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Effects of coagulants on the surface forces of colloidal alumina under water treatment conditions

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Abstract

The effect of sulfate and selenate anions on the rate of coagulation of alumina colloids by Al(III) salts has been investigated under conditions typical of potable water treatment. Methods used included conventional light scattering and jar test coagulation experiments, determination of zeta potential and measurements of surface forces using an atomic force microscope. The presence of sulfate or selenate increases the initial rate of Brownian coagulation of the colloids, compared to an $Al(NO_3)_3$ coagulant by approximately two orders of magnitude. In jar testing, $Al(NO_3)_3$ coagulant produced fluffy, low density flocs with the greatest floc formation occurring at the highest pH (pH 8), whereas with $Al_2(SO_4)_3$, floc density was greater and optimum floc formation occurred at an intermediate pH (pH 6). AFM measurements reveal that sulfate (as Na_2SO_4) exhibits surface forces that cannot be modeled by simple DLVO theory, with a long-range (>10 nm) attractive force dominating, with hysteresis on the compression and decompression curves indicative of a bridging mechanism. The same behaviour was observed with the analogue Na_2SeO_4. With $Al(NO_3)_3$ electrolyte, simple forces that can be modeled using DLVO theory were observed, but the uniformly repulsive forces were independent of pH. The force curves in the presence of $Al_2(SO_4)_3$ were more complex than those with Na_2SO_4, showing van der Waals attraction dominating at small separation at the PZC and largely repulsive forces at other pH values. The overall results underline the unusual surface effects induced by sulfate (and selenate) with aluminium oxyhydroxide surfaces.

Keywords: Coagulation; Alumina; AFM; Aluminium oxide; Aluminium salts; Interparticle forces; Water treatment

1. Introduction

Aluminium salts are widely used for the coagulation of natural water colloids in potable water treatment. These colloids comprised of charged minerals, such as silica, aluminosilicates and ferro-manganese oxides, usually in association with acidic natural organic matter (NOM) [1–5]. NOM is thought to impart stability to colloids mainly through steric stabilization [6,7]. In the water treatment process, an extended hydrous network of alumina (Al_2O_3) is formed which entraps the colloidal material and may also adsorb soluble contaminants. Some alumina colloids display unusually high stability in the presence of indifferent electrolytes, compared to the predictions of the DLVO theory. This is thought to be the result of the formation of a gel layer of Keggin ions $Al_{13}O_4(OH)_x{}^{31-x}$ on the surface of the alumina particles that creates a steric barrier to aggregation or imposes a particular electrostatic barrier that is not described by the classical ζ-potential [8]. However, in the presence of sulfate, alumina colloids display 'normal' DLVO stability properties, presumably because the adsorbed sulfate ion disrupts surface-bound Al_{13} species [8]. It is well known that the presence of sulfate enhances the precipitation of aluminium hydroxide compared to indifferent anions, such as nitrate, chloride or perchlorate [9].

The development of colloidal probes for the atomic force microscope (AFM) has enabled the measurement of forces

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relevant to colloid stability under a range of solution conditions [10]. We have recently applied these techniques to the study of natural water colloids with regard to the effects of NOM on surface forces [11,12]. Karaman et al. [13] have reported AFM measurements that are consistent with the formation of an Al_{13} surface gel layer, however they did not investigate the effect of sulfate ions. Thus, because aluminium salts, and aluminium sulfate in particular, are widely used as coagulants in potable water treatment, we have used AFM colloid probes to investigate the effects of these coagulants on the surface forces between alumina surfaces under solution conditions directly relevant to potable water treatment. The results have been compared to those of conventional light scattering and jar test measurements of aggregation rates, and to electrokinetic (zeta potential) measurements. To extend our understanding of the effects of Al(III) and sulfate, we have also investigated other anions, including the indifferent ion NO_3^- and the sulfate analogue SeO_4^{2-}.

