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Removal of TiO_2 nanoparticles by porous media: Effect of filtration media and water chemistry

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HIGHLIGHTS

- Nano-TiO_2 retention in saturated granular beds depends strongly on the filtration media.
- Sand and activated carbon provided little retention for TiO_2 nanoparticles.
- Diatomaceous earth provided superior nanoparticle capture capacity.
- Solution contaminants greatly influenced nanoparticle retention in all media.

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ABSTRACT

The use of nanoparticles in manufacturing as well as in commercial products continues to rise despite concerns over the environmental release and potentially negative ecological and health effects. Some aqueous waste streams carry a large fraction of released nanoparticles and thus should be targeted for treatment. Conventional porous media filtration has focused on sand as the bed material with discouraging results. This study investigated the effectiveness of three different bed materials, namely, sand, activated carbon, and diatomaceous earth, on the removal of nano-TiO_2 from aqueous streams. Additionally, the impact of solution chemistry (a commercial dispersant and the two organic compounds lysozyme and glycine) on nanoparticle retention by the various bed materials was evaluated. Diatomaceous earth displayed great promise in nanoparticle capture, providing full retention of a 50 mg TiO_2 L^{-1} stream for the 30 bed volumes tested as compared to zero and only 20% TiO_2 capture for sand and activated carbon, respectively. Batch isotherms showed that diatomaceous earth, with specific loading capacities exceeding 25 mg TiO_2 g^{-1}_{medium}, has a high affinity for nano-TiO_2. This loading capacity is 20- and 1000-fold higher compared to activated carbon and sand, respectively. The solution contaminants investigated had varying effects on nano-TiO_2 retention depending on the bed material, indicating the need for investigation of co-contaminants and their role on nanoparticle filtration. This study demonstrates the superiority of diatomaceous earth as a filtration material compared to conventional sand and indicates its suitability as a new material for the removal of nanoparticles in porous media filtration.

1. Introduction

Nanoparticles (NPs) form the basis for development of new nano-enabled technology, which is expected to be worth approximately $1 trillion annually by 2015 [1]. Metal oxide NPs, such as nano-titanium dioxide (n-TiO_2), are of particular interest due to their use in varied commercial products, from sunscreens and cosmetics to abrasives in slurries used for semiconductor manufacturing [2]. A recent study puts the upper bounds of yearly n-TiO_2 production at approximately 2.5 million metric tons by 2025 [3]. Evaluating the health and environmental risks of these emerging contaminants is an active area of research [4]. Effects on human health are of great concern with n-TiO_2 being shown to display neuro-toxicity toward dorsal root ganglion cells, even with commonly applied inorganic coatings [5] and to bring about apoptosis and necrotic death in human umbilical vein endothelial cells [6]. Ecotoxicity is also concerning as n-TiO_2 has been found to be damaging toward both *Bacillus subtilis* and *Escherichia coli*, possibly due to production of reactive oxygen species [7]. The numerous exposure pathways and potential toxicity leads to concerns about the release of these nanomaterials into the environment [8,9].

Wastewater streams have been specifically found to be potential point sources of NP release [10]. A recent modeling of environmental concentrations of n-TiO_2 produced an estimate of over 1500 Tons of n-TiO_2 per year entering sewage treatment plants in the United States, with the majority of release being divided between the soil (~48%) and surface water (~24%) [11]. While no

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current treatment techniques are utilized that primarily target NP removal, the effectiveness of standard wastewater treatment operations has been evaluated in a few studies. Flocculation and sedimentation processes used in primary wastewater treatment were shown to be ineffective in removing 56 nm SiO_2 NPs at 2470 mg L^{-1} due to their stability and slow settling rate [12]. Treatment by activated sludge, the most common element of secondary wastewater treatment, was shown to be more effective at removing NPs, however significant amounts of sub 50-nm n-TiO_2 remain in effluents of these conventional wastewater treatment plants [13]. Additional procedures must be instated to address the treatment of this emerging nano-scale contaminant. Porous media filtration is a standard treatment technique for removing colloidal and particulate matter from water streams and is becoming more common for wastewater treatment [14]. The effectiveness of porous media filtration to remove colloidal substances, which by definition are those between 1 and 1000 nm, indicates the potential of this technique to remove engineered nanomaterials. Understanding the role of this established technique in NP removal is important for potential optimization and targeted use.

The most common type of media filtration used in wastewater treatment is sand filtration [14]. The majority of research performed on NP removal has focused on the use of sand as the bed material [15–17]. Investigations of NP retention in saturated sand media have shown the importance of solution chemistry and its effects on electrostatic interactions between the NPs and the sand surface. Quartz sand typically has a point of zero charge (pH_{pzc}) of approximately 3 and thus will be negatively charged at circumneutral pH values [18]. The pH_{pzc} of TiO_2 ranges from 3.9 to 7.2 [19], thus the surface of n-TiO_2 typically carries a negative to near neutral charge near pH 7. This electrostatic repulsion typically leads to significant (>95%) and rapid elution of TiO_2 NPs in sand columns [16,20,21]. In addition to pH, ionic strength and cation valence can have a great impact on NP aggregation and NP retention by media filtration. Deposition of TiO_2 NPs onto sand has been shown to increase with both ionic strength and cation valence [20]. A mechanistic study of TiO_2 NPs in sand columns determined that electrostatic interactions between the NPs and the sand surface were a significant factor in NP capture. However, site blocking due to adsorbed NPs contributed significantly in electrostatically favorable conditions and physical straining was notable during aggregation inducing conditions [22].

