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Silica nanoparticles separation from water: Aggregation by cetyltrimethylammonium bromide (CTAB)

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\textbf{HIGHLIGHTS}

- The same CCC was gained at $M(\text{CTAB}) = 0.1 \text{ mmol L}^{-1}$ for different 30R50 concentrations.
- More than 95.7% of turbidity can be removed for 30R50 0.15% with CTAB 0.1 mmol L$^{-1}$.
- The “hydrophobic effect” plays an important role in aggregation of 30R25.
- The results show different agglomeration mechanisms.

\textbf{ABSTRACT}

Nanoparticles will inevitably be found in industrial and domestic wastes in the near future and as a consequence soon in water resources. Due to their ultra-small size, nanoparticles may not only have new hazards for environment and human health, but also cause low separation efficiency by classical water treatments processes. Thus, it would be an important challenge to develop a specific treatment with suitable additives for recovery of nanoparticles from waters. For this propose, this paper presents aggregation of silica nanoparticles (Klebosol 30R50 (75 nm) and 30R25 (30 nm)) by cationic surfactant cetyltrimethylammonium bromide (CTAB). Different mechanisms such as charge neutralization, “depletion flocculation” or “volume-restriction”, and “hydrophobic effect” between hydrocarbon tails of CTAB have been proposed to explicate aggregation results. One important finding is that for different volume concentrations between 0.05% and 0.51% of 30R50 suspensions, the same critical coagulation concentration was observed at CTAB = 0.1 mM, suggesting the optimized quantity of CTAB during the separation process for nanoparticles of about 75 nm. Furthermore, very small quantities of CTAB (0.01 mM) can make 30R25 nanosilica aggregated due to the “hydrophobic effect”. It is then possible to minimize the sludge and allow the separation process as “greener” as possible by studying this case. It has also shown that aggregation mechanisms can be different for very small particles so that a special attention has to be paid to the treatment of nanoparticles contained in water and wastewaters.

\textbf{Keywords:}
Separation
Nanoparticles
CTAB
Aggregation
Silica

\textbf{1. Introduction}

For the past decade, nanotechnology industries start to come on line with larger scale production, it is then inevitable that nanoparticles and by-products will reside at some level in our recreational and drinking waters (Daughton, 2004; Moore, 2006; Weinberg et al., 2011). From accidental spillages or permitted release of industrial effluents, nanoparticles could accumulate into the human body via skin contact, inhalation of water aerosols, direct ingestion of contaminated drinking water, or indirect exposure from ingestion of vegetables and aquatic organisms such as fish, molluscs and crustaceans as a part of the human diet (Daughton, 2004; Brar et al., 2010).

Although research on risks of nanoparticles is still limited compared to their plentiful applications, hazards relevant to humans and animals health begin to be listed or investigated (Reijnders,
In fact, the very large surface area of these small particles can result in the direct generation of harmful oxyradicals; that can cause cell injuries. Furthermore, the ability of the nanoparticles to penetrate the body and cells provides potential routes for the delivery of nanoparticle-associated toxic pollutants to sites where they would not normally go (Moore, 2006). Nanoparticles can then behave like a vector on which hazardous compounds are concentrated.

Nanoparticles differ from classical solid particles by their size, smaller by several orders of magnitude, and their specific properties due to their high surface area over volume ratio. These differences could be responsible for a low efficiency of classical water treatment processes. Thus, it is reasonable to begin considering suitable treatment for water and wastewaters containing synthetic nanoparticles that may present novel toxicity.

One important issue was to determine nanoparticle’s types for which the development of water treatments seems to be urgent or the most economically interesting. Today, we used to classify nanoparticles via already known properties, the easiest being their chemical composition. Three main categories are usually distinguished: (a) pure metallic nanoparticles (Fe, Ag, Au, ...), (b) metallic oxides or oxy-hydroxides (SiO$_2$, TiO$_2$,...), (c) carbonaceous nanoparticles (nanotubes, fullerene, ...). Among them, SiO$_2$ and TiO$_2$ nanoparticles are already produced in very large quantities (10$^{-2}$–10$^{3}$ kg$^{-1}$) (Ostiguy et al., 2006).

