Treatment of low turbidity water by sweep coagulation using bentonite

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Abstract: A novel strategy of sweep coagulation to treat low turbidity water is presented herein. Study findings demonstrated that an Na\(^+\)-saturated bentonite with medium cation exchange capacity (CEC) resulted in significant turbidity removal at a bentonite dosage of 30 mg dm\(^{-3}\). Bentonite dispersion with fully delaminated platelets tended to undergo a more porous type of coagulation with intense face-to-face interactions of platelets and effectively entrapped TiO\(_2\) particles in band-type structures. This type of coagulation usually results in a large volume of settled flocs with a fluffy structure and excellent turbidity removal efficiency for sweep coagulation. The sign and magnitude of electrical charge on TiO\(_2\) particles has a minor effect on the efficiency of sweep coagulation.

Keywords: sweep coagulation; bentonite; turbidity; low turbidity water

INTRODUCTION

Treatment of low turbidity water caused by ultra-fine particles is essential to several industries, such as drinking water supply, electronic manufacturing, fine polishing and pure chemical manufacturing. Owing to the low concentration of ultra-fine particles in water, the rate of interparticle contacts limits the overall process of coagulation.\(^1\) Alternative treatment processes such as membrane filtration and centrifugation are effective but high capital and operating costs prohibit their application in large-scale water treatment. Effective coagulation for low turbidity water is generally accomplished by sweep coagulation, which is usually performed with alum (aluminum sulfate).\(^2\) In such a process, high alum dose yields amorphous Al(OH)\(_3\) precipitation, which increases the interparticle collision rate, enmeshes the suspended particles and then removes them via sedimentation. However, in addition to the large amount of waste sludge produced by sweep coagulation using alum, high levels of aluminum remained in the treated water at acidic and alkaline pH, which raised public health concerns.\(^3\) McLachlan\(^4\) discovered that an intake of a large quantity of aluminum salt causes Alzheimer’s disease. In this study a novel strategy of sweep coagulation to treat low turbidity water is explored. This strategy uses flocs formed by flocculation of a dispersion of bentonite with a cationic polyelectrolyte instead of alum during sweep coagulation. Bentonite has been used to remove colloidal impurities in wine.\(^5\) These colloidal impurities are positively charged and are attached and coagulated by the negatively charged bentonite particles. In addition, spreading bentonite on the surface of water has been employed to remedy algal bloom.\(^6\) An outstanding property of dispersed bentonite particles is delaminating into the single silicate layers (platelets) or thin packets of them.\(^7\) Adding cationic polyelectrolyte causes charge neutralization of the negatively charged bentonite platelets and subsequent formation of flocs from all of the bentonite platelets dispersed in water. The turbidity-causing particles may well be entrapped within the aggregates of flocculating bentonite platelets, and is removed subsequently from water by sedimentation.

The aim of this work was to investigate the influence of the properties of bentonite (eg charge density and exchangeable cations) on the treatment efficiency of this new sweep coagulation strategy. In this work, we used a dilute dispersion of nanometer titanium dioxide (TiO\(_2\)) as a model of low turbidity water.

EXPERIMENTAL

Materials

TiO\(_2\) powder used herein was purchased from Degussa Corp (Germany) and was 20–30 nm in size (Fig 1), with a point of zero charge (pzc) at a pH of 6.5 (Fig 2). A reference Ca-saturated bentonite (SAz-1) and an Na-saturated bentonite (SWy-1) obtained from the Clay Source Repository of the Clay Minerals Society (Purdue University, USA) were used as received. Na-saturated SAz-1 was obtained by washing the SaZ-1 three times with 1.0 M NaCl solution followed by washing with distilled water, centrifugation, and freeze-drying. Some properties

of these bentonites are listed in Table 1. The cationic polyelectrolyte used was highly charged polydiallyldimethylammonium chloride (PDADMAC) (molecular weight of 300 000 g mol$^{-1}$, 20% by weight in water) from Aldrich Chemical Co (Milwaukee, WI, USA). Acidic (pH = 1.8) and alkaline (pH = 13.1) TiO$_2$-stock solutions (100 mg dm$^{-3}$) were prepared and sonicated for 30 min. A low turbidity water sample was prepared by adding 10 cm$^3$ of TiO$_2$-stock solution in 500 cm$^3$ distilled water with a final turbidity of 10.6 Nephelometric Turbidity Units (NTU). High pH water samples (pH = 11.2) and low pH water samples (pH = 3.5) were prepared by adding acidic and alkaline TiO$_2$-stock solution respectively.

