Removal of TiO₂ Nanoparticles During Primary Water Treatment: Role of Coagulant Type, Dose, and Nanoparticle Concentration

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Abstract

Nanomaterials from consumer products (i.e., paints, sunscreens, toothpastes, and food grade titanium dioxide [TiO₂]) have the capacity to end up in groundwater and surface water, which is of concern because the effectiveness of removing them via traditional treatment is uncertain. Although aggregation and transport of nanomaterials have been investigated, studies on their removal from suspension are limited. Hence, this study involves the development of scaled-down jar tests to determine the mechanisms involved in the removal of a model metal oxide nanoparticle (NP), TiO₂, in artificial groundwater (AGW), and artificial surface water (ASW) at the primary stages of treatment: coagulation, flocculation, and sedimentation. Total removal was quantified at the end of each treatment stage by spectroscopy. Three different coagulants—iron chloride (FeCl₃), iron sulfate (FeSO₄), and alum [Al₂(SO₄)₃]—destabilized the TiO₂ NPs in both source waters. Overall, greater than one-log removal was seen in groundwater for all coagulants at a constant dose of 50 mg/L and across the range of particle concentrations (10, 25, 50, and 100 mg/L). In surface water, greater than 90% removal was seen with FeSO₄ and Al₂(SO₄)₃, but less than 60% when using FeCl₃. Additionally, removal was most effective at higher NP concentrations (50 and 100 mg/L) in AGW when compared with ASW. Zeta potential was measured and compared between AGW and ASW with the presence of all three coagulants at the same treatment stage times as in the removal studies. These electrokinetic trends confirm that the greatest total removal of NPs occurred when the magnitude of charge was smallest (<10 mV) and conversely, higher zeta potential values (>35 mV) measured were under conditions with poor removal (<90%). These results are anticipated to be of considerable interest to practitioners for the assessment of traditional treatment processes' capacity to remove nanomaterials prior to subsequent filtration and distribution to domestic water supplies.

Key words: water treatment; coagulation; nanoparticle removal; titanium dioxide; TiO₂; nanomaterials

Introduction

THE UNIQUE PHYSICOCHEMICAL, optical, and electrical properties of nanomaterials have resulted in an increased usage in consumer products and industries (Nel *et al.*, 2006), from which nanoparticles (NPs) may be released into aquatic environments (Wiesner *et al.*, 2006). The rapid growth of the nanotechnology industry has led to increased production and consumption of nanomaterials in common household products such as cosmetics, paints, and sunscreens (Weir *et al.*, 2012). Recent studies have shown that nanomaterials can be introduced into the aquatic environment via product use, disposal, and recycling (Wiesner *et al.*, 2006; Robichaud *et al.*, 2009). One nanomaterial that has been detected in biosolids and wastewater treatment effluent is titanium di-

oxide (TiO₂), suggesting it may ultimately end up in the receiving water bodies (Westerhoff *et al.*, 2011; Keller *et al.*, 2013). Exact levels of TiO₂ NPs present in the environment are not known due to limitations in current detection methods (Gottschalk and Nowack, 2011). However, an approximate concentration between 0.180–1.230 mg/L has been reported as levels found in wastewater biosolids (Westerhoff *et al.*, 2011).

Additionally, food grade nanoscale TiO₂ has a higher probability to enter sewage systems due to their frequent presence in personal care products, toothpastes, candies, and chewing gum (Weir *et al.*, 2012). About 5000 tons of nanoscale TiO₂ are produced annually, and is expected to increase annually until 2025 (Weir *et al.*, 2012). Non-nano-based TiO₂ production in industries are predicted to be converted into nano-based TiO₂ where the nanoscale levels will rise from about 200,000 tons in year 2014 to 2.5 million tons by year 2025 (Robichaud *et al.*, 2009). Non-food grade TiO₂ may also make it into waste streams through such mechanisms as paint weathering or industrial discharges.

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Subsequently, they may be introduced into the environment in the form of treated effluent discharge or biosolids applied to agricultural lands, incinerated wastes, or landfill solids (Zhang *et al.*, 2008; French *et al.*, 2009). As such, NPs are considered emerging pollutants that have the capacity to enter and impact water supplies. Thus, it is of critical importance to understand the movement of nanomaterials (Domingos *et al.*, 2009) in various model aquatic environments (Zhang *et al.*, 2008) and determine how they can be most effectively removed through conventional water treatment processes. This is of concern since nanoscale TiO_2 have been reported to cause adverse effects such as oxidative stress in human cells (Long *et al.*, 2006; Xia *et al.*, 2008) and genetic instabilities in mice (Trouiller *et al.*, 2009).