In China and Taiwan, silica nanoparticles are very commonly used as abrasive in chemical mechanical polishing (CMP) industries for the manufacture of integrated circuits and electronic chips (Chin et al., 2006). The studies of several research groups (Lai and Lin, 2003; Hu et al., 2005; Chin et al., 2006; Kin et al., 2006; Lien and Liu, 2006; Yang and Tsai, 2006; Tsai et al., 2007) give a better idea of their composition after an analysis of some samples. To sum up, suspensions are mainly composed of silica particles, with an important total solid content (1.3–8.5 g L$^{-1}$ which corresponds to 0.05–0.36 vol.%) and an average size around 100 nm. These suspensions show a negative charge on particles surface, and the zeta potential [$\zeta$] remains lower than 30 mV leading to their stability. In addition, although silica particles are usually not considered as dangerous even at the nanoscale, other pollutants such as heavy metals in the suspensions may be concentrated and taken by nano-silica into the human body. Summarily, the availability of data concerning these largely produced effluents, as well as the existence of commercially available products necessary for research purposes, confirm to SiO$_2$ nanoparticles the quality of interesting candidate for developing wastewater treatment processes.

Another important issue in the framework is the development of specific treatments (e.g. coagulation, flotation or filtration...) and suitable additives (if necessary) for water containing nanoparticles. Recently, Bizi (2012) has investigated the coagulation and flocculation of nanosilica by some organic polymers. The treatment of CMP effluents by chemical coagulation with polyaluminium chloride has been studied by Chang et al. (2007). Their structural study of the agglomeration of the nanoparticles due to the coagulation demonstrated the interest of the addition of coagulant for a low efficiency of classical water treatment processes. Thus, it is reasonable to begin considering suitable treatment for water and wastewaters containing synthetic nanoparticles that may present novel toxicity.

2. Materials and methods

Klebosol 30R50 and 30R25 colloidal silica suspensions that have different sizes and the same initial solid content of about 15.3 vol.% were purchased from Rohm and Haas Electronic Materials, France. The stability of these manufactured suspensions was obtained by the producer through the addition of Na$_2$O($<0.2\%$) which generates anionic nano-SiO$_2$ surface; particles would thus repel each other, providing a good stability to the colloid. The diluted suspensions (0.05–0.51 vol.%) were prepared with deionised water produced from the urban system, where raw water is filtered to 1 μm, then demineralised by ion exchange resins. The conductivity of the deionized water is 1.7 μS cm$^{-1}$ in average, comparing with that of raw water is 270 μS cm$^{-1}$. The surface tension of water is 0.072 N m$^{-1}$ at 25 °C (Huang, 2009).

The size of the Klebosol 30R50 and 30R25 nanoparticles was measured by transmission electron microscopy (TEM, Philips CM20 (200 kV) and JEOL 100 CX), and dynamic light scattering (DLS) (Nanotrac, Microtrac). The size analysis of nano-SiO$_2$/CTAB/water systems was done by laser diffraction (Mastersizer 2000, Malvern Instruments) for the reason that the size of aggregates might not remain in the range of DLS measurement. The volume of diluted suspensions was measured by electrophoresis with a Zetasizer NanoZS (Malvern Instruments). pH was measured at ambient temperature with a pH-539 pH-meter (WTW) and a SenTix 41 pH-electrode, and turbidity was measured with a 2100N-IS Turbidimeter (Hach).

CTAB ≥ 98% (Carl Roth GmbH KG) was used as the additive for the aggregation of silica nanoparticles. The surface tension of CTAB and water was determined by 35 Tensiometer (GBX), and the conductivity was determined by a LF 538 conductivity meter (WTW). The preparation of aggregated samples was to add certain quantities of CTAB (powder) into certain quantities of nanosilica suspensions in order to have the concentration range of CTAB from 0.01 to 100 mM. The range of nanoparticles was from 0.05% to
0.51% in volume, corresponding from 1.2, 3.6 and 12 g L$^{-1}$ respectively. The sample volume was from 25 to 250 mL.

