation of mixture of NPs for predicting their fate in suspension and in settled solids. Findings of the present work are expected to provide (i) an explicit relationship between water quality constituents and aggregation behaviour of mixture of ZnO and CuO nanoparticles which can be used in characterizing their fate in suspension and in solids and (ii) information on their fate in water under natural conditions.

2. Materials and methods

2.1. Materials

ZnO NPs (CAS Number: 1314-13-2; particle size <100 nm size by dynamic light scattering (DLS); <35 nm size by Aerodynamic Particle Sizer) and CuO NPs (CAS Number. 1317-38-0; particle size <50 nm size) were obtained from Sigma Aldrich Corporation (St. Louis, MO, USA). Fresh stock suspensions of 100 mg/L concentrations of NPs were prepared by sonicating for 15 minutes (Fang et al., 2017) using sonicator (JAISBO Instrument, India).

2.2. Methods

Two types of experiments were performed using a 2$^{4-1}$ factorial approach (Table S2 of Appendix A2) (Montgomery, 2017). The first set of experiments (experiment-1) was done to study effect of presence of CuO NPs on stability of ZnO in suspension. The second set of experiments (experiment-2) was done to study effect of presence of ZnO NPs on stability of CuO in suspension. During design of experiment, nanoparticle type, pH, nanoparticle concentration and ionic strength were presented as A, B, C and D, respectively (a, b, c and d represent levels (high or low)). By looking at highest order interaction factor (ABCD), overall design was divided into two fractions. The combination with interaction factor ABCD value as 1(high) were aliased with combination with ABCD value as −1(low) (Table S2). The first and second order interaction terms have same effects as third and higher order interaction terms (Montgomery, 2017). The combinations underlined in Table S2 are aliased with combinations which are marked as bold texts, as they have same effects. Hence, half of those combinations, i.e., eight combinations (with ABCD = 1 Table S3) were considered to understand the effects of pH, ionic strength, NP concentration and NP type size, turbidity, etc. This design was used to estimate all four main effects and second order effects which are aliased with third and higher order interaction terms.

Suspensions of 1 mg/L and 10 mg/L NP concentrations were used to depict a real condition of environmental pollution. For preparing a suspension containing mixture of nanoparticles with 1 mg/L concentration each, 1 mg/L concentration of ZnO NPs and 1 mg/L concentration of CuO NPs were mixed in de-ionized water. Similar approach was used for preparing suspension containing mixture of NPs both at 10 mg/L alone. Two levels of pH (i.e., 3 and 10) were selected to understand effect of pH change on size, zeta potential, and turbidity. Further, experiments were also conducted under natural water condition. A suspension containing 10 mg/L CuO NPs and 10 mg/L ZnO NPs at 1 mM ionic strength and pH 7 was

studied for 6 h as per the above mentioned experimental plan. Each set of experiment was repeated 3 times and average and standard deviation values of observations were calculated.

For a given experiment, suspensions of different combinations (Table S3) were prepared and liquid samples were collected at seven sampling times (0—6hr, 1hr interval). Turbidity and size values were measured at every hour, whereas, zeta potential values, total metal content of suspension and metal content corresponding to nanoparticles-associated solid fractions were measured only at start and end of the experiment.

2.2.1. Measurement of turbidity values for estimating settling rate constant values

Turbidity values (C_{turb}) in different samples were measured using turbidimeter (Hanna Instruments, HI83414). This parameter has been used earlier also to understand sedimentation (Gambinossi et al., 2015; Wang et al., 2014; Zhu et al., 2014). An exponential model (Equation (1)) was fit to the observed data (C_{turb}/C_{0turb} versus time) to obtain settling rate constant, where, y_0 is initial turbidity at t = 0hr, k is settling rate constant for particles(NTU/(NTU-h)), and t is time in hrs (Mehta et al., 2009; Palimi et al., 2014).

$$y = y_0 e^{-kt} \tag{1}$$

Settling rate constant values were determined only in those suspensions where model fitting resulted in coefficient of determination (R^2) value > 0.75. The calculated settling rate constant values were subsequently used in conducting the analysis of variance (ANOVA).

2.2.2. Measurement of hydrodynamic diameter (HDD) values for estimating aggregation rate constant

The variation of HDD with time was studied to observe change in size of nanoparticles over a period of 6 h in different suspensions. Size value was measured using the dynamic light scattering system (Nicomp Zetasizer ZLS380; wavelength = 633 nm; detector angle = 173 °C). Information about distribution of size of particles in different suspensions was also compiled. Aggregation behaviour was understood by determining aggregation rate constant after doing linear model regression on the data of size versus time (p-value<0.05) (Table S3).

2.2.3. Measurement of zeta potential value and determination of interaction profiles using the Derjaguin—Landau—Verway—Overbeek (DLVO) theory

Zeta potential values of different suspensions were determined using the Smoluchowski equation (Gentile and Fidalgo de Cortalezzi, 2016) from Zetasizer Nano ZS (Malvern Zetasizer Nano ZS90) and used in estimating energy barrier value for understanding possibility of aggregation. Refractive index values of different suspensions were determined with Abbe Refractometer (obtained value = 1.345(for CuO NPs), 1.346 (for ZnO NPs), 1.348 (for mixture of CuO and ZnO NPs). For understanding change in surface characteristics of NPs during their interaction with each other and also with constituents of suspensions, the difference of initial and final zeta potential values (Table S3) was calculated. Values of pH of zero-point charge (i.e., pHzpc) of de-ionized water suspension and suspension with 10 mM NaCl as a background ionic strength were also determined. For analysis of aggregation behaviour of nanoparticle suspensions, the DLVO theory was applied. Interaction profiles of repulsion and attraction energies were drawn to understand phenomenon of aggregation in different suspensions. Values of energy barrier (EB) (Table S3) were calculated for all the combinations where nanoparticles appeared to be

in a repulsion-dominant region.

2.2.4. Microscopic characterization of aggregates

Microscopic characterization of aggregates of the selected suspension (pH = 10; ionic strength = 10 mM; NP concentration = 10 mg/L) was done using Transmission Electron Microscopy (instrument: JEOL 2100F) and elemental mapping. This information was used to study formation of ZnO and CuO heteroaggregates in suspension.

2.2.5. Metal content

Metal content in suspension was determined by taking sample from beaker, digesting it with acid (3050G method (APHA, 1998)) and analysing it with ICP-MS(ICP-MS Agilent 7900).Using obtained values at t = 0 and 6 h, change in metal contents of suspension was calculated.

Metal content associated with solid retained on 20 nm filter paper represents those metals which were present in aggregates of suspension. As this study assumed 20 nm size as a cut-off point for separating ion and nanoparticle, solids retained on the filter paper were assumed to be associated with NP aggregates or nanoparticle. It was determined after passing mixture suspension from 20 nm(Whatman) filter paper(Han et al., 2014), digesting filter paper and determining Zn and Cu metal contents as mentioned above. Using obtained values at t = 0 and 6 h, change in metal contents of solids associated with nanoparticles was calculated. The values obtained as percentage for suspended and solid portions in 6h were used for determining regression equations using the factorial analysis approach and presented in Table 1.

2.2.6. Mathematical methods

The analysis of variance (ANOVA) of different output parameters was conducted using the Minitab version 18 for Windows (Minitab Inc.) software and tested for a 95% confidence level test ($\alpha = 0.05$) (Montgomery, 2017). Before conducting ANOVA, two types of tests were conducted: (1) Tukey HSD test to see if statistically significant difference between two consecutive observations exists and (2) paired *t*-test to see if mean value of two different samples differ statistically. Factors giving statistically significant main effect and interaction effect for every output variable were identified from ANOVA analysis and used in developing equations for predicting settling rate constant, aggregation rate constant. Factorial analysis was used to obtain values of various coefficients for main and interaction effects of various factors (Montgomery, 2017, Mitić et al., 2019). Equation consists of main and interaction effects as variables with coefficient represented by half-of- the-effect. As no other model form, except the form developed as per the factorial design approach, was used, estimation of parsimony of model was not conducted.