**Methods**

A Zetasizer 3000 (Malvern, UK) was used to measure the zeta potential of TiO$_2$ as a function of pH. Three repeats were carried out for every zeta potential measurement that was conducted in 0.01 M NaCl solution.

Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4100 SEM with an energy dispersive X-ray microanalysis (EDAX) detector. Samples of TiO$_2$ and settled flocs after sweep coagulation were prepared by gently drying the samples at room temperature and placing them onto sample studs using sticky carbon tapes.

The light microscopic images were obtained with an Olympus BX50 device in transmission mode with phase contrast filters and recorded with a Polaroid digital microscope camera.

For the bentonite coagulation test, a weighed sample of bentonite was stirred in 500 cm$^3$ of distilled water within a 600 cm$^3$ beaker, fitted with four 0.25” wide baffle plates and 1” diameter propeller, for 10 min. The dispersion was then adjusted to pH 6.5 and further conditioned for 2 min. After conditioning, different amounts of PDADMAC were then added to the dispersion, while the propeller was rotated at 300 rpm. After 3 min of rapid mixing, the sample was stirred for a further 7 min at 30 rpm, then left to settle for 45 min. The bentonite concentration in the dispersion was estimated by turbidity measurements taken with a HACH 2100A turbidimeter. A calibration curve of the turbidity versus bentonite concentration was obtained. Samples were taken before and after coagulation, and the turbidity was determined. The percentage of bentonite removal was calculated as usual. The volumes of settled flocs (sludge volume) were measured in 100 cm$^3$ or 250 cm$^3$ graduated cylinders. After decanting the supernatant, the settled flocs were gently poured into graduated cylinders. For the sweep coagulation test, a pre-weighed amount of bentonite was added to 500 cm$^3$ of low turbidity water and varying amounts of PDADMAC were then added to the dispersion followed by the procedures described earlier (bentonite coagulation test). Supernatant turbidity was measured with a HACH 2100A turbidimeter and expressed in NTU.

The recycling of bentonite in sweep coagulation system was also evaluated. The settled flocs resulting from sweep coagulation using SWy-1 (Na$^+$) were air-dried and heated at 450 °C for 3 h to remove adsorbed PDADMAC. The treated SWy-1 (Na$^+$) samples were ground with a mortar and pestle for 5 min and reused in sweep coagulation tests.

**RESULTS AND DISCUSSION**

**Coagulation of bentonite dispersions**

Bentonite coagulation tests were run to explore the optimum coagulant dosages and flocculating behavior.

<table>
<thead>
<tr>
<th>Bentonite</th>
<th>CEC (meq per 100g)</th>
<th>Turbidity$^a$ (NTU)</th>
<th>Charge distribution$^b$</th>
<th>Tetra</th>
<th>Octa</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWy-1(Na$^{3+}$)</td>
<td>76</td>
<td>139</td>
<td>0.16</td>
<td>0.52</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>SAz-1(Ca$^{2+}$)</td>
<td>102</td>
<td>129</td>
<td>0.14</td>
<td>1.00</td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>SAz-1(Na$^{3+}$)</td>
<td>110</td>
<td>161</td>
<td>0.14</td>
<td>1.00</td>
<td>1.14</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ 700 mg dm$^{-3}$ clay in water.
$^b$ Calculated for O$_{20}$(OH)$_{4}$.$^8$

![Figure 1. SEM images of nano-sized TiO$_2$ particles.](image1)

![Figure 2. Zeta potential as a function of pH.](image2)
Treatment of low turbidity water

Figure 3. Coagulation of various bentonite dispersions as a function of PDADMAC dosage.

