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Effect of $AlCl_3$ concentration on nanoparticle removal by coagulation

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ABSTRACT

In recent years, engineered nanoparticles, as a new group of contaminants emerging in natural water, have been given more attention. In order to understand the behavior of nanoparticles in the conventional water treatment process, three kinds of nanoparticle suspensions, namely multi-walled carbon nanotube-humic acid (MWCNT-HA), multi-walled carbon nanotube-N,N-dimethylformamide (MWCNT-DMF) and nanoTiO_2-humic acid (TiO_2-HA) were employed to investigate their coagulation removal efficiencies with varying aluminum chloride ($AlCl_3$) concentrations. Results showed that nanoparticle removal rate curves had a reverse "U" shape with increasing concentration of aluminum ion (Al^{3+}). More than 90% of nanoparticles could be effectively removed by an appropriate Al^{3+} concentration. At higher Al^{3+} concentration, nanoparticles would be restabilized. The hydrodynamic particle size of nanoparticles was found to be the crucial factor influencing the effective concentration range (ECR) of Al^{3+} for nanoparticle removal. The ECR of Al^{3+} followed the order MWCNT-DMF > MWCNT-HA > TiO_2-HA, which is the reverse of the nanoparticle size trend. At a given concentration, smaller nanoparticles carry more surface charges, and thus consume more coagulants for neutralization. Therefore, over-saturation occurred at relatively higher Al^{3+} concentration and a wider ECR was obtained. The ECR became broader with increasing pH because of the smaller hydrodynamic particle size of nanoparticles at higher pH values. A high ionic strength of NaCl can also widen the ECR due to its strong potential to compress the electric double layer. It was concluded that it is important to adjust the dose of Al^{3+} in the ECR for nanoparticle removal in water treatment.

Introduction

Nowadays, engineered nanoparticles (ENPs) have attracted a great deal of attention because of their increasing production and use (Luan and Tan, 1992). As the use of ENPs continues growing rapidly, it is inevitable that these particles will enter natural aquatic systems if they are not properly controlled during their production, use and disposal. Recent studies on the toxicity of nanoparticles showed that nanoparticles may pose a risk to human health and organisms in aqueous systems if present at sufficiently high concentrations (Lin et al., 2010). Thus finding a proper method to remove ENPs from water is urgently needed.

Coagulation has been widely used to remove suspended matter and some colloid matter in water treatment (Gurusamy

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Annadurai and Lee, 2004). Studies on potable water treatment unit processes (especially coagulation) related to ENP removal have suggested that there are many factors influencing the removal efficiency for nanoparticles. Reijnders (2006) suggested that standard wastewater treatment may be ineffective in the removal of nanomaterials, whereas Wiesner et al. (2006) concluded that the involvement of nanomaterials in current water treatment systems may not become a problem. Meanwhile, Zhang et al. (2008) reported that coagulation removal efficiencies of selected metal oxide nanoparticles ranged between 20% and 60% and Holbrook et al. (submitted for publication) confirmed that multi-walled carbon nanotubes (MWCNTs) could be removed from the aqueous phase *via* coagulation using either ferric chloride or aluminum sulfate (alum). Liu et al. (2012) investigated the removal of dispersant-stabilized carbon nanotube (CNT) suspensions and concluded that the removal efficiency of these particles was dependent on dispersant type, coagulant type and coagulant dosage. Also, Hyung and Kim (2009) found that the removal of nC_{60} depended on coagulant dose.

The above studies showed that the ENP coagulation removal efficiency is closely related to the coagulant type and dosage. In our previous research (Zhang et al., 2014), we found that the $AlCl_3$ dosage can transform the electric charge of C_{60} from a negative to positive charge and re-stabilize the particles in suspension. We believe that the coagulant dosage can significantly affect the stability of nanoparticles by varying their surface charges. As the surface charge carried by nanoparticles is related to their type and size, it is necessary to investigate the variation of the effective concentration range (ECR) of Al^{3+} with the type and size of nanoparticles, which would benefit the manipulation of the coagulant to obtain effective removal of nanoparticle by coagulation in actual water treatment. Therefore, two kinds of nanoparticles, CNT and TiO_2 were dispersed in humic acid (HA) and N,N-dimethylformamide (DMF) to prepare three suspensions with different particle sizes, CNT-HA, CNT-DMF and TiO_2-HA, to investigate how their removal efficiency varied with the dosage of Al^{3+}, and the variation of the ECR of Al^{3+} with nanoparticle size was explored.