3. Results and discussion

This study tried to statistically analyse different parameters like size, zeta potential, and metal content with the help of factorial design. Effects of different factors like nanoparticle type, NP concentration, pH and ionic strength were studied and model equations were developed to understand the significance of each factor. Findings related to all parameters and their effects on rate constant and aggregation behaviour were discussed separately.

3.1. Characterization of suspension containing mixture of nanoparticles

Intensity-weighted size distributions of suspensions were obtained to understand effect of various solution chemistry

Table 1
Percentage change in metal values in suspension and solids retained on filter paper (pore size: 20 nm) in 6 h period (p-values are given in bracket; p-value < α = 0.05 level is highlighted as bold texts).

Combination	Change in metal content in suspension (Zn)[a] (Decrease)	Change in metal content in solid retained on filter paper (Zn)[a] (Decrease)	Change in metal content in suspension (Cu)[a] (Decrease)	Change in metal in solid retained on filter paper (Cu)[a] (Decrease)
1	12.65 ± 0.68 (0.034)	71.80 ± 2.96 (0.025)	NA	NA
2	15.12 ± 4.63 (0.114)	15.47 ± 4.25 (0.122)	64.14 ± 1.19 (0.009)	83.89 ± 3.19 (0.014)
3	17.36 ± 1.83 (0.033)	78.50 ± 3.34 (0.002)	69.52 ± 4.25 (0.018)	89.84 ± 0.77 (0.007)
4	21.53 ± 1.63 (0.016)	6.70 ± 1.73 (0.054)	NA	NA
5	15.29 ± 2.428 (0.019)	38.80 ± 11.68 (0.031)	56.66 ± 5.58 (0.002)	87.88 ± 3.18 (0.006)
6	10.94 ± 1.9 (0.073)	22.07 ± 2.37 (0.023)	NA	NA
7	18.52 ± 2.04 (0.104)	33.87 ± 4.23 (0.129)	NA	NA
8	29.53 ± 1.51 (0.022)	44.50 ± 0.003 (0.003)	21.19 ± 1.71 (0.144)	49.01 ± 9.34 (0.011)

[a] Average ± standard deviation (p value); NA-not available.

parameters on different aggregation behaviour. Figs. 1—4 show size distributions of suspensions containing mixture of particles. Size distributions of particles in suspensions with other combinations are presented in Supporting Information document (Figs. S1—S8). As observed from size distribution data (Figs. 1—4), there has been aggregation between mixture of nanoparticles over time. For combination C2 (ZnO + CuO, 10 pH, 1 mg/L NP Concentration, 1 mM Ionic strength), mean diameter was found to increase from around 200 nm to 650 nm indicating aggregation between mixture of nanoparticles. Similarly, values of mean diameter of particles were found to increase from around 600 nm to 1000 nm (C3, Fig. 2); 500 nm to 700 nm (C5, Figs. 3) and 1000 nm to 1800 nm (C8, Fig. 4), indicating aggregation of particles in mixture suspension over time. The increase in size of particles was found to be maximum in suspension containing high NP concentration (10 mg/L) and high ionic strength (10 mM) (Combination 8, Fig. 4), indicating NP concentration as one of the significant factors.

The suspension containing mixture of nanoparticles (C8: pH10, 10 mM ionic strength, 10 mg/L nanoparticle concentration) was also characterized for zeta potential values and surface morphology. Fig. 5 shows TEM-EDX of mixture of nanoparticles at high level values. Fig. S9 shows TEM-EDX for nanoparticles suspension with single nanoparticles. For mixture of nanoparticle case (Fig. 5), the STEM image at t = 0 h showed high presence of zinc metal than copper metal. The EDX result also showed high peak value of zinc than copper. After 6 h of interaction among particles, similar type of

pattern was obtained with dominance of zinc metal over copper metal through the STEM and EDX data. In addition, the analysis of ion content data for C8 sample indicated higher dissolution of copper ions than zinc ions (copper dissolution rate = 0.067 mg/g/h versus zinc dissolution rate = 0.007 mg/g/h). Zinc content in solid fraction after 6 h was observed to be higher than copper content in solid fraction which was also evident by looking at the EDX data. These observations indicated the possibility of less involvement of copper metal than zinc metal in formation of aggregates in suspension containing mixture of NPs. Further, size values of particles using DLS method and TEM analysis method were compared (Figs. 4 and 5). Although size value from TEM analysis was found to be different from size value obtained from DLS method, as also observed in previous studies(Pabisch et al., 2012), both the method confirmed the increase of size of nanoparticles in 6 h period (Figs. 4 and 5).

Fig. 6 shows trends of variation of zeta potential (ZP) with pH of suspension containing single type of nanoparticles or mixture of nanoparticles. Values of pHzpc of mixture of NPs in de-ionized water and in suspension containing 10 mM NaCl were calculated to be 8.33 and 8.65, respectively. pHzpc value of ZnO NPs suspension (i.e., 9) was observed to decrease to 8.65 in suspension containing mixture of nanoparticles, indicating the effect of addition of one type of NP on overall charge characteristics of suspension containing mixture of NPs. This effect might play a role in aggregation of suspension of mixture of NPs. Further, pHzpc value for
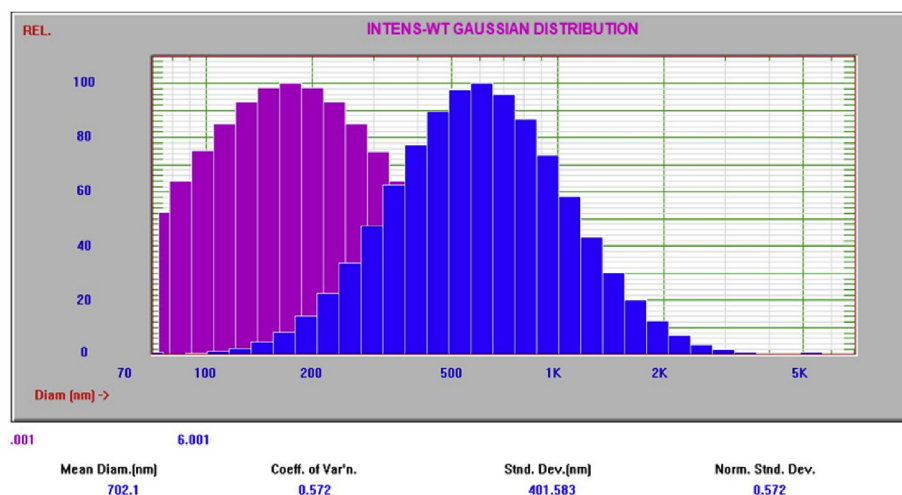