After an immediate agitation by hand, these samples were let to deposit until they reach the equilibrium (no more changes of turbidity in their supernatants). The equilibrium time for different nano-SiO$_2$/CTAB/water systems was different from less than 5 min in the most favorable conditions. The equilibrium time lasted up to 2 wk for unfavorable conditions. Indeed, for samples that would well aggregate, the coagulation process started immediately after the mixture of CTAB and SiO$_2$ suspensions, and the equilibrium time was less than 5 min. The size distribution of these well aggregated samples always showed aggregation without remaining nanoparticles. In other word, they showed only one peak of aggregation. However, for other samples that had two peaks (one for nanoparticles, the other for aggregation), the equilibrium time might last until 2 wk. The samples for laser diffraction analysis were collected after agitation of the samples (mixture of the liquid suspensions with the previously settled aggregates).

The Krafft temperature or critical micelle temperature of CTAB, which is the minimum point below which the CTAB remains in crystalline form, measured by Carolina and Barney (2003) is about 25°C. Therefore, all results of CTAB and nano-SiO$_2$/CTAB/water systems were prepared and measured at a temperature higher than 25°C in order to be sure that the powder of CTAB was sufficiently dissolved in solution.

3. Results and discussion

3.1. Characterizations of nanoparticle suspensions

The detailed characterization has been presented in Liu et al. (2012); here we just make a brief summary. The nanosilica suspensions Klebosol 30R50 and 30R25 are respectively 50 and 25 nm determined by BET (commercial data from the manufacturer). They are firstly observed by TEM and then validated by DLS. From TEM, two populations in 30R50 suspensions have been observed: larger ones about 80–85 nm in diameter and smaller ones about 30–40 nm; while for 30R25 from TEM, particles are monodispersed, and the average size is about 35–40 nm. The mean diameters measured by the Nanotrac (DLS) at SiO$_2$ concentration 0.15 vol.% are respectively 75 and 30 nm for 30R50 and 30R25.

ζ of the particles was measured in order to predict the suitable conditions for the removing process since it is mainly controlled by the interfacial forces. For the initial silica suspensions 30R50 and 30R25, the very high and negative ζ measured (in absolute value $|$ζ$| > 30$ mV) confirmed that the stability of the system was insured by the repulsive interaction. It is worth noting that no aggregation of 30R50 and 30R25 was observed by changing pH (2–11), whatever their final ζ values (between −35 and −2 mV), so the pH of samples were not adjusted to one specific value in the following aggregation study.

3.2. Characterization of CTAB

The critical micelle concentration (CMC) is the concentration of surfactants above which micelles are spontaneously formed. In our experiments, the conductivity and surface tension were used to determine the CMC of CTAB which value was about 0.92 ± 0.05 mM. Modaresi et al. (2007) have reported the CMC of CTAB at 0.89 mM, while Gao et al. (2004) have cited 0.92 mM, and Maiti et al. (2000) have given 0.8 mM; the CMC measured in this work is then comparable with the results of others.

Table 1 gives conductivity, turbidity and pH of different CTAB concentrations. For Klebosol 30R50 suspensions (0.05–0.51%), the turbidity is respectively 61.9, 171 and 542 NTU; and for Klebosol 30R25 suspensions (0.05–0.51%), the turbidity is respectively 4.0, 8.0 and 20.6 NTU. The turbidity values of CTAB concentrations (see Table 1) are much smaller than those of the nanosilica suspensions, indicating that the extra CTAB would not change the turbidity of nano-SiO$_2$/CTAB/water systems in the supernatant liquid after aggregation and sedimentation. Thus, turbidity that is an indication of the clarity of water mainly relates to the sizes and the numbers of particles could be used as a measuring technique for the monitoring of the colloidal nanoparticles concentration along the treatment process. In order to further verify a potential effect of these micelles or molecules on the size measurements, we have measured the sizes of solutions at different CTAB concentrations (0.01–100 mM). Their sizes measured by both DLS and laser diffraction could not be detected whatever the CTAB concentration, certainly due to the fact the size of the CTAB micelles remains very small. So we are confident in considering that the micelles of CTAB would not influence the measurement of aggregation. Moremore, CTAB is easily dissociated into cationic CTA+ and bromide ion and its speciation is not influenced by the pH changes (Lien and Liu, 2006).