Metal oxide NP aggregation in water is a well-known phenomenon. Various groups have demonstrated NP aggregation through a combination of stability tests and transport studies (Zhang *et al.*, 2008; French *et al.*, 2009; Keller *et al.*, 2010; Chowdhury *et al.*, 2011). These studies have shown that aggregation is a significant mechanism governing NP behavior and provides insight into how they may be transported or removed in the environment. Such that observed trends in this current study can be evaluated, the fundamental mechanisms involved in particle separation are described briefly here. It is common to refer to coagulation as the destabilization step, which is induced by the introduction of polymers or salts. Flocculation refers to cases where polymer bridging dominates through fluid motion (i.e., orthokinetic aggregation) and aggregates (flocs) tend to be larger (Benjamin, 2002; Gregory, 2005). It has been reported that metal salts (i.e., aluminum, iron) are effective in removing colloidal particles and dissolved organic substances through charge neutralization and sweep flocculation mechanisms (Duan and Gregory, 2003). Specifically, the Duan and Gregory (2003) study found that charge neutralization can be effective in destabilizing colloidal particles at low dosages of aluminum and ferric salts (5–50 μM), bulk precipitation of metal hydroxide yielded larger flocs from sweep flocculation, and that optimum pH is important for the effectiveness of the coagulant. Sweep flocculation leads to faster aggregation than charge neutralization, and gives stronger/denser flocs (Gregory, 2005). Moreover, an important phenomena involving the effectiveness of metal coagulants is from the pH change caused by hydrolysis of the metal cations (in this case, Al^{3+} and Fe^{3+}); the change in pH of the solution governs the metal coagulants' effectiveness during coagulation since metal ion solubility will be affected (Crittenden and Harza, 2005; Gregory, 2005). Others have demonstrated the use of conventional water treatment processes (i.e., coagulation, flocculation, and sedimentation [CFS]) to effectively remove natural organic matter, suspended solids, disinfection by-product precursors, and other inorganic constituents from water and wastewater (Duan *et al.*, 2002; Domínguez *et al.*, 2005; Beltrán-Heredia *et al.*, 2009; Zhao *et al.*, 2009; Kim *et al.*, 2012). However, even with these studies and many others, the involvement of these removal mechanisms in the destabilization and separation of nanomaterials is yet unknown. Further, even with an extensive body of literature on these initial stages of water treatment and a growing number of articles on nanomaterial stability, the capacity of these treatment stages to remove nanomaterials has not yet been fully determined. Thus, it is imperative to conduct a systematic

study for the assessment of current water treatment infrastructure in removing nanomaterials prior to their entering water distribution systems, groundwater, and surface waters (Lecoanet and Wiesner, 2004; Dunphy Guzman *et al.*, 2006).

The overall aim of this research is to identify the capacity of traditional drinking water treatment processes to remove a model NP (TiO_2). Specifically, the scope of this study involves simulation of the three primary stages of water treatment, which include CFS. While current infrastructure technology has been designed to generally remove particles during water treatment, no study has been done specifically addressing the removal of nanomaterials in these processes. Therefore, systematic jar tests at the traditional (1 L) and reduced scale (100 mL) have been conducted to investigate this issue. The goals are to identify (1) whether a scaled-down version of jar tests could be used to evaluate the effectiveness of primary treatment and (2) what level of removal could be achieved under a range of representative conditions. The objective of developing the scaled-down jar tests is to employ a system that achieves the same degree of removal as the conventional jar tests, while generating far less waste; notably, lower volumes of test solutions (1 L vs. 0.1 L) and amounts of NPs (100 mg/L vs. 10 mg/0.1 L) are utilized. The second objective involves conducting tests under a range of relevant solution chemistries and conditions. The parameters under consideration include coagulant dose and type, NP concentration, source water types (model groundwater and surface water), and general operating conditions. The objective is to evaluate each stage of primary treatment for NP removal capacity prior to subsequent filtration and distribution to domestic water supplies.