Fig. 1. Intensity- weighted Gaussian distribution for combination C2 (ZnO + CuO, 10 pH, 1 mg/L NP Concentration, 1 mM Ionic strength); Pink colour distribution t = 0 h; Blue colour distribution: t = 6 h). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
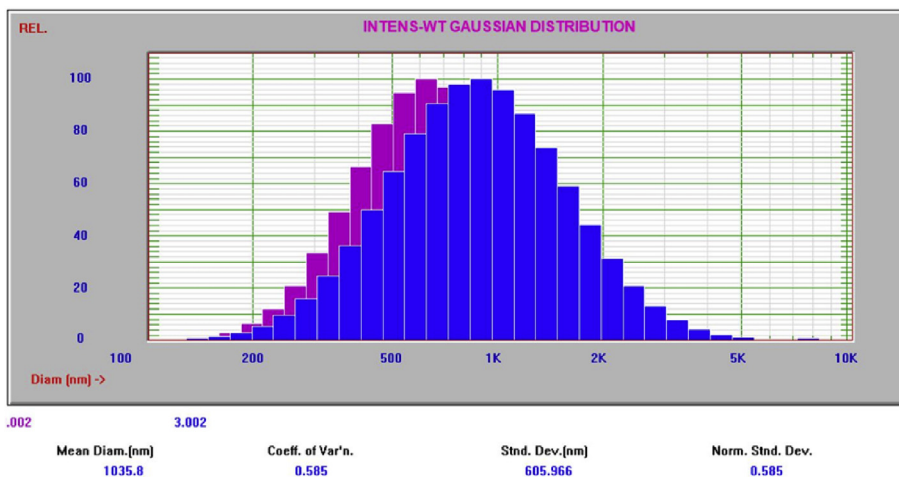
Fig. 2. Intensity- weighted Gaussian distribution for combination C3 (ZnO + CuO, 3 pH, 10 mg/L NP concentration, 1 mM Ionic strength).
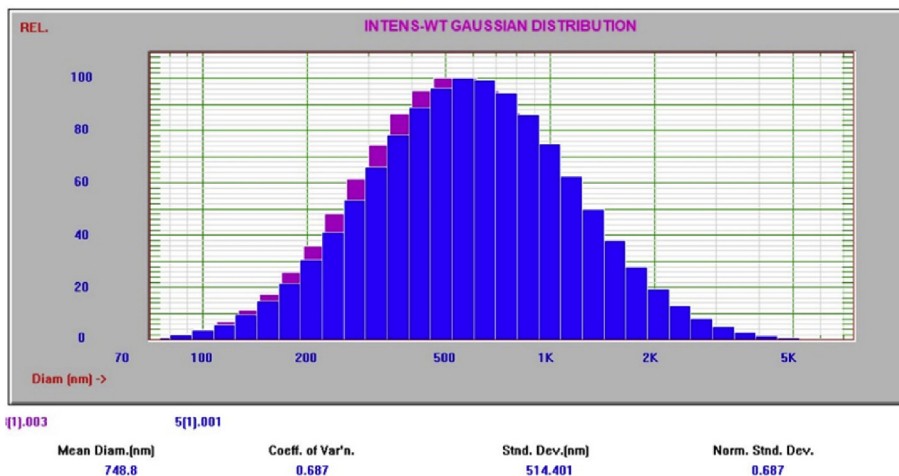

Fig. 3. Intensity- weighted Gaussian distribution for combination C5 (ZnO + CuO, 3 pH, 1 mg/L NP concentration, 10 mM Ionic strength).
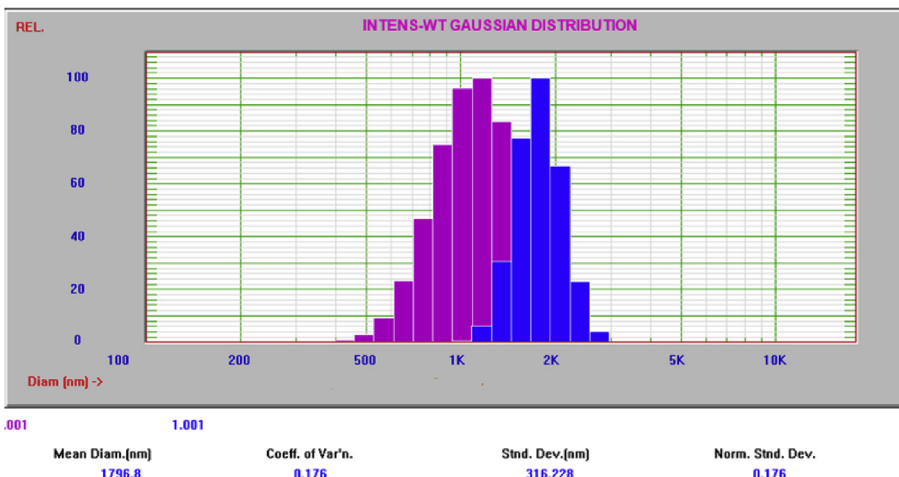

Fig. 4. Intensity -weighted Gaussian distribution for combination C8 (ZnO + CuO, 10 pH, 10 mg/L NP concentration, 10 mM Ionic strength).

ZnO NPs (or CuO NPs) in 10 mM ionic strength suspension was found to be different than that reported in literature for de-ionized water (value = 9.3 and 6.21(Sousa and Teixeira, 2013; Zhou and Keller, 2010)). Two values of pHzpc were observed for ZnO NPs in
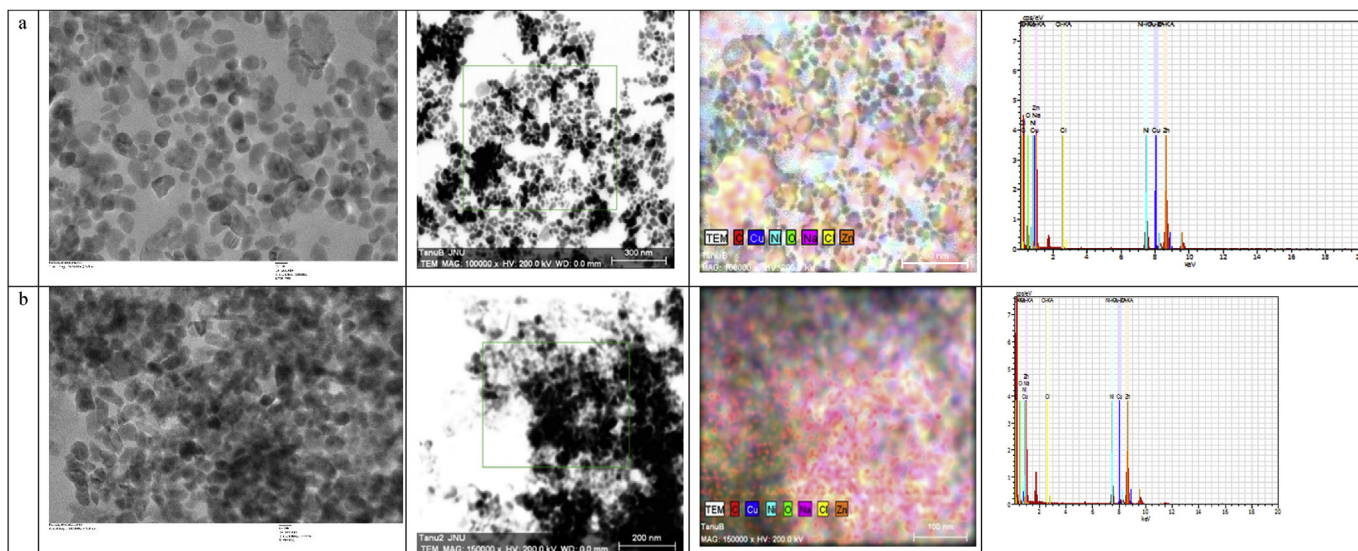
Fig. 5. Transmission electron microscopy along with elemental mapping for seeing formation of heteroaggregate (experimental conditions: 10 mg/L nanoparticle concentration, pH 10, 10 mM background electrolyte concentration): (a) suspension containing mixture of ZnO and CuO nanoparticles at t = 0; (b) suspension containing mixture of ZnO and CuO nanoparticles at t = 6 h
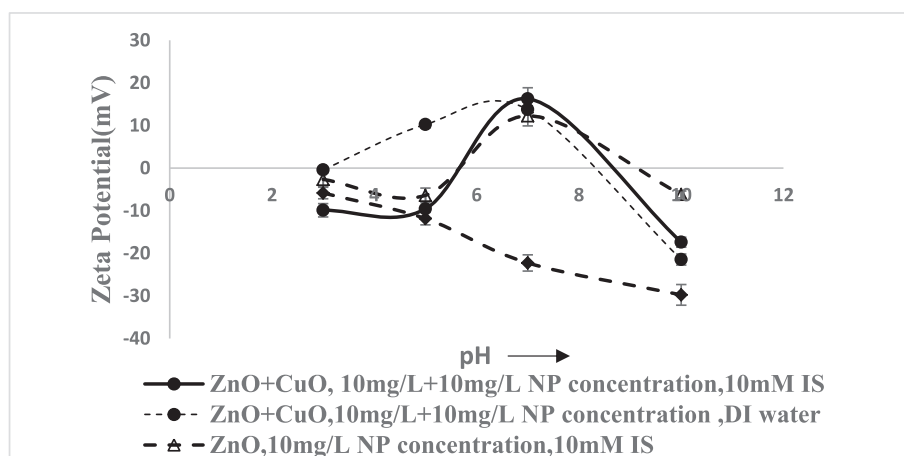

Fig. 6. Variation of zeta potential values of ZnO, CuO and mixture of ZnO and CuO nanoparticles (NPs) in suspension at high level condition. Error bars: ±Standard deviation (n = 3).

this suspension (i.e., pH 5.69 and pH 9.07), whereas, ZP value of suspension containing CuO NPs remained negative throughout the tested pH range. The trend of variation of ZP with pH for suspension containing mixture of NPs was observed to be similar to that of ZnO NPs under similar conditions.

