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Enhanced cadmium immobilization in saturated media by gradual stabilization of goethite in the presence of humic acid with increasing pH

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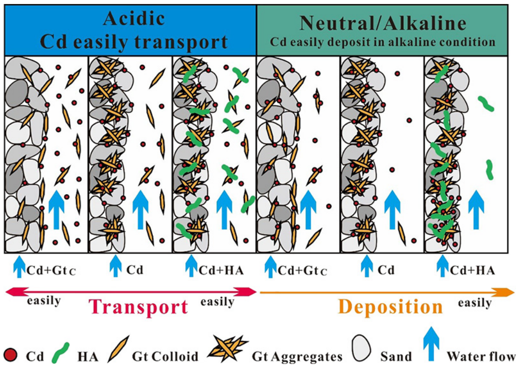
HIGHLIGHTS

- Cd and Gt transports in saturated porous media were easily occurred at pH 4.
- Cd transport was inhibited at high pH, especially in the presence of HA.
- The major fraction of Cd retained in the columns was exchangeable form.

GRAPHICAL ABSTRACT



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ABSTRACT

Goethite (Gt) and humic acid (HA) are important components of soil that significantly affect Cd mobility. In this study, the co-transport of Cd^{2+} and Gt with/without HA in saturated sand columns was investigated by monitoring the breakthrough curves at different pH values. A solute transport model was used to study Cd^{2+} transport and retention in the saturated sand in the presence of Gt and HA, and a colloid transport model was used to describe the Gt colloid (Gt_C) transport in the columns. Our results showed that the transport behaviors of Cd^{2+} and Gt colloids/aggregates were regulated by pH. Cadmium transport was significantly inhibited at high pH due to its adsorption on the sand and Gt. Moreover, Gt retention was gradually stabilized with increasing pH regardless of its forms, i.e., individual colloids (Gt_C) or larger assemblages of particles due to aggregation (Gt_A). This retention was obviously enhanced in the presence of HA. Thus, the superposition of increased Cd^{2+} adsorption on Gt and Gt retention (stabilization) enhanced the immobilization of Cd^{2+} at high pH. In addition to stabilizing Gt, HA further enhance Cd^{2+} adsorption on Gt, thus promoting Cd^{2+} immobilization. However, only a small amount of organic-matter-bound Cd^{2+} was observed in the columns with injected HA. The major fractions of retained Cd^{2+} were exchangeable Cd^{2+} and Fe-oxide-bound Cd^{2+}. Our results provide new insights into the roles of Gt and HA in the transport and mobilization of Cd^{2+} in soil-groundwater systems.

1. Introduction

Cadmium(II) is a hazardous trace metal that can enter and accumulate in soil and the environment through the agricultural application of sewage sludge, fertilizers, wastewater irrigation, and other

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anthropological activities (Kersale et al., 2003; Meeûs et al., 2002). Cadmium is very reactive in the natural environment. Once released from soils and sediments into surface water or groundwater, Cd^{2+} becomes a serious threat to the health of human and other animals, causing kidney and liver dysfunction, weakening the immune system, and adversely affecting reproduction.

Nano-sized colloids are widely dispersed in natural waters and could transport over long distances in vadose zones and aquifers (Tosco et al., 2012; Wang et al., 2012; Wang et al., 2015; Yang et al., 2015). Numerous previous studies have indicated that the transport of heavy metals through subsurface environments can be influenced by various colloids (Hammes et al., 2013; Ma et al., 2018; Ma et al., 2016). For example, the presence of kaolinite colloids appeared to retarded the mobility of Cd^{2+} in porous media at higher ionic strengths (Wikiniyadhanee et al., 2015), and Cu transport was facilitated in association with hydroxyapatite nanoparticles in water-saturated quartz sand at different solution concentrations of NaCl with 0–100 mM or $CaCl_2$ with 0.1–1.0 mM (Wang et al., 2011). Thus, heavy metal (e.g., Cd^{2+}) concentrations in soil solutions are most likely controlled by adsorption-desorption reactions on the surface of soil colloidal materials such as mineral colloids, organic colloids, and organo-mineral complex colloids (Kretzschmar and Schäfer, 2005). Among iron oxyhydroxides, goethite (α-FeOOH, Gt) is the most widespread highly reactive iron oxide in natural environments. It has been reported that Gt and its colloids can strongly affect the environmental behavior of contaminants, such as increasing the amount of Cd^{2+} adsorbed at pH values higher than the isoelectric point of Gt (IEP_{Gt}) (Bäckström et al., 2003; Lai et al., 2002; Li et al., 2007; Venema et al., 1997; Wang and Xing, 2004), and enhancing plutonium transport through a single saturated granite fracture (Lin et al., 2014).

Humic acid (HA) is a reactive fraction of the natural organic matter in soils, sediments, and surface water in terms of metal ion binding (Weng et al., 2006). It can not only adsorb heavy metals such as Cd^{2+} directly but can also enhance Cd^{2+} adsorption on iron oxyhydroxide colloids when HA is adsorbed on these oxides (Abasiyan and Tofighi, 2013; Arias et al., 2002; Lai et al., 2002). Humic acid can significantly alter the surface chemistry and retention-repulsion properties of the water-sand-colloid system by adsorbing on such solid surfaces (Chen et al., 2012; Wang et al., 2012; Wang et al., 2013). In addition, previous studies have indicated that even small amounts of natural organic matter greatly promote the transport of colloid-associated contaminants (Granger et al., 2010; Guo et al., 2011; Ma et al., 2018; Wang et al., 2014); thus, HA plays an important role in regulating the transport and fate of contaminants and colloids (Wang et al., 2012).