Experimental Protocols

TiO₂ nanoparticles

TiO_2 NPs used in this study were Evonik Degussa P25 TiO_2 NPs, which are an industrial grade TiO_2 with a phase composition of 82% rutile and 18% anatase. According to the manufacturer, the NPs were greater than 99.5% pure and have a primary particle size of ~ 20 nm. Previous work with transmission electron microscopy has verified a similar effective diameter of TiO_2 to be $\sim 18 \pm 6.0$ nm (Chowdhury *et al.*, 2011), which is similar to the manufacturer's reported average particle size. Prior to all experiments, a stock suspension of TiO_2 NPs was prepared by a previously reported protocol (Chowdhury *et al.*, 2011) involving 2 min of sonication (Transsonic 460/H; Barnstead/Lab-Line) in the background solution. Nano- TiO_2 was selected as the model engineered NP as it will be one of the most common nanomaterials prevalent in the aquatic environment (Keller *et al.*, 2013). Bulk-sized TiO_2 was not used as the particles selected for this study were effectively micron-sized aggregates based on the solution conditions tested. Additionally, increased reactivity of NPs, despite aggregate sizes compared to bulk-sized TiO_2 , has been shown. Studies have demonstrated that the band gap of TiO_2 changed as a function of primary particle size (< 20 nm) (Lin *et al.*, 2006).

Test solutions

The two test solutions used in this study were artificial groundwater (AGW) (Bolster *et al.*, 1999) and artificial surface water (ASW) (Yip *et al.*, 2011) to simulate environmentally

relevant source waters typically entering water treatment plants. The ionic strength of the two solutions was 0.01 and 0.00183 M for AGW and ASW, respectively. The total salt concentration in AGW is 630.9 mg/L and is comprised of six different salts: CaCl₂·2H₂O, CaSO₄·2H₂O, KNO₃, NaHCO₃, Ca(NO₃)₂·4H₂O, and MgSO₄·7H₂O. ASW has a total salt concentration of 80.1 mg/L that is eight times less in mass concentration than AGW, and it is composed of: MgCl₂·6H₂O, MgSO₄, KHCO₃, NaHCO₃, and CaCO₃. All chemicals used were either ACS grade reagents (purchased from Fisher Scientific) or research grade (from Mallinckrodt Chemical and Acros Organics).

Jar test experiments

The first primary treatment stage in water treatment is coagulation. Coagulation, also known as a rapid or “flash” mixing process, refers to the step where anionic or cationic polymers are added into the water in an effort to destabilize suspended material (Bratby, 2006). Typical operating parameters for coagulation involves 150–300 rpm mixing for 1–2 min (Crittenden and Harza, 2005; Bratby, 2006). Next is flocculation, where the destabilized particles and primary flocs collide and agglomerate to a size and density that will readily settle to the bottom (Bratby, 2006). This process is facilitated by slow mixing, typically 25–40 rpm mixing on the order of 30 min (Spellman and Drinan, 2000; Crittenden and Harza, 2005). Finally, sedimentation, also known as clarification, involves gravity-induced settling of the resulting floc, remaining particulate matter, and precipitates from suspension in the absence of any mixing over 1 to 4 h (Spellman and Drinan, 2000; Crittenden and Harza, 2005).

Two scales of jar test analyses were conducted, at the conventional (1 L) and a novel “scaled-down” (100 mL) version. The operating parameters, which include the mixing speeds and length of three critical treatment steps—CFS—were set based on values reported from actual CFS stages in water treatment plants (Crittenden and Harza, 2005). To simulate flash mixing, both the conventional and scaled-down jar tests employed maximum feasible mixing speeds (300 rpm for conventional jar tests and 150 rpm for the scaled-down version) and lasted for 1 min. Prior to the start of experimentation (i.e., before the coagulation process), the TiO₂ suspension was sonicated and stirred. The equilibration time for the jar test experiments were as follows: (1) after sonication of the TiO₂, there is approximately a 2 min interval for dispensing the NP solution (while stirring) into the four 100 mL jars prior to coagulant addition; (2) then, the coagulant was pipetted immediately (~2 s) prior to turning on the mixer. Flocculation was conducted at 30 rpm for both cases that lasted for 30 min. Finally, a 1 h non-mixing sedimentation stage was implemented. The conventional jar tests were performed with a traditional apparatus of six vertical paddle stirrers (Philips and Bird Unit of General Medical Corp.). The scaled-down jar test was conducted using a stir plate with four, simultaneously spinning magnets (Corning Laboratory Systems) and FDA-grade octagonal magnetic stir bars that measure 2.54 cm in length and 0.79 cm in diameter (Fisher Scientific).