Figure 4. Light microscopic images of (a) flocs formed by the coagulation of SAz-1 (Ca$^{2+}$), (b) flocs formed by the coagulation of SWy-1 (Na$^+$).

for different types of bentonites. Figure 3 presents a comparison of the coagulation of SWy-1 (Na$^+$), SAz-1 (Na$^+$), and SAz-1 (Ca$^{2+}$) dispersions (700 mg dm$^{-3}$) with PDADMAC. The initial turbidity values of these dispersions are listed in Table 1. Optimum PDADMAC dosages for the coagulation of SAz-1 (Ca$^{2+}$), SWy-1 (Na$^+$), and SAz-1 (Na$^+$) dispersions were 0.2 mg dm$^{-3}$, 10.0 mg dm$^{-3}$, and 40.0 mg dm$^{-3}$ PDADMAC respectively. At the optimum dose, apparent solid removal was almost 100% for all bentonites except SAz-1 (Na$^+$). The relatively low optimum PDADMAC dosage for SAz-1 (Ca$^{2+}$) is presumably due to the divalent Ca$^{2+}$ ions as the exchangeable cations in SAz-1 (Ca$^{2+}$). The strong electrostatic attractive force limits the delamination of SAz-1 (Ca$^{2+}$) in dispersion and a small amount of PDADMAC was able to flocculate the closely spaced platelets of SAz-1 (Ca$^{2+}$). For PDADMAC coagulation of Na-saturated bentonites, SWy-1 (Na$^+$) (CEC = 76 meq per 100g) and SAz-1 (Na$^+$) (CEC = 110 meq per 100g), the optimum PDADMAC dosage for SWy-1 (Na$^+$) (10.0 mg dm$^{-3}$ PDADMAC) was only a quarter of that for SAz-1 (Na$^+$) (40.0 mg dm$^{-3}$ PDADMAC). This fact indicated that mechanisms of PDADMAC coagulation of bentonite dispersion are not dominated by charge neutralization of surface charge sites on bentonite (ie CEC of bentonite), instead, mechanisms such as bridging through PDADMAC and interactions among bentonite platelets (edge-to-face and/or face-to-face) may also contribute to the coagulation of bentonite dispersions. Furthermore, Fig 3 indicates a distinct difference between the volumes of settled flocs (sludge volume) for different bentonite dispersions. The coagulation of SAz-1 (Ca$^{2+}$) dispersions (700 mg dm$^{-3}$) produced sediment consisting of large aggregates with a compact structure (Fig 4(a)) and small sludge volume (less than 10 cm$^3$). In contrast, coagulation of SWy-1 (Na$^+$), and SAz-1 (Na$^+$) suspensions (700 mg dm$^{-3}$) resulted in a large volume of settled flocs (more than 100 cm$^3$) consisting of small aggregates with a fluffy structure (Fig 4(b)). It is possible that SAz-1 (Ca$^{2+}$) has a strong tendency to form aggregates of aligned (face-to-face interaction) bentonite platelets in dispersion, resulting in large flocs with a compact structure after coagulation. Coagulation of fully delaminated SWy-1 (Na$^+$) and SAz-1 (Na$^+$) dispersions, however, resulted in small flocs with a fluffy structure, presumably due to a more porous type of coagulation with intense face-to-edge and/or edge-to-edge interactions of platelets. It has been pointed out that edge-to-face contacts leading to card-house structures are only formed in acidic media, at neutral or alkaline conditions face-to-face interactions or band-type structures are formed.9,10 It is speculated that this band-type structure with bentonite platelets arranged in face-to-face contacts

during sweep coagulation is more efficient for capturing TiO$_2$ particles.

