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Removal of nanoparticles by coagulation

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Nanoparticles (NPs) from anthropogenic sources have applications in several commercial products, including cosmetics, pharmaceuticals, and materials. There is evidence that during their usage and disposal, engineered nanoparticles can and will be released into wastewater (Gottschalk et al., 2013; Pasricha et al., 2012; Westerhoff et al., 2013; Zheng et al., 2015). If water and wastewater treatment plants are inefficient or incapable of removing NPs from water, NPs will be released with the treated effluent, entering drinking water sources and natural aquatic environments, increasing exposure for plants, microorganisms, animals, and humans alike (Farre et al., 2010). Although the large surface area to volume ratio of NPs provides unique materials with altered properties and new applications compared to the corresponding bulk materials, this characteristic, as well as the very small size of NPs, may also result in enhancement of the bioavailability of the material and increase in its toxicity. Consequently, there have been extensive studies with the aim of improving our understanding of the behavior and toxicity of NPs (Kahru and Dubourguier, 2010; Oberdorster et al., 2005; Yin et al., 2015; Zhang et al., 2015b).

Efforts have been made to evaluate the release of NPs into the environment and to quantify the environmental concentrations of several NPs (including nano- TiO_2 , nano-ZnO, nano-Ag, carbon nanotubes (CNTs), and fullerenes) using both modeling and analytical methods (Gottschalk et al., 2013). Wastewater treatment plants are a primary route through which many types of NPs enter the environment. The modeling study by Gottschalk et al. (2009) suggests that nano-Ag, nano- TiO_2 , and nano-ZnO in sewage treatment effluents, and nano-Ag in surface waters, pose a risk to aquatic organisms. Therefore, efficient removal of NPs during wastewater treatment is crucial to reduce environmental concentrations of NPs, in order to control the environmental and health risks associated with their exposure.

Conventional water and wastewater treatment methods include coagulation, flocculation, sedimentation, filtration, and disinfection. Coagulation is regarded as a key step for efficient and cost-effective modern water and wastewater treatment processes (Jiang, 2015). Large portions of suspended solids, colloidal particles, natural organic matter (NOM), and other soluble inorganic compounds can be effectively removed through the combined use of coagulation, sedimentation, and filtration processes (Zouboulis et al., 2009). NPs are considered colloidal particles, so for this reason coagulation is a critical process for the effective removal of NPs during water treatment (Fig. 1). Moreover, the coagulation process can influence the morphology of NP aggregates, which will further affect the filtration resistance that appears during the filtration process (Feng and Johnson, 2015).

Silver, TiO_2 , and fullerene NPs have been detected in wastewater treatment plants (Burkowska-But et al., 2014; Farre et al., 2010; Kiser et al., 2009; Westerhoff et al., 2011). It is unclear whether wastewater treatment, under current conditions, is an efficient method for NP removal. Abbott Chalew et al. (2013) simulated conventional wastewater treatment methods, in a bench-scale experiment, to assess the removal efficiency of NPs under conventional treatment conditions. The researchers spiked nano-sized Ag, TiO_2 , and ZnO particles into samples of groundwater, surface water, synthetic freshwater, synthetic

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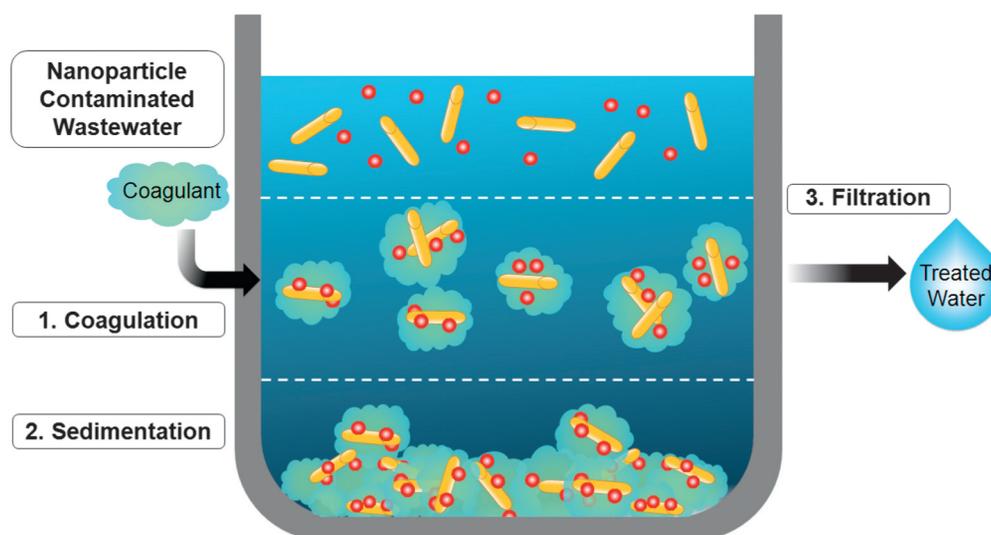


Fig. 1 – Schematic showing removal of nanoparticles by coagulation, sedimentation, and filtration.

freshwater containing NOM, and tertiary wastewater effluent. The optimal alum dose, for each type of water and NP, was determined by turbidity and total organic carbon removal. They observed 2%–20%, 3%–8%, and 48%–99% of spiked Ag, TiO₂, and ZnO NPs, respectively, remaining in the effluent after the treatment process. Additionally, NPs can produce dissolved ions, resulting from the leaching of the NP material into water. These dissolved ions are of additional concern as they can persist in finished water. The best removal of dissolved ions was observed for TiO₂ and the worst removal for ZnO.