Three different coagulants were used in this study: iron chloride (FeCl₃), iron sulfate (FeSO₄), and alum [Al₂(SO₄)₃]. These are commonly used choices in industry (Tchobanoglous

et al., 2003), most notably FeCl₃ and Al₂(SO₄)₃. The TiO₂ concentration was 100 mg/L for all experiments, with the exception for the experiments investigating the role of TiO₂ concentration on removal. Experiments were conducted in both AGW and ASW at NP concentrations of 10, 25, 50, and 100 mg/L. The concentration of NPs was selected to be artificially high such that their concentration could be measured in the spectrophotometer when removal levels of >90% are achieved. The influence of coagulant dose was investigated in AGW with the three coagulants at 30, 40, 50, and 60 mg/L, which are representative of a range commonly used in industry (Tchobanoglous *et al.*, 2003; Crittenden and Harza, 2005).

Jar test experimentation consisted of three coagulants at a constant dosage of 50 mg/L each and NP concentration of 100 mg/L in AGW and ASW. About 1.5 mL samples were drawn from the center point and ~1 mm depth in the beakers at the end of the three treatment stages for both the scaled-down and full-scale jar tests. Sampling times of 0, 30, and 90 min correspond to the end of the following three stages of treatment at which absorbance was read: at 1 min for flash mix, 30 min of flocculation, and 1 h of sedimentation. The samples were measured in a spectrophotometer (DU 800 Beckman Coulter) at a wavelength of 370 nm. This value was determined using the automatic time-scan feature on the spectrophotometer to determine the optimum wavelength for measuring TiO₂. Despite the lack of a distinct peak, TiO₂ does strongly absorb light smaller than 400 nm (band gap energy of 3.0 eV) (Linsebigler *et al.*, 1995; Lin *et al.*, 2006; Palominos *et al.*, 2008) proportionally to the mass concentration of the suspension. There have also been other studies that have successfully employed this technique of using a UV-Vis to measure relative concentration of NPs (Keller *et al.*, 2010; Dalai *et al.*, 2012).

Total particle removal was evaluated at each of the three stages of treatment (CFS). The results are plotted as $1 - A/A_0$ versus time, when A/A_0 is the ratio of measured absorbance over the initial absorbance (initial refers to the experiment at time “0 min” before the addition of coagulant) and time accounts for the minutes elapsed since the NPs were added to the solution. The expression $1 - A/A_0$ is expressed as a percentage and represents the total particle removal from the start of the jar test through each phase of treatment.

Characterization

Electrokinetic characterization (zeta potential) was conducted using a ZetaPALS analyzer (Brookhaven Instruments Corp) and measurements were taken immediately after each of the three treatment processes—CFS—were complete. Hydrodynamic diameter was measured using dynamic light scattering (DLS) (Brookhaven Model BI-9000AT) at the end of each of the three treatment stages. Both the zeta potential and hydrodynamic diameters were determined from the arithmetic average of five runs with each run lasting 2 min. Each measurement required ~2 mL of test sample for both zeta potential and DLS.

Results and Discussion

Conventional versus scaled-down jar tests

Validation of the use of the scaled-down jar tests (100 mL vs. conventional 1 L jars) was conducted to ensure that the

FIG. 1. Conventional versus microscale jar tests were evaluated as a function of total particle removal ($1 - A/A_0$) over time in artificial groundwater (AGW). Times 0, 30, and 90 min correspond to the end of the following three stages of treatment: a 1 min flash mix, 30 min of flocculation, and 1 h of sedimentation. The three coagulants used were iron chloride (FeCl_3) (A), iron sulfate (FeSO_4) (B), and alum [$\text{Al}_2(\text{SO}_4)_3$] (C) at dosage of 50 mg/L. TiO_2 concentration was 100 mg/L. Operating parameters were: 150 rpm coagulation for 1 min, 30 rpm flocculation for 30 min, and 0 rpm sedimentation for 60 min. Error bars indicate one standard deviation of three jar test measurements.

smaller scale experiments achieved the same degree of removal as in traditional jar tests. The results of these comparison tests are presented in Fig. 1.