It is interesting to note in Fig 3 that the sludge volume of SWy-1 (Na$^+$) dispersion (CEC = 76 meq per 100g, initial turbidity = 139 NTU) is higher than that of SAz-1 (Na$^+$) dispersion (CEC = 110 meq per 100g, initial turbidity = 161 NTU). It is possible that adsorption of PDADMAC on the highly charged surface of SAz-1 (Na$^+$) results in an extended conformation of the PDADMAC polymer chain with few loops or trains. In contrast, PDADMAC adsorbed on the low-charged surface of SWy-1 (Na$^+$) has fewer contact points and a portion of the charged groups exist as loops or tails. Loops and tails of PDADMAC dangle into solution and bridge over dispersed platelets. The bridging mode of SWy-1 (Na$^+$) coagulation by PDADMAC resulted in a larger volume of settled flocs with a looser structure compared with the charge neutralization mode of SAz-1 (Na$^+$) coagulation. The bridging mode of coagulation generally requires less dose of coagulant compared with charge neutralization mode$^{11}$ and this will explain the relatively low optimum PDADMAC dosage for coagulation of SWy-1 (Na$^+$) compared with SAz-1 (Na$^+$).

**Sweep coagulation of low turbidity water with bentonite**

Preliminary coagulation tests revealed that PDADMAC coagulation alone was not effective for low turbidity water (with a turbidity of 10.6 NTU) over a wide range of PDADMAC dosages because of the low degree of interparticle contact and fineness of dispersed TiO$_2$ particles. Figure 5 compares the sweep coagulation of low turbidity water with different bentonites at a pH of 11.2, in terms of supernatant turbidity and sludge volume versus dispersed bentonite. The PDADMAC dosages applied (0.2, 10, and 40 mg mg$^{-1}$ bentonite for SAz-1 (Ca$^{2+}$), SWy-1 (Na$^+$), and SAz-1 (Na$^+$) respectively) herein were obtained from Fig 3. With a pzc of 6.5, the surface of TiO$_2$ particles was negatively charged at pH 11.2. Significant turbidity removal was achieved by sweep coagulation using SWy-1 (Na$^+$) (residual turbidity less than 1 NTU at bentonite dosages ranging from 30 to 700 mg dm$^{-3}$). The superior sweep coagulation using SWy-1 (Na$^+$) at pH 11.2 is attributable to the fact that the PDADMAC adsorbed on the low-charged surface of SWy-1 (Na$^+$) existed as loops or tails. Loops and tails of PDADMAC dangle into solution and effectively bridge over dispersed platelets and TiO$_2$ particles. In addition, the high sludge volume produced after SWy-1 (Na$^+$) sweep coagulation (Fig 5) may be caused by a more porous type of coagulation with intense face-to-face interactions of platelets that provided adequate interparticle contacts for TiO$_2$ removal. A bentonite dosage as low as 30 mg dm$^{-3}$ of SWy-1 (Na$^+$) was enough to reduce turbidity significantly. The sweep coagulation using SAz-1 (Na$^+$) at pH 11.2 resulted in a slightly higher residual turbidity (residual turbidity about 6 NTU at bentonite dosages ranging from 30 to 700 mg dm$^{-3}$) even though SAz-1 (Na$^+$) also produced high volumes of sludge. It is possible that this residual turbidity was caused by residual SAz-1 (Na$^+$) platelets due to inadequate PDADMAC coagulation of SAz-1 (Na$^+$) dispersion, as indicated in Fig 3. For the sweep coagulation using SAz-1 (Ca$^{2+}$) at pH 11.2, the residual turbidity decreases with increasing SAz-1 (Ca$^{2+}$) dosage. It has been reported that in the presence of Ca$^{2+}$ ions platelets aggregate to flocs which settle, forming sediments.$^{12,13}$ Apparently, a more compact type of coagulation with intense face-to-face interactions of aligned SAz-1 (Ca$^{2+}$) platelets provided inadequate interparticle contacts for TiO$_2$ removal and produced low volumes of sludge. The degree of interparticle contacts increases with increasing SAz-1 (Ca$^{2+}$) dosage and an SAz-1 (Ca$^{2+}$) dosage as high as 700 mg dm$^{-3}$ was only enough to result in a residual turbidity of 6 NTU.