3.2. Change in metal content

Values of percentage change of Zn contents over 6 h in remaining suspended fraction and in solid fraction retained on filter paper are presented in Table 1. Columns 1 and 3(Table 1) show percentage change in heavy metal content in suspension, i.e., change in Zn and Cu metals present in suspension after 6h. Columns 2 and 4 (Table 1) show the change in metal content in solids retained on filter paper, i.e., metal values in aggregates retained on filter paper after 6h. Within 6 h, Zn content in suspension was observed to decrease which could be attributed to the effect of increase in contents of settled aggregates.

The observed decrease in Zn content in aggregate (i.e., retained on filter paper) could be attributed to the effect of dissolutions of

ions from ZnO particles. ZnO nanoparticles has been observed to dissolve at pH 1, 3 and 6 with higher dissolution of ions at lower pH (Bian et al., 2011). The % change in zinc content on suspended solids in suspension with high pH (combination 8) was found to be smaller than that in suspension with low pH condition which could be attributed to the effect of formation of metastable layer of hydroxide on nanoparticles (David et al., 2012).

In suspension containing mixture of CuO and ZnO nanoparticles, a change in copper ion content value over 6 h was found to be higher than that of zinc ion content within the same period. Earlier, Fang et al. (2017) also observed lesser settling of ZnO nanoparticles than TiO$_2$ nanoparticles in filtered natural water. They attributed this observation to lesser formation of homoaggregates of ZnO because of reduction in overall collision frequency between nZnO nanoparticles. There is a possibility of observing similar effect during interaction of ZnO particles in our case as well, resulting in association of more zinc to solid fraction than copper.

The regression analysis for % change of Zn content indicated that all single factors, such as NP type, NP concentration and pH had significant effects on total metal content; whereas interaction

factors, such as NPtype × pH and NP Type × ionic strength had significant effects on % change in Zn. NP concentration was observed to be the most significant factor. A reduction in total Zn content over 6 h period was observed due to settling of nanoparticles with time. Further, regression analysis for Zn content in aggregates showed that factors (NP type, pH, and ionic strength) affected as significant single factors and factors (NP type × pH, NP type × NP concentration) affected as significant interaction factors. The regression equations obtained from factorial analysis are given in equations (2) and (3). Residual diagnostics for these equations are shown in Figs. S10 and S11. Normal probability plot (Fig. S10a) showed that data points were found to be close to straight line and followed normal distribution trend. Further, residual versus fit plot (Fig. S10b) showed that residuals are randomly distributed and have constant variance.

$$
\begin{aligned}
\textit{Total Zn remaining in suspension}(\% \; change) = &\; 17.611 \\
&+ 1.713 NPType + 1.658 pH + 4.110 NP \; Conc. \\
&+ 0.963 \; Ionic \; Strength + 1.345 \; NP \; Type \times pH \\
&+ 0.008 \; NP \; Type \times NP \; Conc. + 2.130 \; NP \; Type \\
&\times Ionic \; Strength
\end{aligned}
\tag{2}
$$

$$
\begin{aligned}
\textit{Zn associated with nanoparticle}(\% \; change) = &\; 39.20 \\
&+ 5.11 \, NP \; type - 17.03 pH + 1.68 NP \; conc \\
&- 4.41 Ionic \; strength + 2.70 NP \; type \times pH + 15.50 NP \; type \\
&\times NP \; conc. + 1.74 NP \; type \times Ionic \; strength
\end{aligned}
\tag{3}
$$

Earlier, some studies (Wang et al., 2016; Peng et al., 2017; Liu et al., 2018) focused on dissolution of nanoparticles during aggregation studies. For example, Wang et al. (2016) studied effect of dissolved organic matter on dissolution of ZnO (calculated dissolution rate values = 0.072 ± 0.003 (1/minute) and 0.044 ± 0.002 (1/minute)). However, the Wang et al. study did not consider effects of pH, nanoparticle concentration, ionic strength and mixture of nanoparticles on dissolution. Similarly, Peng et al. (2017) studied effect of size, electrolyte concentration and organic carbon on dissolution. However, the Peng et al. study did not consider effect of mixture of nanoparticles on dissolution of ions from nanoparticles. Out study provided information on factors affecting metal distribution in settled and suspended portions of aggregates, which can be useful in estimating exposure dose of nanoparticles-associated metal during inadvertent exposures of these types of suspensions as part of ecological and health risks assessment studies.

3.3. Turbidity

The variations of turbidity of suspensions containing ZnO NPs and CuO NPs (C6 versus C14) with time (Fig. S12) was found to be significantly different (p-value<0.05). For other combinations (C1 versus C9; C4 versus C12; C7 versus C15), the variations of turbidity with time were not found to be significantly different (p-value>0.05). The variations of turbidity values with time for different mixture suspensions are presented in Fig. 7a. Settling rate constants of ZnO nanoparticles varied between 0.05 and 0.16 (NTU/(NTU-h)) whereas these values varied between 0.07 and 0.26 (NTU/(NTU-h)) for CuO nanoparticles alone. Settling rate constants of suspension containing mixture of particles varied between 0.02 and 0.23 (NTU/(NTU-h)) (Table S2). CuO nanoparticles were observed to settle more than ZnO nanoparticles (C6 versus C14), probably due to the effect of greater homo-aggregation of CuO NPs than ZnO nanoparticles in suspension.

The ANOVA analysis for experiment 1 indicated that main factor (i.e., NP concentration) and interaction of factor (i.e., NP type × pH, NP type × NP concentration, NP type × ionic strength) had significant effects on settling rate constant (Table S5; p-value <0.05). Previously, studies have reported a decrease in turbidity value (and thus an increase in settling rate) with an increase in NP concentration (Sousa and Teixeira, 2013). In present study, combinations, such as C3, C4 and C8, had high NP concentration values (i.e., 10 mg/L) which might have increased chances of collision amongst nanoparticles and thus, of aggregation (Keller et al., 2010). The ANOVA analysis for experiment 2 indicated that single factors, NP type and NP concentration, had significant effects on settling rate constant (Table S6; p-value< 0.05). Table S7 presents regression equations for predicting settling rate constant values for all combinations. These equations also indicate the effect of mixture of nanoparticles on settling rate constant value. For example, the presence of CuO NPs in suspension containing ZnO NPs (condition:C1) was observed to increase settling of particles (calculated difference in settling rate constant: 0.0366 per hour). Further, the following equation (Eq. (4)) was developed for predicting settling rate constant of suspension containing mixture of ZnO and CuO nanoparticles (here, $I_{pH} = -1$ for pH 3 and + 1 for pH10; I_{NP} concentration = −1 for 1 mg/L and +1 for 10 mg/L; $I_{ionic \; strength} = -1$ for 1 mM and +1 for 10 mM):

$$
\begin{aligned}
\textit{Settling rate constant}\left(hr^{-1}\right) = &\; 0.09667 - 0.03833 I_{pH} \\
&+ 0.06833 I_{NP \; Concentration} - 0.0300 I_{ionic \; strength}
\end{aligned}
\tag{4}
$$

3.4. Size

For combinations (C4-C12, C6-C14), the variations of size values of CuO NPs were found to be statistically different than that of ZnO nanoparticles (Fig. S13) (p-value <0.05; paired t-test), indicating that both CuO and ZnO NPs aggregate differently under these conditions. For other combinations (C1-C9, C7-C15), both types of particles were observed to follow similar type of aggregation behaviour. Fig. 7b shows variations of size of mixture of nanoparticles with time. Nanoparticle aggregation was observed to be dominant for all combinations except for C5.