As seen from Fig. 1, ~95–100% removal was reached over the entire course of the experiments (as judged by the total particle removal achieved at 90 min, the end of the sedimentation phase). This removal level occurs regardless of coagulant type or scale of system (conventional or scaled-down). For example, the total particle removal achieved subsequent to sedimentation with coagulant FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ remained at combined (both scales) average removal of $99.7\% \pm 0.1\%$ and $99.4\% \pm 1.0\%$, respectively, and the differences between the two scales were statistically insignificant ($p=0.41$) as verified by an ANOVA test run in Microsoft Excel (v. 2007). Removal in the presence of FeSO_4 was a bit lower than the other two coagulants, at about $95.3\% \pm 0.8\%$ effective. The only notable differences occurred during the flocculation stage, where the total removal from across the three stages was greater than 80% in all cases, except in the conventional scale with $\text{Al}_2(\text{SO}_4)_3$ (<60%). However, by the end of the sedimentation phase of treatment the total particle removal achieved was effectively the same. These experiments demonstrated the capacity for the scaled-down (100 mL) jar tests to simulate the conventional (1 L) apparatuses ones; hence, all subsequent jar tests discussed herein are those conducted in the scaled-down system.

Role of coagulant type and dosage

The relative effectiveness of three commonly used coagulants— FeCl_3 , FeSO_4 , and $\text{Al}_2(\text{SO}_4)_3$ —was compared over a range of doses in AGW. These results are presented in Fig. 2. The removal trends are quite similar between the three coagulants across all doses tested, with the greatest removal occurring during the coagulation and flocculation stage. Notably, 90% of the total removal in all cases occurred in these first 30 min of treatment. FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ performed the best, achieving an average removal of $97.5\% \pm 2.0\%$ and $98.0\% \pm 2.8\%$, respectively, compared with a lower value of $92.0\% \pm 1.8\%$ for FeSO_4 . The difference in removal when using FeCl_3 and $\text{Al}_2(\text{SO}_4)_3$ was statistically insignificant ($p=0.11$).

Coagulant doses below 50 mg/L yielded poorer removal levels, indicating a higher dose coagulant was required. An experiment conducted at 30 mg/L of coagulant dose yielded lower removal when compared with increased dosages (>30 mg/L), except at 60 mg/L. Above 50 mg/L, there was an excess of coagulant, causing additional turbidity of the water due to an increased amount of particles present in the suspension, which subsequently increases the absorbance value reading. This performance was optimized based on an NP concentration of 100 mg/L. As such, the subsequent experiments were conducted at the selected coagulant dose of 50 mg/L. In contrast, experiments in the absence of

FIG. 2. Total titanium dioxide (TiO_2) removal plotted as a function of coagulant dose in AGW in microscale jar tests over time with three coagulants using four different dosages: 30, 40, 50, and 60 mg/L. TiO_2 concentration remained constant in all experiments at 100 mg/L. The three coagulants used were FeCl_3 (A), FeSO_4 (B), and $\text{Al}_2(\text{SO}_4)_3$ (C). Operating parameters were 150 rpm coagulation for 1 min, 30 rpm flocculation for 30 min, and 0 rpm sedimentation for 60 min. Error bars indicate one standard deviation of three jar test measurements.

FIG. 3. Total TiO₂ removal plotted as a function nanoparticle (NP) concentration in AGW in microscale jar tests. TiO₂ concentrations ranged from 10, 25, 50, and 100 mg/L. The three coagulants used were FeCl₃ (A), FeSO₄ (B), and Al₂(SO₄)₃ (C). Coagulant dose remained constant at 50 mg/L with all three coagulants for all experiments. Operating parameters were 150 rpm coagulation for 1 min, 30 rpm flocculation for 30 min, and 0 rpm sedimentation for 60 min. Error bars indicate one standard deviation of three jar test measurements.

coagulants were also conducted to demonstrate TiO₂ removal with no chemical aid. Results showed that the total particle removal after sedimentation was 71.5% ± 4.89% in AGW and 69.5% ± 1.91% in ASW, respectively.