2. Materials and methods

2.1. Light scattering studies

In initial experiments, we tested the effects of the various Al(III) coagulants on the rate of colloid aggregation by measuring the changes in absorbance at 390 nm of a colloid suspension in an unstirred spectrophotometer cell. The relationship between light scattering measured in this way and the colloid particle concentration and size spectrum is complex, but with a suspension that is initially approximately monodisperse, the results should provide a good comparative measure of the initial coagulation rate. The use of an unstirred suspension means that only perikinetic coagulation induced by Brownian motion will be observed. After rapid mixing of the colloid suspension and coagulant and pH adjustment, the cell was placed in a Hewlett Packard 8453 spectrophotometer and absorbance measurements were taken every 60 s for 2–4 h against a Milli-Q water reference. These measurements were performed on a suspension of AR grade γ-Al_2O_3 (99.99% purity) containing 40 mg L^{-1} of solid. Samples were ultrasonicated to ensure a uniform particle size immediately before use.

Three coagulant solutions were used in this preliminary study. The first comprised of $Al(NO_3)_3$ and was intended to measure the effects of Al(III) only, under the assumption that NO_3^- functions as an indifferent anion. The second, consisting of $AlK(SO_4)_2$, represents an alum-like coagulant as used in water treatment. Finally, a mixture of $Al(NO_3)_3$ and Na_2SeO_4 was used to investigate the effects of the alternative anion to sulfate because the aluminium selenate salt was not available. All salts were AR grade and were prepared as 10 mM stock solutions. The appropriate volume of each coagulant solution was added directly to the alumina suspension to achieve the required final coagulant concentration and the pH adjusted to nominal values of 5.0, 6.0 and 7.0, respectively, covering the range typically used in water treatment, using 0.1 M NaOH or HCl as required. pH is one of the most important factors that influences the flocculation process because it is thought to exercise an important control on the surface electrical charge of the particles [14]. The $AlK(SO_4)_2$ and $Al(NO_3)_3 + Na_2SeO_4$ coagulants contained the same concentrations of Al(III) (0.258 mM) and SO_4^{2-}/SeO_4^{2-} (0.518 mM), while the $Al(NO_3)_3$ solution concentration was 0.388 mM, which has the same ionic strength as that containing $AlK(SO_4)_2$ but a 50% higher [Al(III)].

2.2. Zeta potential measurements

Forty milligrams per litre suspensions of either 0.3 μm α-alumina particles or 0.015 μm γ-alumina (both BDH) in 0.388 mM $Al(NO_3)_3$ or 0.258 mM $AlK(SO_4)_2$ electrolytes (same ionic strength of 2.33 mM) were employed after pH adjustment with 0.01 M NaOH or HNO_3. These are the same experimental conditions as the light scattering experiments already described. Zeta potentials were then measured with a Malvern ZetaSizer 3000 instrument using the non-aqueous “dip-in” plate cell at 25 °C.

2.3. Jar test coagulation experiments

These experiments were carried out using the standard jar test procedure employed in the water treatment industry to simulate conventional water treatment [15]. In contrast to the light scattering measurements, the use of the stirred jar test apparatus involves orthokinetic coagulation induced by fluid shear in the stirred suspension [15], and is concerned with the growth of much larger aggregates than are observed by our light scattering experiments.

Our apparatus (Fig. 3) used four 1 L tall form cylindrical beakers each fitted with rectangular, stainless steel paddles (7.5 cm × 2.5 cm). The colloid suspension was prepared using 0.3 μm diameter α-Al_2O_3 suspended in either tap water or Milli-Q water at a concentration of 15 mg L^{-1} This oxide has an isoelectric point around pH 8.5–9.0, resulting in a positive surface charge at the pH of most natural waters. Although the colloid levels in natural river waters vary greatly, a concentration of 15 mg L^{-1} is reasonably typical. The procedure involved addition of the coagulant to the suspension followed by rapid mixing at 120 rpm for 1 min to ensure thorough mixing. After this, the pH was adjusted again (if necessary) and was monitored during the remainder of the experiment. Next, slow mixing at 40 rpm for 30 min followed to allow flocs to grow by coagulation, after which photographs were taken to provide a visual record of floc sizes and sedimentation properties. All solutions were buffered with $NaHCO_3$ to ensure a stable pH during experiments. As before, the pH was adjusted with 0.1 M NaOH or HCl as required.

The Al(III) coagulant used was a Fernz® product “kibbled alum”, considered to be $A1_2(SO_4)_3 \cdot 14H_2O$, that is widely