3.3. Surface modification and aggregation of silica nanoparticles by CTAB

3.3.1. Aggregation of nanosilica 30R50 with CTAB

Fig. 1 gives the ζ and pH profiles of 30R50 (0.15%) at different concentrations of CTAB. The adsorption of CTAB (0.01–100 mM) modifies the silica surface (ζ) from negatively to positively charged. The isoelectric point for 30R50 0.15% is at about CTAB = 0.1 mM. Size distributions of these samples are further shown in Fig. 2. All measurements were done after reaching the equilibrium; otherwise the results would be changed continuously.

While adding CTAB 0.01 and 100 mM to 30R50 (0.15%), the size distributions of these two samples are nearly the same as 30R50

![Fig. 1. Zeta potential and pH profiles of the 30R50 (0.15%) at different concentrations of CTAB (0–100 mM).](image)
0.15% without CTAB, except a few aggregates of 10–1000 μm observed. This result suggests that CTAB 0.01 mM might be too low to induce an efficient aggregation, and most of the silica nanoparticles are still stable and separated, in agreement with the 30 mV. At CTAB 100 mM, no obvious aggregation can be observed from Fig. 2. The ζ = 46 mV implies the formation of a bilayer of CTAB molecules at the silica surface, leading to the stabilization of the nanoparticles suspension by positive surface charges; but the possibility of micelles formation could not be eliminated, since 100 mM far exceeds the CMC (0.92 ± 0.05 mM) of CTAB. From Fig. 2, CTAB 0.1 and 1 mM give better aggregation results and very few silica nanoparticles stay in solution after aggregation. In these conditions, ζ < 30 mV also characterizes a probable aggregation.

However, when CTAB = 10 mM, the aggregates exist at ζ > 30 mV, this special phenomenon will be explicated in the following. We have to remember that, as shown in Liu et al. (2012), the observed aggregation is not due to the change in pH.

It could be proposed that the interactions between silica nanoparticles and CTAB act as follows: small quantities of CTAB could firstly act in a monolayer formation that is controlled by electrostatic interaction between positively charged surfactant headgroups and siloxane groups (−SiO−) on the nanosilica surface. Furthermore, it is well known that adsorption of CTAB on silica surface could overcome the micelles formation in bulk water (Bi et al., 2003; Bryleva et al., 2007). This may be the reason why even if the CTAB concentrations are near or higher than the CMC, a good aggregation can still be obtained.

However, when the concentration of CTAB is much higher than the CMC (e.g. 100 mM), whatever the concentration of 30R50, as it will be shown in the next part, the bilayer owing to hydrophobic interaction between surfactant hydrocarbon tails could be formed, leading to the restabilization of nano-SiO2/CTAB/water systems. Fig. 3 describes the possible interactions between CTAB and nanosilica particles. It is worth noting that charge neutralization seems to be the major reason of 30R50 nanosilica aggregation, but hydrophobic effect from hydrocarbon tails of CTAB may contribute to the aggregation as well.

3.3.2. Effect of particle concentration on aggregation of nanosilica 30R50 by CTAB

The aggregation of 30R50 0.05% and 0.51% by CTAB was further explored in order to investigate the effect of different nanoparticles concentrations. Fig. 4a shows zeta potential and particle size profiles of 30R50 (0.05% and 0.51%) at different concentrations of CTAB, in which only average sizes of aggregates were presented. For the aggregation of 30R50 0.05%, when CTAB = 0.1 mM, corresponding to |ζ| < 30 mV, efficient aggregation can be obtained. When CTAB = 0.01 and 100 mM, only a few aggregates form probably due to high surface charge of particles (|ζ| > 30 mV); but when CTAB = 1 and 10 mM (ζ > 30 mV), aggregates still exist under the

![Fig. 2. Size distributions of the 30R50 (0.15%) at different concentrations of CTAB (mM) analyzed by laser diffraction.](image)

![Fig. 3. Simplified scheme of CTAB mono- and bilayers on SiO2/water interface, when the CTAB concentration increases; counterion Br− is omitted for clarity (suggested by Bryleva et al., 2007).](image)

![Fig. 4. (a) Zeta potential and particle size profiles of 30R50 (0.05% and 0.51%) at different concentrations of CTAB (mM). (b) Zeta potential and pH profiles of the 30R25 (0.15%) at different concentrations of CTAB (mM).](image)
condition of high $\zeta$ (> 30 mV). This phenomenon is almost the same as that of 30R50 0.15% with CTAB = 10 mM and neither of them can be explained by the charge neutralization.