Role of TiO₂ NP concentration

The contribution of NP concentration to total removal during treatment, tested in both AGW and ASW with a constant coagulant dose of 50 mg/L, is reported in Figs. 3 and 4, respectively. Figure 3 presents the total removal data with FeCl₃ (3A) with FeSO₄ (3B) and with Al₂(SO₄)₃ (3C). FeCl₃ and Al₂(SO₄)₃ resulted in similar trends in AGW with an average total particle removal of 95.2% ± 0.4% with FeCl₃ and 97.4% ± 0.6% with Al₂(SO₄)₃ after sedimentation for the four TiO₂ concentrations. In FeSO₄, the removal was similar to the other coagulants at 100 mg/L TiO₂ (94.2% ± 0.6%), but was notably lower removal at NP concentrations <100 mg/L (60.7% ± 1.4%, 81.5% ± 0.9%, and 89.6% ± 0.1% total removal at 10, 25, and 50 mg/L, respectively). Poorer removal of the NPs occurs at the lower concentrations (particularly at 10 mg/L) due to insufficient collisions occurring between particles during the mixing stages. This indicates that the presence of a coagulant aid such as bentonite clay particles is needed (Yang *et al.*, 2012), as the coagulant aid can induce a higher collision frequency between the coagulant and NP and, thus, improve aggregation between particles (Kim *et al.*, 2012).

The trends described above are observed in the ASW as well. Figure 4B and C display similar total particle removal

trends with FeSO₄ achieving about a 91.8% ± 1.7% effectiveness and Al₂(SO₄)₃ nearly 100% ± 0.6% after sedimentation across all four TiO₂ concentrations in ASW. However, FeCl₃ resulted in much poorer removal levels (Fig. 4A), with removal dropping off nearly two times less than that of FeSO₄ and Al₂(SO₄)₃. The total particle removal at 10, 25, 50, and 100 mg/L TiO₂ when using FeCl₃ was 32.5% ± 4.4%, 46.2% ± 1.0%, 68.5% ± 5.1%, and 47.9% ± 21.7%, respectively. Clearly, there is a notable difference in removal capacity with FeCl₃ when comparing the two source waters (95% effective in AGW; only 48% in ASW). Out of the three coagulants tested, FeCl₃ demonstrated the most consistent removal of TiO₂ at high concentrations of 50 and 100 mg/L, regardless of solution chemistry (water type) and particle concentration. This is further confirmation that the coagulant type and dose must be selected for the water source at a particular site.

Characterization of TiO₂ NPs

Extensive electrokinetic characterization of the NPs was conducted in an effort to mechanistically explain the results of the jar tests. Outcomes of this characterization are reported in Fig. 5. The TiO₂ NPs became less negatively charged across the range of aquatic parameters tested as the pH values became more acidic with the addition of coagulant (albeit the pH was still above the isoelectric point for TiO₂) (Chen and Li, 2010). As expected, the zeta potential (Fig. 5) was observed to be sensitive to the type of water and coagulant used.

FIG. 4. Total TiO₂ removal plotted as a function NP concentration in artificial surface water (ASW) in microscale jar tests. TiO₂ concentrations tested were 10, 25, 50, and 100 mg/L. The three coagulants used were FeCl₃ (A), FeSO₄ (B), and Al₂(SO₄)₃ (C). Coagulant dose remained constant at 50 mg/L with all three coagulants for all experiments. Operating parameters were 150 rpm coagulation for 1 min, 30 rpm flocculation for 30 min, and 0 rpm sedimentation for 60 min. Error bars indicate one standard deviation of three jar test measurements.

FIG. 5. Zeta potential (mV) measurements of TiO_2 for each of three coagulants in both AGW (A) and ASW (B) measured over the course of the jar tests. Times 0, 30, and 90 min correspond to the end of the following three stages of treatment: a 1 min flash mix, 30 min of flocculation, and 1 h of sedimentation. Zeta potential ranged between 0–12 mV in AGW and 10–45 mV in ASW. The pH of AGW was 8.01 and 9.4 for ASW. Error bars indicate one standard deviation of five zeta potential measurements.