Figure 6 compares the sweep coagulation of low turbidity water with different bentonites at a pH of 3.3, in terms of supernatant turbidity and sludge volume versus dosage of bentonite. With a pzc of 6.5, the surface of TiO$_2$ particles was positively charged at pH 3.3. In this case, interparticle contacts provided by positively charged PDADMAC-loaded platelets (heterocoagulation) were not beneficial to TiO$_2$ removal. Significant turbidity removal was

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*Figure 5. Sweep coagulation of low turbidity water with various bentonites at pH 11.2.*

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achieved, however, by sweep coagulation using SWy-1 (Na+) at pH of 3.3 (residual turbidity less than 1 NTU at SWy-1 (Na+) dosages ranging from 30 to 700 mg dm\(^{-3}\)). This suggests that physical entrapment of TiO\(_2\) particles within the flocculating SWy-1 (Na\(^+\)) platelets may be the primary mechanism responsible for TiO\(_2\) removal in this case. Again, the high sludge volume of SWy-1 (Na\(^+\)) produced after sweep coagulation (Fig 6) indicated a more porous type of coagulation with intense face-to-face interactions of platelets that effectively entrapped TiO\(_2\) particles in band-type structures. For the sweep coagulation using SAz-1 (Na\(^+\)) and SAz-1 (Ca\(^{2+}\)) at pH 3.32, the residual turbidity decreases with increasing bentonite dosage. Apparently, the aggregation processes of platelets of SAz-1 (Na\(^+\)) and SAz-1 (Ca\(^{2+}\)) during sweep coagulation at pH 3.32 were not so effective for entrapment of TiO\(_2\) particles. This speculation was confirmed by the observation that lower sludge volume resulted from SAz-1 (Na\(^+\)) and SAz-1 (Ca\(^{2+}\)) sweep coagulations (Fig 6). The close-up SEM image of Fig 7 reveals flocs formed by sweep coagulation. It shows the entrapped TiO\(_2\) particles within flocculated bentonite flocs.

A potential advantage of bentonite sweep coagulation processes would be the reuse of bentonite. Good turbidity removal was achieved by sweep coagulation using recycled SWy-1 (Na\(^+\)). The residual turbidity was less than 1 NTU at recycled SWy-1 (Na\(^+\)) dosage of 50 mg dm\(^{-3}\).

CONCLUSIONS
1 There is no stoichiometric relationship between CEC and PDADMAC dosage for the PDADMAC coagulation of bentonite dispersions. Surface charge density and exchangeable cations of bentonite influencing the configuration of adsorbed PDADMAC molecules and the arrangement of dispersed bentonite platelets respectively dictated the coagulation of bentonite dispersions.
2 Bentonite dispersions with fully delaminated platelets tended to undergo a more porous type of coagulation with intense face-to-face interactions of platelets and effectively entrapped TiO\(_2\) particles in band-type structures. This type of coagulation usually results in a large volume of settled flocs with a fluffy structure and excellent turbidity removal efficiency for sweep coagulation.
3 Results of this study indicated that excellent turbidity removal might be attained due to physical entrapment of TiO\(_2\) particles within the flocculating bentonite platelets. The sign and magnitude of electrical charge on TiO\(_2\) particles has a minor effect on sweep coagulation.
4 The successful treatment of low turbidity water by sweep coagulation with bentonite has been demonstrated in this study. An Na\(^+\)-saturated bentonite with medium CEC (SWy-1 (Na\(^+\))) resulted in significant turbidity removal at a dosage of 30 mg dm\(^{-3}\). In addition, bentonite has a potential to function as a recyclable material for sweep coagulation after removing the adsorbed PDADMAC and TiO\(_2\) particles.

REFERENCES
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