For aggregation of 30R50 0.51%, not only CTAB = 10 mM ($\zeta$ > 30 mV) can make nanosilica particles form aggregates, but also the CTAB = 0.1 mM ($\zeta$ < –30 mV). Better aggregation results are found for CTAB = 10 to 100 mM, but 0.01 and 100 mM CTAB can also form a few aggregates of silica nanoparticles.

Overall, the aggregation is observed at CTAB = 10 mM ($\zeta$ > 30 mV) for all three concentrations of 30R50, while it should have a stable state according to zeta potential prediction. It is likely that another mechanism called “depletion” or “volume-restriction” (Furusawa et al., 2002) contributes to the aggregation at high concentrations of CTAB. As the concentration of CTAB 10 mM is much larger than its CMC (0.92 ± 0.05 mM), the formation of micelle could not be avoided. When two particles approach in a solution within free micelles of CTAB, hydrocarbon chains leave the gap, generating a local region with almost pure solvent. The osmotic pressure in the fluid surrounding the particle pair exceeds between the particles and may force the particles together (Furusawa et al., 2002).

Moreover, it was also observed that all of the satisfying aggregation of 30R50 (0.05–0.51%) begin at CTAB = 0.1 mM, whatever their surface zeta potential. This suggests that the “depletion flocculation” may not only occur at very high zeta values (10 mM CTAB for all three concentrations of 30R50 as mentioned above), but also very low ones (30R50 0.51% with 0.1 mM CTAB corresponding to $\zeta$ ≈ –40 mV). Of course, at the concentration of 0.1 mM CTAB, the formation of micelles from CTAB can be neglected. However, as nanoparticles come closer together, the intercolloidal region consists of a region that is depleted in CTAB. The depletion effect (Shi, 2002) is induced by their osmotic pressure, due to the difference of CTAB concentration between the inside and outside regions. Solvent between the nanoparticles then tends to diffuse out to reduce the concentration gradient, causing the nanoparticles to aggregate.

Table 2 shows the turbidity of different nano-SiO$_2$/CTAB/water systems. For all of the samples, the turbidity of the solution increased as soon as the CTAB was added, but only for some of them, the ones that could give efficient aggregation and sedimentation, the turbidity (taken in the supernatant liquid) subsequently decreased below the original turbidity of the 30R50 suspensions. For example, the sample 30R50 (0.15%) with CTAB 0.1 mM lost more than 96% of turbidity after aggregation and sedimentation compared with the original value (171 NTU). Moreover, these better aggregated samples can also reach their final turbidity in a short time (less than 5 min), but the samples without efficient aggregations have to wait from 5 min to 2 wk to get their final and relatively stable turbidity.

In conclusion, for the aggregation of 30R50 (0.05–0.51%) with CTAB, charge neutralization mechanism could be sometimes overcome by “depletion flocculation”, but finally the same (0.1 mM CTAB) is the lowest concentration tested that induces aggregation of the system. This result would give a better knowledge to develop environmentally friendly separation technology such as coagulation–flocculation in order to minimize the sludge, as well as the optimized quantity of CTAB for the treatment of water containing silica nanoparticles with a diameter of about 75 nm; but for nanosilica with smaller size such as 30R25, the suggestion may no longer fit.

### Table 2

<table>
<thead>
<tr>
<th>MCTAB (mM)</th>
<th>30R500.05%</th>
<th>30R500.15%</th>
<th>30R500.51%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>61.9</td>
<td>71.1</td>
<td>54.2</td>
</tr>
<tr>
<td>0.01</td>
<td>78.6–30.6</td>
<td>46.4</td>
<td>75.7</td>
</tr>
<tr>
<td>0.1</td>
<td>2.1</td>
<td>7.4</td>
<td>703</td>
</tr>
<tr>
<td>1</td>
<td>23.3</td>
<td>84.7</td>
<td>80.3</td>
</tr>
<tr>
<td>10</td>
<td>250</td>
<td>491</td>
<td>–</td>
</tr>
<tr>
<td>100</td>
<td>88.3</td>
<td>274</td>
<td>–</td>
</tr>
</tbody>
</table>

* As the 2100N-IS Turbidimeter cannot measure the turbidity more than 1000 NTU, “–” was used to stand for values higher than 1000 NTU.