Aggregation rate constant values of suspensions containing only ZnO nanoparticles (Table S3) varied between 0.004 nm/s and 0.24 nm/s whereas these values varied between 0.008 nm/s and 0.017 nm/s for suspension containing CuO NPs only. Further, these values varied between 0.001 nm/s and 0.004 nm/s for suspension containing mixture of ZnO and CuO NPs. These observations indicated that aggregation happens slowly in suspension containing mixture of nanoparticles than in suspension containing single type of nanoparticles. This information is important as it indicates that mixture of nanoparticles might remain suspended in water for a long time and thus one might have higher chances of exposure of mixture of nanoparticles than single type of nanoparticles during inadvertent exposures of contaminated water.

NP concentration was not observed to affect aggregation rate constant (p > 0.05) (Tables S8 and S9). All other single factors were observed to affect aggregation rate constant significantly (p < 0.05). NP type was found to affect aggregation of particles more than other parameters. The interaction of factors, NP type and NP concentration, was found to affect aggregation rate constant of particles significantly (Experiment 1), indicating that the significance of the effect of NP concentration on aggregate rate constant depends on NP type. Further, the interaction of factors, NP type and pH, was found to affect aggregation rate constant of particles significantly (Experiment 2), indicating that the significance of the effect of pH
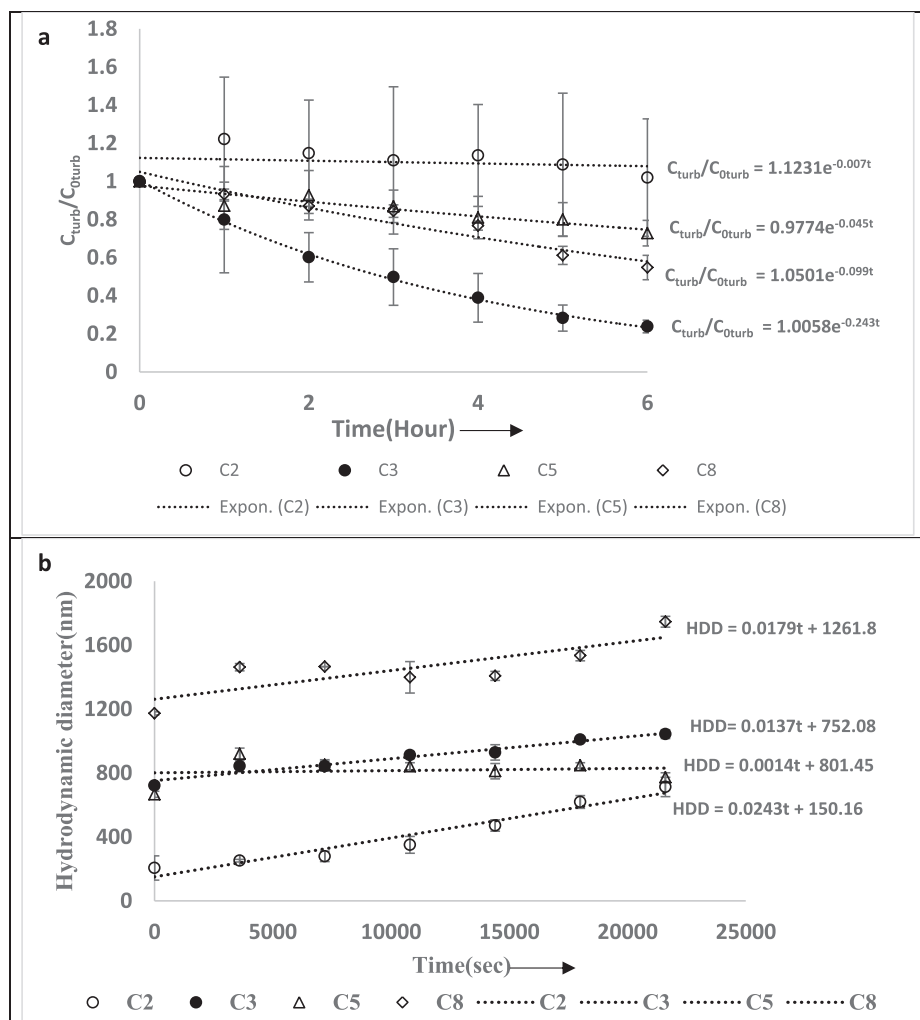
Fig. 7. Variations of (a)turbidity (C_{turb}/C_{oturb} where C_{turb} is turbidity at time t and C_{oturb} is turbidity at time t = 0) and (b) size of mixture of nanoparticles with time in suspensions with parameters (C2: 10 pH, **1mg/LNP concentration, 1mMIS; C3: 3** pH, **10mg/LNP concentration, 1mMIS; C5: 3** pH, **1 mg/L NP concentration, 10mMIS; C8: 10** pH,**10 mg/L NP concentration, 10mMIS)** Model fitting using exponential expression (coefficient of determination >0.9); Error bars indicate one standard deviation value of three replicates around average values.

on aggregate rate constant depends on NP type as well.

Using calculated aggregation rate constant values, following equation (Eq. (5)) was developed for predicting aggregation rate constant of suspension containing mixture of ZnO and CuO nanoparticles.

$$Aggregation\ rate\ constant \left(\frac{nm}{sec}\right) = 0.013767 + 0.0069I_{pH}$$
$$+ 0.002067I_{NP\ concentration} - 0.0048I_{ionic\ strength} \qquad 5$$

3.5. Zeta potential difference

The zeta potential (ZP) values of suspension containing mixture of nanoparticles at t = 0 and 6 h are presented in Fig. S14. For other conditions, ZP values are presented in Table S3. Zeta potential value was observed to fluctuate between −1.8 and −9.1 mV with pH change (from 4.4 to 6.0). Similarly, earlier studies (Omar et al., 2014; Fatehah et al., 2014) have also observed variations of zeta potential value of ZnO nanoparticles with pH.

The analyses of conductivity, pH and zeta potential values of combinations (1,3,4,5,7, and 8) at t = 0 and 6 h (Table S13) indicated that values of zeta potential were observed to differ significantly when values of conductivity and pH also differed significantly within 6 h. Similarly, values of zeta potential of combinations 2 and 6 did not change significantly within 6 h when values of conductivity and pH of these combinations also did not change significantly. These trends indicate that as ion content changes with change in pH and conductivity values, zeta potential value also change.

Overall, a change in value of ZP within 6 h (ΔZP) could be attributed to the combined effects of following simultaneous processes: (a) Dissolution of ions over time from particles (Bian et al., 2011; Omar et al., 2014), (b) Adsorption of ions on particles (Ho et al., 2018), (c) Settling of particles, and (d)Aggregation of particles.