1. Materials and methods

1.1. Nanoparticles

Multi-walled CNTs were purchased from Nanotech Port Co., Shenzhen, China (Model CN3016). Before their use, CNTs were dispersed into a 150 mL flask containing 40 mL concentrated acid solution (30 mL HNO_3, 10 mL H_2SO_4) for 24 hr to remove residual metal catalyst. Then, CNTs were washed by deionized water. Finally, the CNT-containing solution was filtered by a 0.45 mm glass-fiber filter and dried at 80°C in a hot air oven overnight to obtain purified CNTs. TiO_2 (25 nm) was purchased from Sigma-Aldrich. Aldrich HA was purified according to a previous study (Pan et al., 2006). Briefly, 0.1 mol/L NaOH and 0.1 mol/L $Na_4P_2O_7$ were mixed with Aldrich HA (50:1, V/W) to extract the HA. The supernatants were filtered and collected. The supernatants were then precipitated by HCl. The precipitated HAs were washed using distilled water until a chloride test using $AgNO_3$ was negative for chloride, freeze-dried and ground to <500 μm particles. The purified HAs were then dissolved into deionized water and adjusted to pH 12 with 0.5 mol/L NaOH. After 10 hr stirring, the solution was filtered through a 0.20 μm cellulose acetate membrane filter and stored at 4°C. The concentration of HA in the filtrate was 525 mg/L quantified by total organic carbon (TOC). DMF was purchased from Tianjin BODI Company, China.

1.2. Carbon nanotube and TiO_2 suspensions

HA and DMF were used as dispersants to prepare MWCNT-HA, MWCNT-DMF and TiO_2-HA suspensions. 50 mg of nanoparticles was dispersed into 25 mL HA solution (525 mg/L) and pure DMF solvent, respectively. The mixture was shaken for 12 hr at 25°C in a thermostat oscillator. Then, the mixture was poured into 750 mL super pure water. After that, the pH of the mixture was adjusted to 10.0 with 0.1 mol/L NaOH. The suspension was then sonicated for 1.5 hr at 40 KHz with an intensity of 150 W/L (2000U, Ultrasonic Power Co, China) and stored at 25 ± 2°C for no longer than 10 hr before its use.

1.3. Coagulation experiments

A jar test was used to evaluate the removal efficiency of nanoparticles by the coagulation process in a Jar Mixer (Tianjin, China) with six paddles. 250 mL water samples containing nanoparticles were used in the experiments and their characteristics are shown in Table 1. $AlCl_3$ was used as coagulant. The jar tests were performed in three steps: (1) rapid mixing for 2 min at 200 r/min, (2) slow mixing for 20 min at 100 r/min, and (3) settling for 30 min. After the settling step, the supernatants at 1 cm below the surface were extracted for measurement.

1.4. Analytical methods

The size of nanoparticles was analyzed by dynamic light scattering (DLS) using a Zetasizer (Zetasizer ZS90, Bedford Co, MA, USA) equipped with a folded capillary cell at 25°C. The zeta potential was analyzed using a Zeta 90 Plus Zeta Potential Analyzer (Brookhaven Instruments Co., Holtsville, NY, USA). The initial concentration of CNT in the suspensions was quantified by TOC (TOC-5000, Daojin Co., Japan) with subtraction of the TOC of the dispersant. The quantification of TiO_2 was measured by an Inductively Coupled Plasma Atomic Emission Spectrometer (ICP) (Optima 7300, Perkin Elmer Co, MA, USA). Briefly, 3.0 mL of the TiO_2 suspension was collected in a test-tube and 2.0 mL pure HF was added. Then the tube was heated at 155°C 1 hr. After that, 1.0 mL pure $HClO_4$ was added into the tube and heating was continued at 165°C until the liquid volume was about 1 mL. In this process, the tube cap should not be fastened tightly to let the vapor escape. The resulting liquid was diluted by HNO_3 solution (2.0%) according to its concentration. Finally, the sample was used for measurement by ICP.

The turbidity was used to quantify the removal efficiency of MWCNT and TiO_2 by the formula (1-Turbidity end) /Turbidity initial × 100% after coagulation. All samples were run in duplicate.