Hydrochars and phosphate enhancing the transport of nanoparticle silica in saturated sands

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HIGHLIGHTS

- $nSiO_2$ aggregates can be restablized by the adsorption of P at low pH.
- Hydrochars facilitate the transport of attached $nSiO_2$ at pH 6.0.
- The retention of $nSiO_2$ is more significant with hydrochars or P at high pH (9.0).
- When hydrochars and P coexist, the enhancement of $nSiO_2$ deposition occurs.

GRAPHICAL ABSTRACT
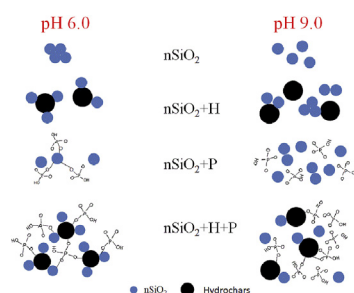
ABSTRACT

Due to the potential negative impact of nano silica ($nSiO_2$) on human's health and living environments, it is important to investigate their transport in soil environments. Hydrochars has been widely used in agricultural soil and phosphate (P) is an important nutrient, thus the aggregation and transport of $nSiO_2$ in saturated sand columns were investigated in single and binary systems of hydrochars and P. The experimental results showed that the $nSiO_2$ aggregates can be restablized by the adsorption of P or the attachment of hydrochars at high IS (>100 mM) and low pH (<7.0). Accordingly, the transport of $nSiO_2$ in sand columns is enhanced due to the smaller particle size. However, the $nSiO_2$ presents the distinct surface characteristics at pH > 7.0 from that at pH < 7.0. Thus, $nSiO_2$ has a better dispersivity in 300 mM NaCl solution at high pH (9.0). Nevertheless, their deposition to sands becomes pronounced in the presence of hydrochars and/or P. In particular, the formation of $nSiO_2$-hydrochar-Phosphate clusters associated with the larger size mainly contributes to the enhancement of $nSiO_2$ retention in sand columns during the wide pH range, when hydrochars and P coexist in suspensions. The two-site dynamic model fitting results showed that the reversible retention is related to k_2 (First-order straining coefficient on site 2). The results in this study will provide the theoretical basis for assessing the retention of $nSiO_2$ in soil environment with the presence of hydrochars and phosphate.

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1. Introduction

Nano silica ($nSiO_2$) is one of the largest industrial productions of inorganic non-metallic materials (Wang et al., 2016). Silica particles are produced on an industrial scale as additives to cosmetics, drugs,

printer toners, varnishes, and food (Hirsch et al., 2003), because it can provide materials with a desired consistency and prevents separation of various ingredients (Napierska et al., 2010). It is also particularly used in paints, surgical tools, medical equipment, textiles and various surfaces of substrates due to its high water repellence (Diener et al., 2013). Moreover, since the negative charge of $nSiO_2$ can provide a high number of electrostatic binding sites, it has been developed in biomedical or biotechnological applications, such as cancer therapy (Laranjeira et al., 2017), drug delivery (Jin et al., 2009), and enzyme immobilization (Vijayanathan et al., 2002). Nevertheless, the extensive applications of $nSiO_2$ may have potential risks to aquatic ecosystem and human health. Several researches have studied the toxicity of $nSiO_2$ toward the biological systems in vitro and in vivo (Jin et al., 2009; Monobe et al., 2011; Nabeshi et al., 2011a, 2011b). For instance, the $nSiO_2$ can induce the severe liver damage in mice and the inflammatory responses in vitro (Nabeshi et al., 2011a, 2011b). The presence of $nSiO_2$ in living systems leads to a series of damages to the internal organs, the reactive oxygen species generation, and the intracellular genes and proteins (Jin et al., 2009). In addition, $nSiO_2$ may present potential hazards to human by penetrating the intracellular targets in the lung and systemic circulation (Napierska et al., 2010). Furthermore, $nSiO_2$ (as adsorbents or mobile carriers) can facilitate the transport of nutrients and pollutants in subsurface environments resulting in environmental contamination due to its high dispersivity (Kobayashi et al., 2005; Fujita and Kobayashi, 2016). Therefore, it is necessary to investigate the behavior of $nSiO_2$ in the water environment.