For Experiment 1, suspension pH was found to affect ΔZP significantly. In addition, the interaction of factors, NP type and NP concentration, was found to affect ΔZP significantly (Table S10). For Experiment 2, main factors (pH and electrolyte concentration) were found to affect ΔZP significantly. Further, the interaction of NP type with NP concentration (interaction factor 1) and also of NP type with electrolyte concentration (interaction factor 2) were found affect ΔZP significantly (Table S11). Following equation (Eq. (6)) was

developed for predicting ΔZP values for suspension containing mixture of ZnO and CuO nanoparticles.

$$Zeta\ Potential\ Difference(\Delta ZP) = 9.763 + 3.169 I_{pH} \qquad 6$$

3.6. Variation of total energy between two nanoparticles with separation distance

The analyses of calculated values of energy barrier (EBs) and debye length of particles in different suspensions at $t = 0$ and $t = 6\ h$ (Table S12) indicated that particles in suspensions of C2, C4, C6 and C12 were observed to be in the repulsion force predominant regions(Fig. S15), whereas particles in other suspensions were observed to be in the van der Waals force pre-dominant regions. For example, particles of suspension with low pH and low ionic strength conditions were found to be in aggregated state with no repulsive energy (i.e., ZP value close to zero). Earlier also, unfavourable NP-NP interaction and high energy barrier value have been observed in solution with low ionic strength, i.e., in a solution with reaction −limited regime (Han et al., 2014). For combination 2 (i.e., high pH, low concentration and ionic strength), the DLVO interaction profile shows that repulsion forces dominate interaction between two types of particles, resulting in possibilities of stabilization of ZnO nanoparticles and destabilization of CuO nanoparticles (Fig. 8). For all other combinations, the dominance of high van der Waals −based attractive forces was observed on particles in the suspension at $t = 0$. For combination 2, the EB value @2 nm separation distance at $t = 0$ (i.e., 49.8 kT) was observed to decrease to 6.67 kT after 6 h, indicating a shift of total energy in the attraction force-dominant region.

3.7. Aggregation and settling behaviour of nanoparticles at natural water conditions (i.e., near neutral pH, 1 mM ionic strength)

Under natural water condition, settling rate constant values of nanoparticles ranged from 0.046 (1/h)to 0.136 (1/h) and aggregation rate constant values ranged from 0.004 nm/s to 0.036 nm/s (Fig. 9). Variations of settling rate constant and aggregation rate constant with pH (3 and 10) and nanoparticle type are also presented in this figure. The ANOVA analysis indicated that each of the main factor (NP type or pH) affected aggregation rate constant significantly ($p < 0.05$). Aggregation rate constant of suspension containing mixture of nanoparticles was observed to differ significantly with that of suspension containing one type of nanoparticles ($p < 0.05$). As observed from Fig. 9, settling rate constant values of different types of nanoparticle were found to be higher at pH 10 than at pH 7 and pH 3($p < 0.05$). Aggregation rate constant of ZnO nanoparticles was observed to be highest, indicating that these nanoparticles aggregate quickly under natural water condition than other types of nanoparticles studied in this work. Particles in suspension containing mixture of ZnO and CuO nanoparticles were observed to aggregate faster than that in suspension containing CuO NPs only. Further, zeta potential values for nanoparticles suspension under natural water condition (Fig. 10) were found to decrease within 6 h. For ZnO nanoparticles, zeta potential value was observed to decrease significantly within 6 h ($p < 0.05$). For suspension containing mixture of nanoparticles, zeta potential value was observed to be negative.

Earlier, Keller et al. (2010) also observed metal oxide nanoparticles to be more stable at near -neutral pH in a mesocosm freshwater with low ionic strength (1−10 mM). Similarly, Sousa and Teixeira (2013) did not find change in size of CuO nanoparticles, indicating the stability of CuO nanoparticles suspension. The present study also observed the similar trend of no change in size of CuO nanoparticles, resulting in lesser settling of CuO nanoparticles from suspension. Previously, Velzeboer (2014) also observed no change in sedimentation of particles in fresh and estuarine water at pH7.9 and 584 μs/cm conductivity. Overall, the suspension containing mixture of nanoparticles was found to be stable. These settling and aggregation behaviour information are useful in estimating mass of mixture of ZnO and CuO nanoparticles present in surface water which aquatic species, plants or human beings might be exposed to. However, this aspect needs to be separately confirmed by (i) measuring number and mass concentration of nanoparticles and (ii) obtaining information related to size, surface charge and composition before it can be used in exposure assessment steps.

3.8. Relating settling rate constant, aggregation rate constant and energy barrier values for understanding aggregation and settling of nanoparticles

3.8.1. Aggregation and settling of ZnO and CuO nanoparticles

Homoaggregation of ZnO NPs (or CuO NPs) might have resulted in reduction in turbidity (and thus, an increase in settling rate constant value). This phenomenon has been shown to depend on the combined effects of pH, ionic strength, humic acid and cations (French et al., 2009; Liu et al., 2012). The analysis of calculated EB values of suspension containing ZnO NPs (Table S12) indicated that observed aggregation of ZnO NPs for combinations (C2 and C7) could be attributed to the effect of dominance of van der Waals forces of attraction whereas observed aggregation of ZnO NPs for combinations (C4 and C6) could be attributed to the effect of dominance of electrical double layer (EDL) compression and charge neutralization. Similar to the aggregation behaviour of ZnO NPs, the observed aggregation of CuO NPs for different cases could be attributed to the effect of van der Waal forces of attraction (for combinations C9, C14 and C15) and effect of EDL compression and charge neutralization (for C12). Further, a comparison of settling and aggregation characteristics of ZnO and CuO NPs indicated that settling patterns of both types of NPs appeared to be similar except for the one condition (pH10, 10 mM ionic strength, 1 mg/L NP concentration). This observed difference could be attributed to the effects of difference in (1) size values of ZnO NPs (529 nm at 0 h to 1194 nm at $t = 6$ h) and CuO NPs (433 nm at 0 h to 681 nm at $t = 6$ h) and (2) zeta potential values (−23 mV at 0 h to −7.43 mV at 6 h) for ZnO NPs and (−33 mV at $t = 0$ to −21 mV at $t = 6$ h).

This study observed variations of settling rate constant values from 0.07 to 0.23 (1/h) which were found to be comparable to previously reported values. For example, these values were found to be comparable to findings of study which observed sedimentation rate constants of ZnO, TiO_2, and CeO_2 NPs to vary between 0.00036 and 0.36 (1/h) in different aqueous matrices (Keller et al., 2010). Similarly, Fang et al. (2017) reported faster homoaggregation of TiO_2 NPs than CeO_2 NPs. In our study, settling rate constant value of CuO NPs was observed to be higher than that of ZnO NPs.

