Facilitated transport of anatase titanium dioxides nanoparticles in the presence of phosphate in saturated sands
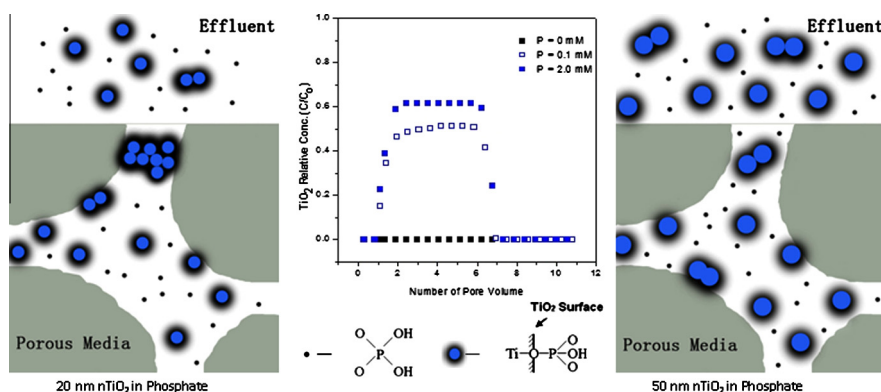
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GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Soil and water environments are inevitably contaminated by the excess of artificial nanoparticles (NPs) and phosphorus (P) fertilizers. There is a possibility of phosphate facilitating or inhibiting the transport of nanoparticles titanium dioxides (nTiO$_2$). It is a great urgency and high priority to investigate the nTiO$_2$ retention mechanisms and accurately describe the transport of nTiO$_2$ in the presence of phosphate. Anatase nTiO$_2$ with two sizes of 20 and 50 nm through the saturated porous sand columns were observed under the conditions (0–50 mM NaNO$_3$ electrolyte, influent P concentrations of 0.10 mM and 2.0 mM, pH 6.5 and 7.5). The experimental results show the phosphate favor the dispersion of nTiO$_2$, and consequently improve their transport patterns. The likely mechanism is that phosphate adsorption increasing the negative charge on the surface promotes the transportability of nTiO$_2$ resulting from the low deposition rate and attachment efficiency of NPs. In particular, the facilitated transport of nTiO$_2$ (50 nm) is greater than those relative smaller as 20 nm. In addition, this enhancement of nTiO$_2$ transportability by phosphate at pH 6.5 is increased at higher pH of 7.5 due to the more negative zeta potential of surface, which indicates the potential risks to groundwater systems.

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1. Introduction

Properties of nano-materials with dimension less than 100 nm, such as small size and high surface energy, are giving to mass

production and varieties of potential applications. As an important inorganic functional material, nanoparticle titanium dioxide ($nTiO_2$) has good application in the fields: paints, sunscreens cosmetics, opacifiers, semiconductors, and electronic ceramics [1,2]. However, during their industrial productions and/or applications, nanoparticles (NPs) may inevitably enter soils leading to the potential risk to human health and living environments. It has been reported that $nTiO_2$ and nZnO are harmful to soil environments resulting in significant reduce of wheat biomass [3].

Lots of attentions have been paid to the fate and transport of NPs (i.e. industrial fullerenes nC_{60} [4–6], carbon nanotubes [7,8], and cerium dioxide particles [9]) in saturated porous media and the related factors including solution pH, ionic concentration (IC), and flow velocity. In particular, $nTiO_2$ attract the more researchers [10–14]. However, limited knowledge is available about the size effect of $nTiO_2$. Note that the properties of inorganic NPs with size <30 nm are different from those >30 nm [15]. Therefore, it is necessary to study the retention and transport of $nTiO_2$ with different size ranging 1–100 nm and 1–30 nm.

Recent years, NPs facilitating the transport of organic materials [16,17], and heavy metals [18,19] are proposed to be a potential risk to underground water systems. Additionally, application of phosphorus (P) fertilizers in farmland can influence the leaching of heavy metals [20]. It has been demonstrated that the mobilization of molybdate [21], arsenate [22], and lead [23] in soils can be induced by soluble P. Particularly, due to excess of fertilizers in cropland, a large number of nutrient ions are discharged into water body through surface runoff and drainage, or leached into underground water causing eutrophication. In general, metal ions in the soil solutions and groundwater environments play an important role in impact on the aggregation and transport behavior of NPs than anions [12]. It is interesting to note that phosphate as one of predominant anions can be adsorbed onto TiO_2 colloidal particles [24], altering their surface properties, and consequently affecting their transport patterns. Does the presence of phosphate facilitate or inhibit the transport of $nTiO_2$? However, there are scarce the related reports available. To the best of our knowledge, it is the first report to clarify the effects of phosphate on the transport of $nTiO_2$ in porous media of soils and the corresponding retention of phosphate, especially with regard to particle size, pH and phosphate level effects.