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3.3.3. Effect of size: aggregation of nanosilica 30R25 with CTAB

The aggregation of 30R25 0.15% with different concentrations of CTAB was studied to compare with that of 30R50 0.15%. Fig. 4b gives the properties of 30R25 0.15% with CTAB, from which CTAB = 0.01–100 mM corresponding to $|\zeta|$ ≈ 30 mV or $|\zeta|$ > 30 mV would stabilize 30R25 nanoparticles according to the zeta potential prediction.

However, from Fig. 5, all of these samples form aggregates. Nearly no nanoparticles remain in the suspensions after aggregation and sedimentation except in the one with CTAB = 100 mM. This phenomenon can be explained neither by charge neutralization nor by “depletion flocculation”, because the aggregates exist at very low CTAB concentrations (0.01 mM). Nevertheless, as the particle size is about 30 nm for 30R25, the aggregation by hydrophobic chains interaction between surfactant hydrocarbon tails is more likely to happen. Based on DLVO theory, the stability of a particle in solution is dependent upon its total potential energy function $V_T$:

$$V_T = V_A + V_R$$

(1)

where $V_A$ is the van der Waals interaction energy, and $V_R$ is the electrostatic repulsion energy. For the van der Waals interaction between two particles, theoretical derivation starts with the assumption that the particle separation distance $D$ is much larger compared to the two particle radii $a$. For spherical particles, the van der Waals interaction energy can be expressed as:

$$V_A = \frac{Aa}{12D}$$

(2)

where $A$ is the Hamaker constant, $A = 8.3 \times 10^{-21}$ J (Kobayashi et al., 2005).

The electrostatic repulsion energy is:

$$V_R = 2\pi\varepsilon_0\varepsilon_0a^2\ln(1 + \exp(-kD))$$

(3)

where $\varepsilon$ is the solvent permeability, $\varepsilon_0$ is the permittivity of free space (8.854 × 10$^{-12}$ F m$^{-1}$), $k$ is the dielectric constant of the suspension medium and is approximately 78.4 for an aqueous system at 20 °C and $\kappa$ is a function of the ionic composition (Lu, 2007):

$$\kappa = \left(\frac{e^2N_a\sum_i z_i^2}{k_B T}\right)^{\frac{1}{2}}$$

(4)

where $e$ is electron charge, $N_a$ is Avogadro’s number, $c$ is the molar concentration of ions, $z$ is the valence of each ion and $k_B$ is Boltzmann’s constant (1.381 × 10$^{-23}$ J K$^{-1}$), $T$ is the temperature.

Fig. 6 gives DLVO prediction of particle size effect on particle interaction for 30R50 and 30R25 suspensions based on the calculations from Eqs. (1)–(4), in which particle concentration is 0.15 vol.%; [Na$_2$O] = 0.2% w/w; [H$^+$] and [OH$^-$] in the suspensions were calculated from the zeta potential (−35 mV for 30R50 and −30 mV for 30R25) and pH measurement (pH = 6.83 for 30R50 and 8.76 for 30R25); $A = 8.3 \times 10^{-21}$ J (Kobayashi et al., 2005).

According to the theory calculation, the barrier of interaction energy between 30R25 nanoparticles is smaller than that of 30R50. It is then more possible for the hydrocarbon tails of absorbed CTAB to touch each other and then aggregate 30R25 nanosilica.
As the concentration of CTAB increases, the Klebosol 30R25 would undergo four steps. When a little quantity of CTAB is adsorbed on the silica surface, the repulsion between negatively charged surface reduces, but it may not be enough to destabilize the suspension (step 1, this step could present at CTAB < 0.01 mM). As increasing the quantity of CTAB, the negative surface charge of 30R25 could further reduce. The aggregation may occur even before complete charge neutralization, owing to hydrophobic interaction of CTAB (step 2). By continuously increasing the quantity of CTAB, the silica surface would be neutralized, even altered to be positive, and the hydrophobic interaction could still act on the aggregation (step 3). Lastly, when the CTAB concentration is high enough, a bilayer of CTAB could envelop the particle surface and thus restabilize the nanosilica suspension (step 4).