Previous studies on Cd^{2+} transport mainly focused on solute transport (Moradi et al., 2005; Pang et al., 2002; Qi et al., 2012). However, in the natural subsurface environment, changes in environmental conditions, such as pH, result in the release of natural colloids (Hu et al., 2009). Until now, few studies have considered the co-transport of Cd^{2+} with kaolinite colloids (Wikiniyadhanee et al., 2015, 2016). The mechanism and extent of the effect of goethite on the fate and transport of Cd^{2+} in saturated porous media, as well as in the presence of HA, have not been reported. Goethite generally exhibits positive surface charges with a high IEP at pH < 9.3 (Weng et al., 2006), while HA shows negative surface charges (with $IEP_{HA} < 3$) at the prevailing natural pH (>3) in aqueous solutions (Kosmulski, 2012; Kumar et al., 2006). Generally, both the adsorption and transport of soil colloids and heavy metals in porous media are pH-dependent (Lai et al., 2002; Ma et al., 2016; Warwick et al., 1998). With increases in pH (especially above 9.3) the surface of Gt changes from positively charged to negatively charged and HA also becomes more negatively charged due to the higher adsorption of OH^-. This results in a change from electrostatic attraction (pH < 9.3) to electrostatic repulsion (pH > 9.3) between the two colloids (Gt and HA), and also induces electrostatic attraction between Cd^{2+} and those two more negatively charged colloids. Therefore, an increase in the solution pH drastically increases Cd^{2+} adsorption on Gt and HA but decreases HA adsorption on Gt (Lai et al., 2002). For ferrihydrite, which exhibits a slightly lower IEP than Gt at pH around 8.2–8.7 (Kosmulski, 2009, 2014), a low pH ($<IEP_{ferrihydrite}$) prompted ferrihydrite colloid deposition due to the reduced repulsive interaction energies between the ferrihydrite colloid and the sand surfaces in the water-sand-colloid system, while easy transport of ferrihydrite colloids occurred at high pH ($>IEP_{ferrihydrite}$) due to increased repulsive forces that prompted ferrihydrite colloid release (Ma et al., 2018). However, whether a similar transport phenomenon occurs in the presence of Gt remains unknown. Moreover, the presence of HA could modify the surface charge heterogeneity of the iron oxyhydroxides (Wang et al., 2012; Yang et al., 2015), resulting in a much more complicated Cd^{2+} transport at varying pH values.

In this research, the aim was to unravel the roles of environmentally relevant pH conditions in the co-transport of Gt and Cd^{2+} with/without HA in saturated quartz sand columns. In the natural soil environment, it is difficult to achieve extremely low or high pH levels; so, we adopted a pH range of 4.0 to 9.0. Because both colloidal Gt (in the liquid phase) and aggregated Gt (in the solid phase) exist in paddy field, an intimate mixture of sand and Gt was packed to evaluate the difference between the effects of Gt colloid (Gt_C) and agglomerated Gt on Cd^{2+} transport. The latter material—i.e., Gt aggregates wet-packed with quartz sand in the column—was designated as Gt_A to differentiate it from Gt_C. The effects of Gt and its colloid on Cd^{2+} transport at different pH values were assessed by monitoring the breakthrough curves (BTCs). In addition, a solute transport model (Cameron and Klute, 1977; Selim et al., 1976) was used to simulate Cd^{2+} transport and evaluate the retention sites of sand. Gt_C transport mechanisms were revealed using a colloid transport model (Bradford et al., 2003).

2. Materials and methods

2.1. Colloid suspension

Humic acid was extracted following the classic alkali/acid fractionation procedure of Valdrighi et al. (1996), and Gt was prepared using the method of Venema et al. (1998); these are described in the Supplementary Material (S1). The Gt purity was confirmed by X-ray diffraction analysis (Fig. S1). Its BET specific surface area measured by the Brunauer-Emmett-Teller N_2 adsorption isotherm method was $87.65\ m^2 \cdot g^{-1}$ and its IEP determined by acid-base titration was 9.3. The molecular weight and Fourier-transform infrared spectroscopy analysis results of HA can be found in Ma et al. (2018). Humic acid solution and the Gt suspension were prepared with Milli-Q water at concentrations of 200 and 50 $mg \cdot L^{-1}$, respectively. For HA solution preparation, a trace amount of NaOH was added to accelerate HA dissolution. The Gt suspension was homogenized by stirring, and then sonicating for 1 h, and then centrifuging at 2000 rpm for 1 min to remove large aggregates; the remaining supernatant contained colloidal goethite (Gt_C). The pH values (4.0, 7.0, and 9.0) of the Gt_C suspension and HA solution were carefully adjusted using HCl and NaOH. The Gt_C suspensions at pH 4.0 and 7.0 were stable for 24 h due to their high positive zeta potentials, but no Gt_C suspension was attained at pH 9.0 due to Gt sedimentation resulting from its homo-aggregation (Fig. S2). Thus, the effects of Gt_C on Cd^{2+} transport at this pH were not considered since similar Gt_C sedimentation would probably occurs in the natural environment.

Goethite colloid concentrations were determined by measuring the Fe contents by atomic adsorption spectroscopy (AAS, AAnalyst 900T, PerkinElmer, Germany) after digestion. The particle size distributions and zeta potentials of the colloids and column-packed sands (only zeta potentials) were measured using a dynamic light scattering analyzer (Zetasizer Nano ZS, Malvern Instruments). The colloid particle sizes and zeta potentials results are presented in Table S1.