In this study, the transport behavior of $nTiO_2$ with P in saturated porous sand columns was assessed. The details are to address the following specifics: (i) research the surface electrokinetic properties of $nTiO_2$ and quartz surfaces; (ii) study the dispersion and aggregation behavior of $nTiO_2$ NPs in the different concentrations of electrolyte and phosphate; (iii) investigate the effects of phosphate concentration, particle size and solution pH on the breakthrough curves (BTCs) of $nTiO_2$ in the presence of phosphate in sand columns; (iv) examine the applicability of classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory to describe the transport of $nTiO_2$ in the sand columns in the presence of phosphate.

2. Materials and methods

2.1. Preparation of $nTiO_2$ suspension

$nTiO_2$ (99 + % purity) with two sizes (20 nm and 50 nm) were purchased from Gaoquan Chemical, Inc., Shanghai, China. $nTiO_2$ were characterized by Powder X-ray diffraction (XRD, D8-Focus, Bruker AXS Co., Ltd., Germany), Scanning Electron Microscope (SEM, Quanta 400 FEG), Transmission Electron Microscopy (TEM, FEI Tecnai G2 F20 S-Twin). Samples for TEM images were prepared with thin carbon film. The XRD patterns were obtained by a diffractometer with a Cu Ka radiation. The scanning range was from 10 to 70 at a speed of 2 min^{-1}. All of above analysis results were enclosed in Fig. S1 in Supporting Information (SI). Prior to being used in each transport experiment, $nTiO_2$ suspension was prepared by adding 0.20 g of $nTiO_2$ powder to 200 mL of $NaNO_3$ electrolyte solution containing different P concentrations (diluted with P stock solution) at pH 6.5 and 7.5. The P stock solution was prepared by NaH_2PO_4 (analytical grade) dissolved in DI water. And then the $nTiO_2$ suspension was homogenized by stirring on a magnetic plate for 1 min and sonicated for 30 min at room temperature.

2.2. Adsorption of P on $nTiO_2$

Adsorption isotherms were conducted by adding 1.0 g L^{-1} different size of $nTiO_2$ to series of P solutions in 50 mL vials at different pH (6.5 and 7.5). The series of phosphate solutions were diluted by the prepared P stock solution. The pH was adjusted by adding the diluted HCl or NaOH solutions. And then the vials were placed on rolling incubator about 15 h. At the end of equilibration time, the suspensions were centrifuged for 90 min by high speed centrifuge, and then passed through 0.45 μm pore size filters. Soluble P concentration by colorimetry was analyzed using the molybdenum blue method [25]. The equilibrated pH was recorded and the fraction of P absorbed onto $nTiO_2$ was then determined by the difference between the initial and equilibrium P concentration in filtrate.

2.3. Column transport experiments

The column transport experiments were performed in glass chromatography columns (2.5 cm in diameter and 20 cm in length) which were packed uniformly with the prepared quartz sand and at both ends with 80 μm nylon net film. The procedure details were similar as described in other studies [26]. Once packed, the column was flushed with DI water by peristaltic pump (BT100-2J, Baoding Longer Precision Pump Co., Ltd., China) at a constant Darcy velocity (0.204 cm min^{-1}) to saturate quartz sand for at least 24 h. Transport experiments thereafter were conducted following three steps. Firstly, 5 pore volumes (PVs) of $NaNO_3$ solutions as background electrolyte were pumped upward to sand columns. Secondly, another 5 PVs of $nTiO_2$ (1.0 g L^{-1}) suspended in the same electrolyte were then introduced. Meanwhile, the outflow from sand columns was collected into 10 mL glass tubes at time intervals by a fraction collector (BS-100A, Huxi Analytical Instrument Factory Co., Ltd., Shanghai, China). And then another 5 PVs of $NaNO_3$ electrolyte and DI water was pumped into sand columns until no $nTiO_2$ in effluent, respectively. In addition, the suspension solution of $nTiO_2$ in different concentrations (0.10 mM and 2.0 mM) of P solutions were also injected into sand columns at certain pH adjusted using the diluted HCl or NaOH solutions. Finally, the concentrations of $nTiO_2$ and P in influent (C_0) and effluent (C) were analyzed to obtain the breakthrough curves (BTCs) of C/C_0 as a function of pore volumes passing through columns. The detailed physical conditions for column transport experiments are summarized in Table 1. All experiments were conducted at room temperature. Additional information about the sample analysis is provided in SI.

2.4. Theoretical consideration

The Darcy velocity (q), that is specific discharge, is related to the volumetric flow rate (Q, cm^3 min^{-1}) by dividing by the cross section area (A, cm^2) perpendicular to the flow direction. Thus, the Darcy velocity is the volumetric flow rate per unit surface area as follows: