Dispersion and diffusivity of halloysite and bentonite nanoclays in aqueous Pb (II): Effect of particle concentration, temperature, and pH

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Abstract. This study investigates the influence of particle concentration, temperature, and pH to the dispersion properties and diffusivity of nanoparticles – halloysite and bentonite nanoclays in water, with and without the presence of lead (II) ions. Light scattering analyses were conducted to observe the changes on hydrodynamic radius, zeta potential, and diffusion coefficient of the nanoparticles. Results showed that with the increase of particle concentration and as pH increases, the average hydrodynamic radii for the two nanoclays seems to decrease, and were much smaller in the presence of Pb (II) ions. Conversely, the size of the nanoparticles appears to increase as temperature increases for the halloysite sample while the opposite was found for the bentonite dispersion. Sizes increase and decrease even more upon Pb (II) additions for the halloysite and bentonite dispersions respectively. In terms of zeta potential, both lead-free nanoparticles showed a more negative surface net charge as concentration and pH increases indicating an improvement in suspension stability. This was not the case with respect to temperature changes where halloysite dispersions become more unstable. Pb (II)–bentonite samples on the other hand exhibit a rather unpredictable trend in the zeta potential as the temperature increases but were both more stable than pure bentonite. Lastly, the diffusion coefficients were obtained and data suggest that temperature has the highest influence among all parameters while the addition of Pb (II) ions increases the overall diffusivities except for low-zeta potential dispersions.

1. Introduction

Nanotechnology is considered an emerging technology due to the possibility to advance well-established products and create new products with totally new characteristics, functions, and enormous potential in a wide range of applications [1,2]. These include soft materials such as those in suspensions and colloidal systems encountered in a variety of industries like in ceramic suspensions, liquid abrasives, inks and medicines [3]. Halloysite and bentonite clays are among the most widely used nanoparticles in the scientific community that can extend the applications of dispersions due to their interesting attributes [4-10]. Halloysite is a dioctahedral 1:1 clay mineral of the kaolin group. As nanoparticles, they are in the form of ultra-tiny hollow tubes with diameters typically smaller than 100 nanometers, with lengths typically ranging from about 500 nanometers to over 1.2 microns. HNTs are formed as a result of strain caused by lattice mismatch between adjacent silicon dioxide and aluminum...
oxide layers. One of the specialties of the halloysite is the different surface chemical properties at the inner and outer sides of the tubes [1]. Chemically, the external surface of the halloysite nanotubes has properties similar to SiO$_2$ while the inner cylinder core is related to Al$_2$O$_3$. The negative net surface charge of halloysite particles in solvents is attributed to the negatively charged siloxane outer surface outweighing the positively charged aluminol of the lumen. Below pH 8.5, HNTs can be loaded with negative macromolecules due to the positive charge of the inner lumen which are repelled by the negatively charged outer surface [2,11,12]. Loading and surface modification of HNTs are vital considerations for stability and compatibility with other systems [2,11,12].

Meanwhile, bentonite, which mainly contains montmorillonite, has a plate-like assembly with layers of central octahedral sheets inserted between two tetrahedral sheets; it has negatively charged faces and edges that take up less than 5% of the total surface area [13]. The negative charges of the montmorillonite layers are due to substitution and pH-dependent charges developed on the surface hydroxyls groups at broken edges. Isomorphic substitution in montmorillonite leads to a negative charge associated with cation replacement in the tetrahedral sheet (Al and Si), whereas a much more diffuse negative charge comes from cation replacement in the octahedral sheet (Mg and Al). Additional polar sites, mainly octahedral Al-OH and tetrahedral Si-OH groups are situated at the broken edges. These amphoteric sites are conditionally charged, so variable charges can develop at the edges by direct H$^+$ or OH$^-$ transfer from aqueous phase depending on the pH [14,15]. The size of nanoparticles typically ranges from 100 to 500 nm because of their surface characteristics and is highly dependent on size reduction procedures like high frequency sonication.

Halloysite and bentonite clays have been utilized in several fields of nanotechnology such as in drug-delivery systems as nano-carriers [4-7], as reinforcements for the fabrication of composites used in filtration and biomedical applications [8], and as nanoparticles for heavy metal removal [9,10]. These systems along with the mentioned industries that use suspensions require stability and sometimes, property-modifications on the dispersed phase [3]. By simply varying parameters like solvent viscosity, temperature, pH, and addition of other species – polymers and/or ions, the overall condition of the solute can change and a new set of properties in terms of particle size, diffusivity and zeta potential can be obtained [3]. The diffusivity and size of solute particles in suspensions are usually determined using a method called Dynamic Light Scattering (DLS); a non-invasive technique for characterizing macromolecules and a broad range of particles in solution [16]. In DLS, the speed at which the particle diffuses due to Brownian motion is determined by measuring the rate at which the intensity of the scattered light fluctuates when detected using a suitable optical arrangement [16]. The diffusivity and particle size is then determined through the Stokes-Einstein equation:

$$D = \frac{kT}{6\pi n \eta r} \quad (1)$$

where D is the diffusion coefficient, k is the Boltzmann constant, T is the cell temperature, \( \eta \) is the viscosity of the solvent and r is the hydrodynamic radius.

The zeta potential on the other hand indicates the stability of the particles in a solvent or solution [17]. Under the influence of an applied electric field, charged particles suspended in the liquid move towards the electrode of opposite charge. Faster movements are achieved if particles exhibit higher magnitudes of surface charge. However, ions present in the liquid with charges opposite to the particle can adhere to the surface lowering the effective net surface charge. This then retards the velocity of the particles when voltage is imposed. The charge at the boundary where a double layer of ions is formed is called the zeta potential. Higher zeta potential values suggest lower tendency for aggregation and can yield a stable dispersion. The velocity of the particle, also known as the electrophoretic mobility, \( U_{ph} \), is also dependent on the strength of electric field or voltage gradient, the dielectric constant, \( \varepsilon \), and the viscosity, \( \eta \), of the medium [18,19]. The zeta potential (Z) can then obtained using the Smoluchowski equation:
Particle dispersion and diffusivity are relevant properties for controlled drug delivery [4-7], property-enhancements in nanocomposite materials [8] and for the effective removal of contaminants in liquid media [9,10]. To date, there is no record comparing the scattering behaviour of halloysite and bentonite clays in water, nor in the presence of a metal ion. It is imperative to study the possible changes in the dispersion characteristics of nanoparticles in liquids since it can influence the processes involved for the mentioned applications. Herein, changes in particle size, zeta potential and diffusivity of halloysite and bentonite nanoclays were investigated by varying the concentration of the nanoparticles, temperature and pH of the solutions with and without lead (II) ions.

2. Materials and methodology

2.1. Materials

Lead (II) nitrate, halloysite nanoclay, and hydrophilic bentonite were purchased from Sigma-Aldrich. The continuous phase used in the experiment was deionized water obtained through the Direct-Q 3 UV filtration systems from Merck. Adjustments in pH were made through the additions of HCl and NaOH.

2.2. Experimental procedure

The nanoparticles were tested separately and in triplicates having three levels each parameter; particle concentration was varied to 10, 100, and 500 mgL\(^{-1}\), cell temperatures at 20, 35, and 50°C, and pH of the dispersions at 4, 7 and 10. Each level had four samples in which two were infused with a lead (II) solution on a 1:10 volumetric ratio with concentrations of 0.1 and 10 mgL\(^{-1}\). Unless stated, the default levels were at 500 mgL\(^{-1}\) particle concentration and 25°C cell temperature.

The pH of the samples for the pH parameter were adjusted first before sonication. The rest of the samples were immediately sonicated after preparation. For samples with changes in temperature, the required temperature was set and equilibrated in the particle analyser (Beckman Coulter DelsaMax Pro) before any measurements were done. The dielectric constant, viscosity, and refractive index of water at 20, 35, and 50°C data was then manipulated in the settings. Other parameters such as acquisition time, laser power, and attenuation were also set in the instrument. The prepared dispersions were injected in a flow cell of the particle analyser and data on hydrodynamic radius, zeta potential and diffusivity were gathered afterwards.