To sum up, “hydrophobic effect” from the hydrocarbon tail of CTAB seems to play an important role in the aggregation of 30R25. For all concentrations of CTAB investigated, there were always aggregations of 30R25. It is then possible to add very small quantities of CTAB for the treatment of water containing nanosilica of about or less than 30 nm in diameter, which may allow the separation process much more eco-friendly.

4. Conclusion

After a review of a few papers dealing with the potential hazards of nanoparticles released in the water resources, we observe that it would be an important challenge for the recovery of nanoparticles from water in the near future. Our work is then focused on the separation of nanoparticles from waters. Industrial waste waters containing silica nanoparticles have already been identified and their treatment by coagulation and sedimentation needs a large amount of additives. Flotation with CTAB as additive seems to be a promising treatment alternative because of a lower quantity of sludges, but the use of CTAB for flotation also generates silica aggregation, in competition with bubble-nanoparticle heterocoagulation. Thus, in this paper, the aggregation of silica nanoparticles by CTAB was investigated. Coagulation mechanisms of silica nanoparticles with CTAB have been proposed. From the results, charge neutralization is the main mechanism for the aggregation of 30R50 suspensions. At low CTAB concentration such as CTAB = 0.01 mM, the negative surface charge of the nanoparticles was not affected enough, so the silica nanoparticles usually remained stable. On the contrary, if the CTAB concentration was much above the CMC, a bilayer of CTAB would be formed and restabilizes the silica nanoparticles by positive surface charge. Other mechanism such as “depletion flocculation” or “volume-restriction” was proposed to explain the aggregation of nanosilica at high [l] conditions.

More than 96% of the turbidity can be removed after aggregation and sedimentation for the sample 30R50 0.15% with CTAB 0.1 mM, the negative surface charge of the nanoparticles was not affected enough, so the silica nanoparticles usually remained stable. On the contrary, if the CTAB concentration was much above the CMC, a bilayer of CTAB would be formed and restabilizes the silica nanoparticles by positive surface charge. Other mechanism such as “depletion flocculation” or “volume-restriction” was proposed to explain the aggregation of nanosilica at high [l] conditions.

It has been found that for different particle concentrations (0.05–0.5%) of 30R50 suspensions, 0.1 mM CTAB is the lowest concentration tested that induced aggregation of the system. More than 96% of the turbidity can be removed after aggregation and sedimentation for the sample 30R50 0.15% with CTAB 0.1 mM, suggesting efficient separation of nanosilica from water at this CTAB dosage. Moreover, in our previous study (Liu et al., 2012) on SiO$_2$ nanoparticle separation from water by aggregation with AlCl$_3$, more than 99% of the turbidity could be removed after sedimentation, but sometimes this process was time-consuming due to the hydrolysis of AlCl$_3$; while the aggregation of SiO$_2$ nanoparticle with CTAB consumes shorter time (5 min in the most favorable conditions) to have turbidity removal efficiency more than 96%. Compared with experiments carried out by Zhang et al. (2008) that at an alum dosage of 60 mg L$^{-1}$, coagulation of TiO$_2$, ZnO, Fe$_2$O$_3$, NiO and SiO$_2$ commercial nanoparticles followed by sedimentation could remove 20–60% of the total nanoparticle mass, it seems to be more reasonable to aggregate SiO$_2$ nanoparticles by CTAB.
The aggregation of 30R25 with CTAB may combine the charge neutralization effect and hydrophobic effect (bridging effect), and the latter seems to have a remarkable influence. Therefore, it is likely to separate nanoparticles of about 30 nm with very small quantity of CTAB and minimize the sludge in the further separation process. The results concerning the smaller silica nanoparticles show different agglomeration mechanisms comparing with those for large particles. This is of great importance for water treatment: a special attention has to be paid to the treatment process of wastewaters containing nanoparticles.

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