The mobility and deposition of nanoparticles (NPs) in the water and soil environments are dependent on their characteristics. At present, many studies are focusing on the study of NPs including the industrial fullerene nC_{60} (Chen and Menachem, 2008; Tong et al., 2010; Isaacson et al., 2011), carbon nanotube (Jaisi et al., 2008; Jaisi and Menachem, 2009), nano zero-valent iron (Johnson et al., 2009; Yang et al., 2015), zinc oxide (ZnO) (Jiang et al., 2010), cerium dioxide (CeO_2) (Li et al., 2011) and titanium dioxide (TiO_2) (Chowdhury et al., 2011, 2012). Due to the complexity of natural environment, the transport behavior of NPs can be affected by environmental factors for instance: pH, ionic species, ionic strength, flow rate, soil organic, bacteria, and clays. Nevertheless, there are limited information in the effect of environmental factors on aggregation and transport of $nSiO_2$ so far. It has been reported that the transport of $nSiO_2$ is inhibited with decreasing water saturation at low pH (Fujita and Kobayashi, 2016). Humic acid promotes the aggregation of larger particle size of $nSiO_2$ in $CaCl_2$ solution due to the formation of bridging between the two calcium ions and humic acid (Liu et al., 2011). The deposition of small $nSiO_2$ shows the different mechanism from large particles which exhibit features similar to the predictions of classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory (Kobayashi et al., 2005). $nSiO_2$ with smaller particle size has the higher retention and faster deposition (Wang et al., 2014). Our previous study found that phosphate favors the dispersion of $nTiO_2$, and consequently improve their transport patterns (Chen et al., 2015). To our best knowledge, the effect of phosphate on the transport and retention of $nSiO_2$ remains unknown.

Chars can be obtained by different technologies, such as thermochemical pyrolysis, slow/fast pyrolysis, gasification, hydrothermal carbonization, or flash carbonization of biomass (Meyer et al., 2011). Biochar is generated via the pyrolysis of biomass. The final solid product is termed as hydrochar when biomass is converted into carbonized material by hydrothermal carbonization (Hu et al., 2010). In recent years, those chars have been widely used in many applications: carbon sequestration, reducing greenhouse gas emissions, renewable energy (Lehmann et al., 2006; Castaldi et al.,

2011). For the diverse and widespread environmental pollution in soils (i.e. pH decreasing, metal leaching, and excess fertilizers), various soil amendments have been developed to deal with those problems. Particularly, chars have been proposed as a cheap amendment for polluted soils, since they can be used to improve soil fertility, increase soil carbon sequestration and effectively immobilize a large quantity of heavy metals (Lehmann et al., 2003; Cao et al., 2009; Jeong et al., 2012; Wagner and Kaupenjohann, 2014). Furthermore, the potential applications of biochars and hydrochars in crop soils have received much more concerns. Much of the interest can be attributed to the studies of Amazonian Dark Earths (also called *Terra preta de índio* soils) that demonstrated the significant improvements in soil quality and crop yields due to the abundant biochars (Glaser et al., 2001; Lehmann et al., 2006; George et al., 2012; Glaser and Birk, 2012). In addition, phosphate widely exists in the crop soils by application of phosphate fertilizers in soils. Thus, in hydrochar-amended soils with the enrichment of phosphate fertilizers, $nSiO_2$ may enter and coexist in the soil environment. However, it has been reported that the dissolved chars or char particles has the mobility and can carry environmental pollutants and promote their transport (Jeong et al., 2012). Their environmental impacts, compatibility with agricultural and horticultural systems, and the treatment in subcritical water have received the considerable attention over the last few years (Gajić and Koch, 2012; George et al., 2012; Abel et al., 2013). Furthermore, our previous studies reported that the presence of phosphate and ammonium facilitated the transport of $nTiO_2$ in sands (Chen et al., 2015; Xu et al., 2017). However, the information in dealing with the transport and deposition of NPs in the presence of hydrochars remains limited. Thus, it is urgent to know whether the existence of hydrochars and phosphate promotes or inhibits the mobility of SiO_2 in soils.

In this study, the aggregation and transport of $nSiO_2$ in saturated quartz sand columns will be mainly investigated in the single and binary systems of hydrochars and P. To avoid the formation of precipitation, the NPs are suspended in monovalent (Na^+) instead of divalent (e.g. Ca^{2+} and Mg^{2+}) electrolyte solution due to the presence of phosphate in this system. By means of modern characterization and analysis, their hydrodynamic radius and zeta potentials were characterized, and the interactions between hydrochars and phosphate were revealed. In particular, the two-site kinetic retention model was employed to simulate breakthrough curves (BTCs) for $nSiO_2$ under various conditions to investigate the likely mechanism.

2. Materials and methods

2.1. Preparation of hydrochar NPs and various $nSiO_2$ suspensions

The rice hull is used for preparing hydrochars with the hydrothermal method (Wang et al., 2010). Firstly, rice husk (RH) was washed thoroughly with DI water, then dried and porphyrized to 60 mesh before employment. The treated RH was mixed with 72% (wt. %) of sulfuric acid (H_2SO_4) in a beaker with a ratio of 1:10 (mass: volume). The mixture was stirred in 50 °C water bath before liquid was collected as hydrolysis solution. Then, the diluted hydrolysis solution was heated in water bath at 95 °C for about 6 h. The solid product was collected by using water-circulation multifunction vacuum pump (SHB-III, Zhengzhou Great Wall Scientific Industry and Trade Co., Ltd., China), and washed thoroughly with DI water for 3 times. The final products were obtained after dried at 120 °C. At last, the materials were ground with an agate mortar.

Silica NPs (purity 99.8%) were purchased at the Aladdin reagent company. Its specific surface (200 m^2 g^{-1}) was determined by a nitrogen multi-point BET isotherm. The $nSiO_2$ (1.0 g L^{-1})