3. Results and discussion

The figures below present the plots of the hydrodynamic radius and zeta potential against the particle concentration, temperature, and pH for the halloysite nanoclay, shown in Figure 1, and hydrophilic bentonite, in figure 2.

3.1. Effect of particle concentration

In the absence of Pb (II) ions, both nanoparticles showed a reduction in mean hydrodynamic sizes as the quantity of particles increases. The halloysite radius in figure 1(a) showed a dramatic change from 350 nm to 175 nm at particle concentrations of 10 to 100 mgL\(^{-1}\), followed by a slight decrease to 150 nm at 500 mgL\(^{-1}\). This trend can also be observed for the bentonite dispersions in figure 2(a). For the zeta potential shown in figures 1(b) and 2(b), both lead-free dispersions of halloysite and bentonite exhibit an increase in value (becomes more negative) at increasing particle concentrations. The results show a possible scenario between particle size and zeta potential – that is, competition for adsorbing ions arises as the number of particles grew; this may lead to a smaller effective size caused by a higher zeta potential because of the reduced amount of counter-ions on a particle surface [3]. This change in hydrodynamic radius for the lead-free nanoparticles did not transpire for the Pb (II) dispersions as particle concentration increases. Nonetheless, it appears that the radii of the two dispersions were smaller in the presence of the heavy metal regardless of the low and almost constant zeta potentials of
Figure 1. Hydrodynamic radii and zeta potentials of halloysite dispersions with respect to (a – b) nanoparticle concentration, (c – d) temperature, and (e – f) pH. Dispersions containing Pb (II) are shown in broken lines.
Figure 2. Hydrodynamic radii and zeta potentials of bentonite dispersions with respect to (a – b) nanoparticle concentration, (c – d) temperature, and (e – f) pH. Dispersions containing Pb (II) are shown in broken lines.

the 10 mgL⁻¹ Pb (II)–halloysite and 0.1 mgL⁻¹ Pb (II)–bentonite respectively. This implies that zeta potential is not the limiting factor and can be attributed to a plausible improvement in hydrophilic
dispersion upon adsorption of the metal ions on the nanoclays surface. A possible hampering of this effect as particle concentration increases from 10 to 100 mgL\(^{-1}\) leads to an increase on the average sizes of the particles particularly for the 0.1 mgL\(^{-1}\) Pb (II)–halloysite, and, for both 0.1 and 10 mgL\(^{-1}\) Pb (II)–bentonite dispersions. This trend however did not manifest for the 10 mgL\(^{-1}\) Pb (II)–halloysite samples due to a higher Pb (II) concentration and lower cation exchange capacity (CEC) of halloysite [9,10]. Meanwhile, the average zeta potential still increases with increase in halloysite and bentonite concentration regardless of the heavy metal inclusions. Even so, because the components of the outer and inner surfaces differ for the two particles, their capacity for Pb (II) interactions also differs rendering the distinct zeta potential results for the two dispersions.

3.2. Effect of temperature
From figures 1 and 2 ((c) and (d)) it shows that both dispersions have acquired bigger hydrodynamic radii and lower zeta potentials at higher temperatures. This was caused by the increased Brownian motion of the matrix phase forcing the particle constituents to have a secondary minimum or flocculate according to the DLVO theory [3]. Lower zeta potentials were then obtained due to the lowering of the overall surface area caused by the aggregation [3]. The additions of the heavy metal then causes an inverse effect, predominantly on the particle size and zeta potential for the nanoparticle samples. The results might be attributed to the cation exchange capacity of bentonite [9,10] that is, under hydrophillic conditions, they have a higher capacity to hold Pb (II) ions within the interstices of the layered structure lowering the chance for heavy metal adsorption on its outer surface. This may reduce the overall size of the units due to contraction of the layers from electrostatic attraction and might have been the reason why the zeta potentials of bentonite particles, in most of the conditions, were higher compared to the halloysite nanoparticles. The increase therefore in zeta potentials upon Pb (II) inclusion particularly at higher temperatures can be ascribed to a forced insertion of Pb (II) and solvent ions within the bentonite layers. Higher zeta potentials were then obtained which may have contributed also to the decrease in particle radii.