The sensitivity to water source is linked to the pH of the two model solutions, which was found to be 9.4 and ~ 8 for ASW and AGW, respectively. With the addition of each coagulant, the pH of the two model waters was reduced even further. The most notable impact on pH was seen with FeCl_3 , where the pH dropped almost six log units to 3.9 in ASW. The pH of the water, in addition to the ionic content, impacted the subsequent electrokinetic properties of the NPs. Stability of the NPs is affected by pH changes since TiO_2 will interact with other particles based on its isoelectric point (~ 6.2). The pH of AGW was ~ 8 and became more acidic with the addition of coagulant (pH 6.56, 7.58, and 7.42 for FeCl_3 , FeSO_4 , and $\text{Al}_2(\text{SO}_4)_3$, respectively). As seen from the zeta potential data for particles in AGW (Fig. 5A), even with this change in pH, the relative magnitude of zeta potentials were similar between all three coagulants. After sedimentation, the zeta potential values for FeCl_3 , FeSO_4 , and $\text{Al}_2(\text{SO}_4)_3$ were 5.0 ± 3.0 , 1.6 ± 4.9 , and 6.8 ± 2.1 , respectively. These values directly correspond to the removal data trends as seen in Fig. 3 with an average of about 90% removal in all cases, except with FeSO_4 at 10 mg/L TiO_2 concentration. When comparing the zeta potential and removal data, a correlation between removal and zeta potential is seen (with removal decreasing with more substantial zeta potential values). pH clearly impacts the results because TiO_2 normally has a point of zero charge at a pH of about 6.2 under similar conditions (Chowdhury *et al.*, 2011). In this study, the pH of AGW was ~ 8 and the addition of the coagulant made the solution more acidic. The lower zeta potential value indicates that the NPs were less stable and, therefore, more effectively removed during the jar test. Hence, the selection of coagulant impacted the removal efficiency due to the coagulants influence of solution chemistry and subsequent particle charge, which is consistent with other studies looking at the removal of organic matter, turbidity, and metal oxides (Domínguez *et al.*, 2005; Morfesis *et al.*, 2008; Zhang *et al.*, 2008; Yu *et al.*, 2010).

In contrast, zeta potential values for NPs in ASW had dissimilar results between the three coagulants as seen in Fig. 5B. The pH of ASW is ~ 9.4 and becomes more acidic when each of the three coagulants was added (3.92, 7.23, and 7.21 for FeCl_3 , FeSO_4 , and $\text{Al}_2(\text{SO}_4)_3$, respectively). pH was not controlled in the experiments to determine the coagulants' effectiveness in solutions simulating "natural" water sources—especially as groundwater and surface water are mildly basic by nature (Winter, 1999; Crittenden and Harza, 2005). The zeta potential of the NPs in ASW ranged from 42.4 ± 2.5 , 12.9 ± 2.4 , and 18 ± 2.5 mV in the presence of FeCl_3 , FeSO_4 , and $\text{Al}_2(\text{SO}_4)_3$, respectively. This data helps

explain the poor removal phenomena with FeCl_3 from Fig. 4, as the larger zeta potential indicates greater stability and reduced capacity for the particles to aggregate and be removed by gravitational sedimentation.

Zeta potential measurements provide insight into the particle stability as greater the magnitude of the zeta potential, higher the particle stability. In general, the zeta potential trends agree with the total removal data as presented in Fig. 4. For example, total particle removal was the lowest in ASW for FeCl_3 (only 48% removal compared with the >91 –100% removals with the other two coagulants in Fig. 4A). The zeta potential of the TiO_2 was the greatest under these same conditions, suggesting highly stable particles. Specifically, the magnitude of zeta potential in ASW ranged from 42.4 ± 2.5 , 12.9 ± 2.4 , and 18 ± 2.5 mV for FeCl_3 , FeSO_4 , and $\text{Al}_2(\text{SO}_4)_3$, respectively.

Size of TiO_2 NPs and aggregates

Figure 6 presents the hydrodynamic diameter of the particles as measured by DLS after each stage of treatment. As seen in Fig. 6, TiO_2 aggregated to sizes on the order of ~ 2000 – 2700 nm for all cases except for FeCl_3 in ASW, which was ~ 1200 nm. The hydrodynamic diameters measured correspond to the zeta potential data (Fig. 5) in that under conditions where the particles exhibit greater zeta potential values, they are more stable and result in smaller measured diameters (lower DLS signal). Previous studies have also shown TiO_2 (100 mg/L) to aggregate anywhere from 1000 nm to 3000 nm in KCl during a similar time duration as this study (0–1.5 h) (Chowdhury *et al.*, 2011). Another group showed that aggregation occurs for zinc oxide (~ 400 nm), cerium dioxide (~ 1000 nm), and TiO_2 (~ 1200 nm) NPs in seawater and freshwater over a settling time of 60 min (Keller *et al.*, 2010). Aggregation phenomena has also been observed in nanoscale zero-valent iron, which ranges anywhere between 125 nm to 1200 nm with a NP concentration of 2 to 60 mg/L, respectively (Phenrat *et al.*, 2006). As observed from these examples, NP aggregation occurs regardless of solution chemistry and settling time.