3.8.2. Aggregation and settling of mixture of nanoparticles

Figure S16 shows a comparison of aggregation rate constant values of this study and of literature-reported studies. Literature indicated that observed values of aggregation rate constant of mixture of NPs lie in the range of 0.0002−0.5 nm/s. Values observed in this study were found to differ possibly due to the combined effects of pH, ionic strength, and NP concentration, study period, and types of NPs present in mixture. Although some of the studies focused on understanding aggregation of (i) mixture of nanoparticles and natural colloids or (ii) nanoparticles and
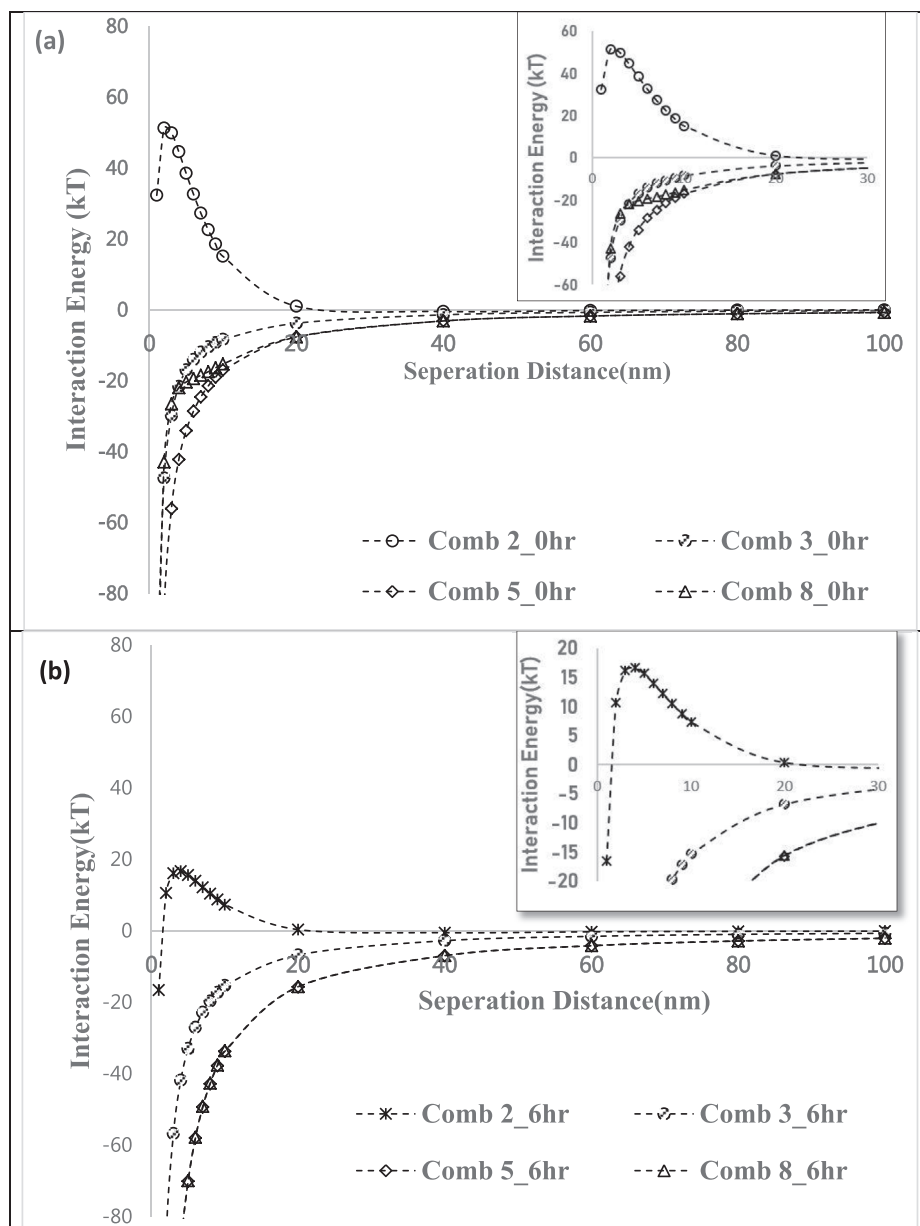
Fig. 8. Total interaction energy curves of mixture of nanoparticles in different suspensions: (a) At t = 0 h and (b) At t = 6 h (the inset figure for separation distance <30 nm).

nanotubes, their findings cannot be used for developing understanding on aggregation of mixture of nanoparticles. Overall, the aggregation rate constant value of suspension containing ZnO and CuO NPs lie within the range of previously reported aggregation rate constant values of metal oxide nanoparticles and depends on pH, ionic strength and NP concentration.

3.8.3. Comparison of aggregation behaviour of single and mixture of nanoparticles

Our study indicated that mixture of nanoparticles aggregates faster than single type of nanoparticle. As a system, particles might have aggregated due to reduction in Debye length and energy barrier values. Earlier studies have attempted to attribute possible mechanisms to observed heteroaggregation of mixture of NPs. For example, mechanisms, such as compression of electrical double layer (EDL), charge screening and charge neutralization have been attributed to the observed heteroaggregation between TiO_2 NPs

and CeO_2 NPs (Luo et al., 2017). In another study, electrostatic attractions between engineered nanomaterials, van der Waals attraction force, and adsorption of dissolved organic carbon were identified as main mechanisms for the observed aggregation (Fang et al., 2017). Further, the effect of binding of cations on another type of NPs on compression of EDL was attributed as a possible reason of heteroaggregation between nano ZnO and nano TiO_2 (Tong et al., 2014).

The review of data of EB (Table S12) for the case of aggregation of mixture of NPs indicated that aggregation might have happened due to the combined effects of ionic layer compression and dominance of van der Waals forces. In our study, pH and ionic strength were observed to affect aggregation of nanoparticles significantly, even if present as alone or in mixture. Similarly, the Sousa and Ribau Teixeira study reported an increase in HDD value of CuO NPs between pH2 and pH10 (HDD = 169 nm at pH2 versus 1581 nm at pH 10) and suggested that extent of aggregation increases near
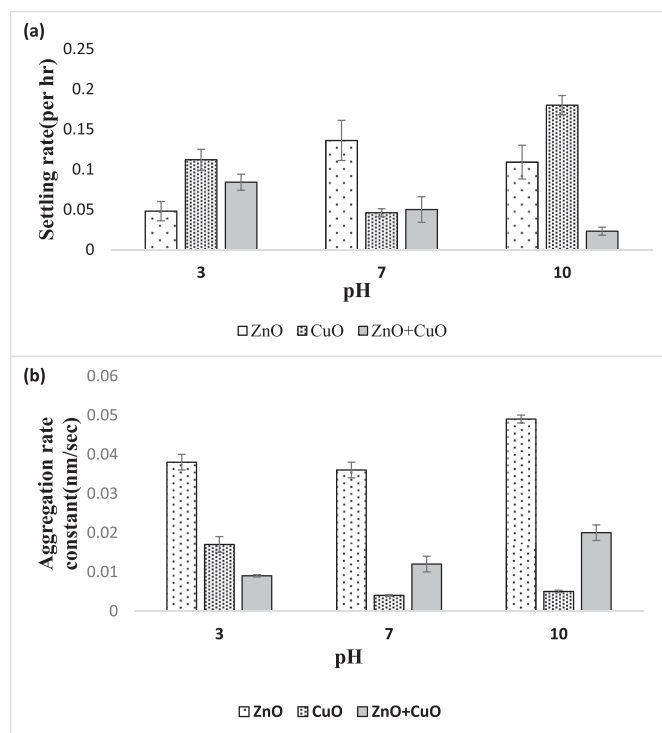
Fig. 9. *Aggregation and settling behaviour of particles in water at natural water conditions (i.e., near neutral pH, 1 mM ionic strength): (a) settling rate constant, (b) aggregation rate constant (n = 3; error bar indicates one standard value about average value).*
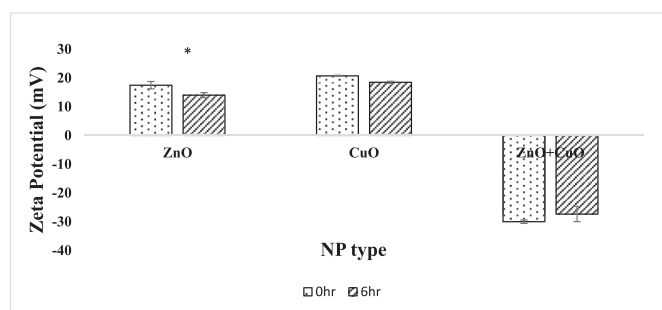

Fig. 10. Variation of zeta potential values for two types of nanoparticles and their mixture at t = 0 and 6h in water at natural water (*: $p < 0.05$, significantly different).

Fig. 8). Counter-cations (Zn^{2+}, Cu^2), in our case, might decrease electrical double layer, act through adsorption and charge neutralization coagulation mechanisms, and, hence, increase the aggregation of particles (Fig. 11). Studies, such as Luo et al. (2017) and Wang et al. (2015) investigated the effect of ion type on aggregate composition. Clavier et al. (2019) studied ion distribution (counter-ion) around nanoparticles using Monte Carlo method and reported that the presence of divalent and trivalent cations strongly modify the NP properties by decreasing the effective charge on NP and improving the condensation state around the nanoparticle. Peng et al. (2015) suggested that co-ions and counter ions affect aggregation by EDL compression and charge neutralization. Overall, the observed aggregation of mixture of NPs in this study could be attributed to the effects of electrical double layer compression, charge neutralization and van der Waals forces of attraction. As per author's knowledge, no study has focused on understanding effect of counter cations released from nanoparticles on aggregation of mixture of nanoparticles. There is a need for exploring this aspect in detail in future studies.