3.3. Effect of pH
The pH – zeta potential relation is quite well known – that is, the higher the pH (more basic), particles acquire a more negative net surface charge or zeta potential, and vice versa. In figures 1 and 2 ((e) and (f)), the first scenario was manifested by the two nanoparticles as pH increases without the heavy metal presence. The increase in zeta potentials was then translated as a decrease in hydrodynamic radii suggesting that particle aggregation was inhibited. Though this was also the case even when Pb (II) ions were present, higher concentrations of the heavy metal exhibited smaller particle radii for the bentonite and halloysite samples similar to the results in Section 3.1. It shows that the increase in hydrophillic dispersion outweighs the potential particle aggregation in acidic conditions yielding smaller particles in the liquid bulk. So while it is highly probable that the smaller particle radii for the Pb (II)–bentonite particles was attributed to the high zeta potentials, the above postulate may also apply. In terms of the zeta potential, for the halloysite samples, there seems to be a slight transition at the acidic and basic region upon metal additions due to a possible saturation of cations and anions on the surface. This was not the case for bentonite particles because of their high CEC.

3.4. Diffusion coefficients
Tables 1 and 2 summarizes the diffusion coefficients for the two dispersions – halloysite and bentonite nanoclays at increasing particle concentration, temperature and pH. Noticeably, in the absence of the heavy metal, diffusion coefficients for the two nanoparticles increase with the said parameters. In terms of concentration and pH effects, the smaller particle radii formed at these conditions can be directly associated to the diffusivity of the nanoparticles since smaller objects diffuse faster [16]. However, the temperature factor exhibits a superior influence when bigger particles formed at higher temperatures, displayed faster diffusions. Likewise, the smaller hydrodynamic sizes upon inclusions of the Pb (II) ions shows predominantly higher coefficients than their lead-free counterparts except for
the Pb (II)– halloysite samples under the temperature parameter – here, bigger particles are generated as possibly caused by a higher rate of Pb (II) adhesion on the outer surface that lowers the zeta potentials.

Table 1. Estimated diffusion coefficient of halloysite in water (∗ 10^8 cm^2 s^-1).

| Pb(II) (mgL^-1) | Concentration (mgL^-1) | Temperature (°C) | pH |
|----------------|------------------------|-----------------|----|
|                |                        | 10              | 100| 500| 20 | 35 | 50 | 4 | 7 | 10 |
| 10             |                        |                 |    |    |    |    |    |   |   |    |
| 0.1            |                        |                 |    |    |    |    |    |   |   |    |
| 0              |                        |                 |    |    |    |    |    |   |   |    |

Table 2. Estimated diffusion coefficient of bentonite in water (∗ 10^8 cm^2 s^-1).

| Pb(II) (mgL^-1) | Concentration (mgL^-1) | Temperature (°C) | pH |
|----------------|------------------------|-----------------|----|
|                |                        | 10              | 100| 500| 20 | 35 | 50 | 4 | 7 | 10 |
| 10             |                        |                 |    |    |    |    |    |   |   |    |
| 0.1            |                        |                 |    |    |    |    |    |   |   |    |
| 0              |                        |                 |    |    |    |    |    |   |   |    |

4. Conclusion
Halloysite and bentonite nanoclay dispersions in deionized water with and without Pb (II) ions were prepared and subjected to light scattering analyses to examine the changes in the particle size, zeta potential and diffusivity. For the lead-free dispersions, results infer that change in particle concentration and pH has a direct effect on the zeta potential or surface chemistry of the nanoclays and can be evoked to predict the corresponding hydrodynamic sizes. The effect of temperature on the other hand was more explicit on the particle size transition which can then be utilized to estimate the surface net charge. In the presence of a heavy metal, it was suggested that while Pb (II) moieties may decrease the zeta potential for the negatively charged nanoclays, a plausible improvement in hydrophilic dispersion can also yield smaller hydrodynamic sizes. The corresponding changes in particle size and zeta potential at different conditions upon the addition of the heavy metal can also confirm the difference in cation exchange capacity of the two nanoclays. Lastly, diffusivity results for the two dispersions have been shown to satisfy the Stokes-Einstein relation concluding that bigger particles at higher temperatures diffuse faster.

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