Environmental Implications

This study provides evidence that typical primary treatment (CFS) can effectively remove metal oxide NPs (i.e., TiO_2) within the range of concentrations tested in this work. Additionally, it was demonstrated that the total removal capacity at the scaled-down level resulted in the same removal capacity as the conventional scale system with ≥ 1 -log removal for all three coagulants. Also, the ideal choice of

FIG. 6. Hydrodynamic diameter values measured via dynamic light scattering (DLS) for particles remaining in suspension for AGW and ASW after each stage of treatment (coagulation at 0 min, flocculation at 30 min, and sedimentation at 90 min). A concentration 100 mg/L TiO₂ and 50 mg/L dose of each coagulant was employed in all experiments. Error bars indicate one standard deviation of five DLS measurements.

coagulant is dependent on the water source. Based on the results, FeCl₃ was more effective in total particle removal in AGW (>95%) than in ASW (<70%). Overall, FeSO₄ performed more effectively in ASW at all four TiO₂ concentrations tested (>91%) than in AGW (>90% at 50 and 100 mg/L; but 60–80% at 10 and 25 mg/L, respectively). Moreover, Al₂(SO₄)₃ was effective in both waters with similar removal results (nearly 100%). Based on the concentrations of metal coagulant used in this study, it is anticipated that removal via sweep flocculation is the dominant mechanism in particle removal (Duan and Gregory, 2003; Gregory, 2005). The effect of NP concentration was significant—generally, the higher TiO₂ concentrations (50 and 100 mg/L) were more effectively removed when compared with the lower concentrations (10 and 25 mg/L), and it was also coagulant specific as discussed previously. This phenomenon suggests that a coagulant aid may be added to the low concentration systems to induce greater collision frequency between the NP and coagulant, an appropriate scaling factor for the optimum dose of coagulant.

Mechanistically, electrokinetic interactions will also be important, as the relative charge on the particle surface in the various water conditions relate to particle stability. Electrostatic repulsion may occur due to the TiO₂ particles in water having a net positive surface charge at these solution conditions (Crittenden and Harza, 2005). Bridging effects between the high amounts of divalent ions (Ca²⁺, Mg²⁺) and the metal coagulants may be occurring on the surface of TiO₂. Also, bridging affects the separation distance between the particles (Biggs, 1995), and in turn, can cause larger aggregates of particles (Gregory, 2005). Also, change in charge effects may be caused by the presence of ions due to the dissolved constituents in the two source waters. Complexation occurs in waters of high ionic content and may induce the formation of ligands, which will solubilize metal complexes in water (Welton, 1999; Crittenden and Harza, 2005). Aluminum sulfate reacts with natural alkalinity in water to form aluminum hydroxo complexes (Viessman, 2009) that also involve the production of H⁺ ions, which

will lower the pH. These reactions are also analogous to the ferric-based coagulants with similar mechanisms (Viessman, 2009). Further, the source water impacts both the pH and ionic strength, and subsequently, affects the stability of the particles. The more acidic the solution is, greater the zeta potential, and thus, a lower removal efficiency is observed. The decrease in pH observed in both source waters is due to chemical reactions associated with the metal coagulants. When salts of iron (Fe²⁺ or Fe³⁺) or aluminum (Al³⁺) ions are added to water, they will dissociate to yield trivalent Fe³⁺ or Al³⁺ and divalent Fe²⁺ (Crittenden and Harza, 2005). These ions then hydrate to form aquometal or hydroxo complexes. During these reactions, the production of H⁺ will occur, which will depress the pH values (Viessman, 2009).

Overall, results presented herein suggest that the chosen operating conditions and coagulant dose are critical based upon particle concentration levels and source waters. Environmentally relevant molecules such as natural organic matter may significantly impact operating parameters; therefore, further investigation is merited under such conditions. By understanding the optimum operating parameters and solution chemistries of these systems, best practices may be developed to remove TiO₂ (and other NPs) via conventional water treatment methods before they enter the environment, and ultimately, drinking water supplies (Kumar, 2012).

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