The majority of studies have investigated NP retention in columns packed with glass beads or quartz sand. Investigation of more efficient adsorptive media capable of attaining high loading capacities is necessary to promote the potential use of media filtration as a technique for NP abatement in aqueous waste streams. The objective of this study is to determine a suitable bed media for the abatement of TiO_2 NPs and determine the major mechanisms guiding NP–media interactions, ultimately leading to an improved treatment design. In order to attain this objective, this study evaluated three different filtration materials including sand as a reference material, as well as activated carbon and diatomaceous earth, which have never previously been applied to NP filtration schemes. In addition, the impact of three model water contaminants, an anionic dispersant and two organic compounds with disparate points of zero charge, on n-TiO_2 fate and transport in porous media was evaluated.

2. Materials and methods

2.1. Materials

The NPs used were TiO_2 (Aeroxide P25, Evonik Industries, Essen, Germany) with a reported primary particle size of 21 nm. Aeroxide P25 is a well documented composite of both anatase and rutile forms. A recent study found that composition ranged from 73–85% anatase, 14–17% rutile and 0–18% amorphous TiO_2 [23].

Three bed materials were examined: quartz sand (Acros Organics, Geel, Belgium) with an average diameter of 190 μm, activated carbon (AC) (KCI-40AD, KC International, Thousand Palms, CA, USA), an acid washed activated carbon with 1000 μm average diameter, and diatomaceous earth (DE) (Celite 545, Sigma Aldrich, St. Louis, MO, USA) with a reported size of <125 μm. DE is a siliceous compound with varied deposits of other compounds. According to the manufacturer, the batch of DE utilized contained: silicon dioxide (89.0%), aluminum oxide (1.0%), calcium oxide (6.73%), ferric oxide (0.46%), as well as sodium oxide and potassium oxide (1.88% combined). The DE was sieved and the material retained on a 200 mesh (74 μm) sieve was separated for use. Sand and DE were washed prior to use: soaked in diluted hydrochloric acid (HCl, 5%), rinsed by deionized water, and dried in an oven for 8 h (105 °C). The AC was rinsed with deionized water to remove associated fines.

Three contaminants were used to simulate varying contaminants commonly found in aqueous streams. An ammonium polyacrylate surfactant (MW $\sim$ 3000–3500; Dispex A40, BASF, Freeport, TX, USA) was selected as a model surfactant and dispersant. Lysozyme and glycine, both obtained from Sigma Aldrich, are two model organic compounds with disparate pH_{pzc}: 9.60 and 5.97, respectively [24,25].

2.2. Porous media and nano-TiO_2 characterization

Scanning electron microscopy imaging of the porous media was done on a Hitachi S-4800 field-emission SEM (Hitachi, Ltd., Tokyo, Japan) at 5 keV after fixing as previously reported [26]. TiO_2 NPs were imaged by transmission electron microscope using a Hitachi H8100 at 200 keV. Surface area measurements were obtained by nitrogen gas adsorption using a Beckman Coulter SA 3100 (Beckman Coulter, Inc., Brea, CA, USA) and the pore distribution data was deduced using a cylindrical pore model.

The measurement of net surface charge of the various media in relation to pH was determined using an acidimeteric–alkalimeteric titration [27]. Vials with a 50 mL capacity were filled with 20 mL of 0.01 M NaCl solution and 0.2 g of media. Seven vials had aliquots of HCl (0.1 M) ranging from 0.05 to 1.5 mL added and equal additions of NaOH (0.1 M) were added to seven additional vials. One vial was left with no addition giving a total of 15 samples. The equilibrium pH was measured after 24 h shaking at room temperature (23 ± 2 °C). The surface charge was determined using a site balance [27].

The zeta potential and particle size distribution of NP dispersions was measured immediately after sampling with a ZetaSizer Nano ZS (Malvern, Inc., Sirouthborough, MA, USA) using laser doppler velocimetry and dynamic light scattering (DLS), respectively. The hydrodynamic diameter of the NPs was calculated as the intensity mean. The pH_{pzc} of n-TiO_2 was determined using the above instrument with pH control provided by an autotitrator accessory (MPT-2, Malvern, Inc.). All measurements were conducted at 25 °C.

2.3. Adsorption isotherms

Batch experiments for determining equilibrium isotherms of the TiO_2 NPs with the three bed materials were conducted in duplicate using a weak phosphate buffer solution (0.5 mM, pH 7.0, 1.0 mM ionic strength) in glass serum flasks (166 mL) at room temperature (23 ± 2 °C). The solution volume was 50 mL and the initial NP concentration ranged from 5 to 200 mg L^{-1}. From 0.1 to 1.0 g of bed material was added to each flask. NP-free and porous