3.8.4. Constitution of aggregates of mixture suspension

This study observed simultaneous happening of homoaggregation and heteroaggregation between nanoparticles. It was hypothesized (Fig. 11) that observed aggregates in a mixture system (aggregation rate constant: $K_{agg, overall}$) might have been formed from aggregates (1) resulting from ZnO NP-ZnO NP interaction (homoaggregation rate constant: $K_{agg, ZnO}$)(reaction type 1, Rxn1), (2) resulting from CuO NP-CuO NPs interaction (homoaggregation rate constant: $K_{agg, CuO}$) (reaction type 2, Rxn2), and (3) resulting from ZnO NP-CuO NPs interaction (heteroaggregation rate constant, $K_{hetero, ZnO-CuO}$) (reaction type 3, Rxn3). The possibility of formation of aggregates through a particular reaction type depends on suspension pH and ionic strength, NP surface charge, NP concentration and pH_{ZPC}.

In a suspension containing both ZnO and CuO nanoparticles, the released Cu ions might also get adsorbed on the ZnO nanoparticles and thus, contribute to change in aggregate composition. An analysis of ion contents of zinc and copper in aggregates of mixture suspension (suspension condition: pH 10, 10 mg/L NP concentration, 10 mM ionic strength) at t = 0 and t = 6 h (Fig. S17) indicated effect of dissolution on metal contents in aggregates over time. The observed increase in zinc content in aggregates of mixture systems indicated the possibility of higher contribution of zinc-associated aggregates in the formation of mixture aggregates than copper-
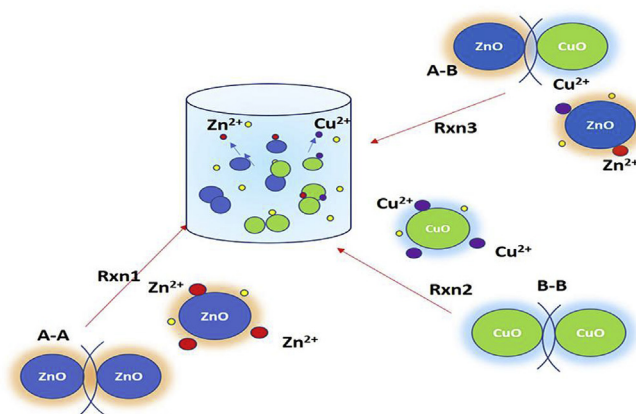
pH_{ZPC} and decreases as pH shifts away from pH_{ZPC} value. In our case, lower pH value of 3 might be the reason for observed lower aggregation phenomenon. Conditions, such as high ionic strength and high pH, might have reduced energy barrier values (EB = 0 for the C8 case; Table S12) and hence, resulted in aggregation of NPs at primary minimum condition (Cerbelaud et al., 2016). The addition of Na^+ in form of electrolyte (1 mM and 10 mM) might have led to charge screening and increase in chances of aggregation of nanoparticles. Earlier also, the observed reduction in HDD values of ZnO and TiO_2 NPs in filtered natural water had been attributed to the observed effects of the compression and neutralization of the electrostatic double layers (Fang et al., 2017).

The aggregation of particle has also been observed due to the effect of presence of counter cations as presence of ions lead to a) ionic layer compression and b) formation of surface complexes on particle. For combinations 2, 4, and 6, aggregation of particles was attributed to effect of non-van der Waals force (i.e., van der -Waals force was not found to be the primary mechanism for aggregation;

Fig. 11. Schematic of hypothesized settling and formation of aggregates in suspension containing mixture of nanoparticles (Rxn-reaction; A-A or B-B indicates aggregation of similar types of nanoparticles).

associated aggregates. It also relates with the observed slow settling of zinc-related particles than copper-related particles. For the CuO and ZnO NPs mixture suspension, this study obtained values of $K_{agg,\ overall}$, $K_{agg,\ ZnO}$, and $K_{agg,\ CuO}$. However, the value of $K_{hetero,\ ZnO-CuO}$ could not be calculated due to lack of explicit relationship between these aggregation rate constants. More work is underway to develop this relationship for getting a better understanding of aggregation of mixture of nanoparticles.

4. Conclusions

Results of this study showed that homoaggregation as well as heteroaggregation processes might be happening simultaneously in suspension containing mixture of ZnO and CuO NPs. The combined effects of pH, ionic strength, and nanoparticle concentration on the aggregation and settling behaviour of mixture of nanoparticles were studied and empirical equations for predicting settling rate constant, aggregation rate constant and zeta potential difference were developed. Settling rate constant was found to be mostly affected by nanoparticle concentration, whereas aggregation rate constant was found to be dependent on pH and ionic strength and NP type. The findings of this study are important as these types of information were not available earlier, even though, previous studies had focused on stability of NPs (Labille et al., 2015; Quik et al., 2014). This study showed that interaction of multiple factors is responsible for aggregation behaviour of nanoparticles (Single/mixture), rather than single factor. Although, one factor may be dominant but interplay of factors (pH, ionic strength, concentration) was highly significant in predicting aggregation/stability of nanoparticle in aquatic system.

This study provided pH_{zpc} values of suspensions containing mixture of 10 mg/L ZnO and 10 mg/L CuO NPs (in de-ionized water solution and in 10 mM ionic strength solution). Energy barrier values using the DLVO theory were calculated which could be used in understanding chances of aggregation of particles in this system. Colloidal behaviour of mixture of particles was predicted with the help of the DLVO interaction energy profiles and possible mechanisms of aggregation between ZnO NPs and CuO NPs were hypothesized (i.e., ionic layer compression, charge neutralization and adsorption, van der Waals force of attraction). More studies are required for collecting data, such as number concentration, density of mixture of particles, aggregate composition, adsorption of ions on nanoparticles, etc. to properly understand aggregation mechanism.

4.1. Implications

Implications of findings of this study are presented in this section. With respect to contribution to nanoparticle research, this study (i)provided information on values of aggregation and settling rate constant for mixture of nanoparticles at various solution chemistry, (ii) characterized metal content values of suspension and in aggregates, (3) developed regression equations for predicting aggregation rate constants of ZnO and CuO NPs. The developed equation could be used in understanding chances of aggregation and settling of mixture of ZnO and CuO nanoparticles and also in knowing possibility of water and sediment pollution if they were to be present together in natural water. However, these equations cannot be used for different types of metal oxide nanoparticles. A detailed experiment is required for developing such relationships (for example, quantitative nanoparticles structure-sedimentation relationship) for mixtute of different types of metal oxide nanoparticles under environmentally-relevant conditions.

Given that there is a lack of information on mixture of nanoparticles, the findings of this study are useful for providing information on water pollution status. Information of total metal content and ion content in aggregates can be used in understanding characteristics of nanoparticles, one might be inadvertently exposed to from ingesting water contaminated with these types of nanoparticles and thus helps in risk assessment. The observed aggregation and sedimentation rates of ZnO and CuO nanoparticles can be used in designing sedimentation units for removing them from water.

Supporting Information

Literature review compiling studies for mixture of nanoparticles, size data, DLVO based estimation of energy barrier and Debye length value, characterization of mixture of nanoparticles(TEM), turbidity, size and zeta potential variation with time, regression equations with residual diagnostics, ANOVA analysis for settling rate constant, aggregation rate constant, zeta potential difference, interaction energy profile, pH and conductivity variation, comparison of observed aggregate rate constant values of this study and literature reported studies, mechanisms of formation of aggregates and settling of aggregates, abbreviations used in study.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.06.171.

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