Hydrolysing metal salts, such as Al³⁺ and Fe³⁺, and their pre-hydrolysed forms are widely used as coagulants in conventional water and wastewater treatment (Duan and Gregory, 2003). Several studies have investigated the efficiency of NP removal using alum or iron coagulants for SiO₂ NPs (Zhang et al., 2013), CuO NPs (Wang et al., 2015), Ag NPs (Sun et al., 2013), NPs from semiconductor wastewater (Yang et al., 2012), as well as the two most commercialized NPs, nano-TiO₂ (Honda et al., 2014; Kinsinger et al., 2015; Wang et al., 2013) and carbon NPs, including fullerene (Hyung and Kim, 2009) and CNTs (Liu et al., 2012).

Though the NP removal efficiency varies across different studies, researchers share a common finding that removal efficiency depends on the type and surface properties of the NPs, source water quality, alkaline concentration, pH, type of coagulant, and dosage of coagulants. Honda et al. (2014) investigated the effectiveness of three types of coagulants, namely FeCl₃, FeSO₄, and Al₂(SO₄)₃, in removing TiO₂ NPs from artificial groundwater (AGW) and artificial surface water (ASW). All three types of coagulants showed high performance in AGW, while FeCl₃ had poor removal efficiency in ASW. In a follow-up study, Kinsinger et al. (2015) examined additional factors influencing the removal efficiency of TiO₂ NPs, including surface coating, presence of NOM, and water chemistry. The researchers observed that bare TiO₂ NPs in complex waters containing divalent cations were more easily removed. The surface coating with meso-2,3-dimercaptosuccinic acid and the

presence of NOM can decrease the removal efficiency. A pH adjustment, under realistic water chemistries, was essential for effective TiO₂ NP removal. In addition to coagulant type and presence of NOM, alkalinity and the presence of ions affect TiO₂ NP removal (Wang et al., 2013). In a study focusing on CNT removal, similar factors were observed to affect removal efficiencies (Hyung and Kim, 2009).

It is feasible to determine the effective dosage of coagulants to remove NPs from water, considering the factors previously mentioned. In a recent paper, Zhang et al. (2015a) conducted a systematic study evaluating how the type (TiO₂ and multi-walled carbon nanotubes (MWCNTs)) and size of NPs, type of suspension solution (in humic acid (HA) and N,N-dimethylformamide (DMF)), pH, and ionic strength affect the effective concentration range (ECR) of AlCl₃.

Zhang et al. (2015a) showed that the curve of the NP removal efficiency with varying Al³⁺ concentration displayed a reverse “U” shape, providing an ECR of Al³⁺ for NP removal at the apex or plateau of the curve. The authors proposed a mechanism that explains the distinctive reverse “U” shape, by dividing the curve into three regions. The first region, the “no significant removal zone,” is where the concentration of Al³⁺ is low and insufficient to cause the destabilization of NPs; the removal efficiency is low. The second region, the “effective coagulation zone”, is where the NP removal efficiency sharply increases, reaching a plateau, due to the destabilization of the NPs. When the dose of AlCl₃ is within the ECR, the NP removal efficiency could surpass 90%, within 1 hr of the coagulation process under the experimental conditions. The reported ECRs of MWCNT-HA, TiO₂-HA, and MWCNT-DMF removal were 0.05–0.4 mmol/L, 0.1–0.4 mmol/L, and 0.05–3.5 mmol/L of AlCl₃, respectively. The third region, the “re-stabilization zone,” is where the NPs are re-stabilized and the removal efficiency decreases. The authors studied the zeta-potential of the NPs in order to address one of the four common mechanisms used to describe the colloidal removal of NPs, adsorption charge neutralization, which Liu et al. (2012) regard as the major

mechanism responsible for dispersant NP removal by alum. The ECR is explained by the surface charge of negative NPs being neutralized by the adsorption of the positively charged hydrolysis product of alum, resulting in reduced electrostatic repulsion between NPs and destabilization, aggregation, and precipitation of the NPs. At high concentrations, the positive alum ions could over-saturate the surface of the negative NPs, producing a reversed (positive) zeta potential, which could re-stabilize the NPs due to the recurrence of the inter-nanoparticle electrostatic repulsion (Liu et al., 2012).

Zhang et al. (2015a) determined that particle size, pH, and ionic strength were all factors affecting the width of the ECR. Smaller NPs, increasing pH, and increasing ionic strength of NaCl each produced a wider ECR. The effect of pH on the ECR can be explained by the small, non-aggregated, particle size of NPs at higher pH. Similarly, increasing ionic strength broadens the ECR due to its stronger capacity to compress the electric double layer of NPs. In the future, optimization of pH and ionic strength conditions can provide the highest removal efficiency of NPs by coagulants.

In actual wastewater, the water chemistry is more complex and subject to change. The effects of water chemistry on the ECR for additional NPs and different coagulants will require further research. Moreover, in addition to TiO₂ and CNT NPs, studied by Zhang et al. (2015a), efforts should be made to study NPs with high toxicity potential, such as quantum dots, to enable their effective removal during water and wastewater treatment in order to reduce exposure. Finally, the ECRs of different NPs can be used to guide the optimization of coagulation conditions needed for the removal of NPs in wastewater treatment plants, where mixtures of NPs are inevitable.

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