Journal of Contaminant Hydrology 182 (2015) 146–156

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Effects of kaolinite colloids on Cd^{2+} transport through saturated sand under varying ionic strength conditions: Column experiments and modeling approaches

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ARTICLE INFO

Article history:
Received 31 May 2014
Received in revised form 19 August 2015
Accepted 24 August 2015
Available online 31 August 2015

Keywords:
Cd^{2+} transport
Colloids
Hydrus-1D
Kaolinite
Ionic strength

ABSTRACT

Column experiments were performed under various ionic strengths (0.0–0.9 mM) using 10 mg L^{-1} of Cd^{2+} without kaolinite colloids and 10 mg L^{-1} Cd^{2+} mixed with 100 mg L^{-1} kaolinite colloids. The nonequilibrium two-site model (TSM) described the behavior of both Cd^{2+} transport and Cd^{2+} co-transported with kaolinite colloids better than the equilibrium model (CD_{eq}) ($R^2 =$ 0.978–0.996). The results showed that an increase in ionic strength negatively impacted the retardation factors (R) of both Cd^{2+} and Cd^{2+} mixed with kaolinite colloids. The presence of kaolinite colloids increased the retardation factors of Cd^{2+} from 7.23 to 7.89, 6.76 to 6.61 and 3.79 to 6.99 for ionic strengths of 0.225, 0.45 and 0.9 mM, respectively. On the other hand, the presence of kaolinite colloids decreased the retardation factor of Cd^{2+} from 8.13 to 7.83 for ionic strength of 0.0 mM. The fraction of instantaneous sorption sites (f) parameters, kinetic constant for sorption sites (α) and Freundlich constant (K_f) were estimated from HYDRUS-1D of TSM for Cd^{2+} transport. The fraction of instantaneous sorption sites was found to increase for an increase in ionic strength. K_f values of Cd^{2+} transport without kaolinite colloids for 0.0, 0.225 and 0.45 mM were found to be higher than those of Cd^{2+} transport with kaolinite colloids, except for ionic strength of 0.9 mM. Hence, the presence of kaolinite colloids probably retarded the mobility of Cd^{2+} in porous media for higher ionic strengths. Furthermore, retardation factors and K_f values of both Cd^{2+} transport and Cd^{2+} co-transport were shown to decrease when ionic strength increased. Interestingly, according to TSM, the fraction of instantaneous sorption sites tends to increase for an increase in ionic strength, which imply that the mechanism of Cd^{2+} sorption onto quartz sand can be better described using equilibrium sorption rather than nonequilibrium sorption for an increase in ionic strength.

1. Introduction

Due to their sorption affinity for pollutants, colloidal particles in groundwater from soils and waste sites have attracted considerable interest in the fate and transport of pollutants and the potential of increased health risks to humans (Hu et al., 2008). Colloidal particles have surface charges and/or organic components and are generally smaller than inter-granular pores or fractures in rock; and therefore, can be transported over long distance via groundwater flow (Sen et al., 2004). Migration of pollutants can be potentially enhanced when the pollutants are adsorbed onto the colloids and transported in subsurface environment (McCarthy and McKay. 2004). Depending on the nature of the colloids, cations, anions and

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http://dx.doi.org/10.1016/j.jconhyd.2015.08.008
0169-7722/

nonpolar and polar organic compounds can be adsorbed and transported (Kersting et al., 1999; Sen et al., 2002). Cationic forms of metals have a tendency to sorb onto soil colloids such as clay minerals which can act as a carrier for metals (McGechan and Lewis. 2002; Bradl. 2004; Sen et al., 2004; Usman et al., 2005).

There is some research on the effects of colloids on heavy metals transport. For example, Sun et al. (2010)examined the effects of kaolinite colloids on the transport of lead (Pb) in saturated porous media by using column experiments. They found that the transport of kaolinite was faster than that of Pb and the delayed Pb transport indicates that Pb had interacted with the porous medium in the column. When they compared the transport of Pb to the of kaolinite–Pb complex, they found that the latter complex displayed a faster breakthrough than Pb itself. In addition, they speculated that sorbed Pb from the media surface can be scavenged by the mobile kaolinite which would further enhance the mobility of Pb in the presence of kaolinite. Similarly, Saiers and Hornberger (1996) found that kaolinite colloids enhanced cesium (Cs) migration in a packed sand column. Noell et al. (1996) found that amorphous silica colloids increased Cs transport through glass bead columns. In an aquifer, colloidal particles are commonly attached to the porous medium during normal water flow and ionic strength conditions. Many researchers have studied various factors affecting the transport of organic and inorganic colloids such as pH (Ryan and Elimelech, 1996; Grolimund et al., 1998), ionic strength (Ryan and Elimelech, 1996; Grolimund et al., 1998; Saiers and Hornberger, 1999; Walshe et al., 2010) and ionic composition (Israelachvili, 1992; Elimelech et al., 1998). Ionic strength and ionic composition are known to have an influence on the transport behavior of colloids associated with contaminants. Cheng and Saiers (2010) reported that the binding capacity of sediment-colloids for ^{137}Cs decreased with increasing ionic strength, leading to a decrease in the mass of ^{137}Cs released from the columns packed with Hanford coarse sand. Cadmium (Cd), which naturally presents in ores together with copper (Cu), zinc (Zn) and lead (Pb), is a toxic heavy metal and it can come from natural sources, such as wildfires and volcanic activities, and anthropogenic sources, such as metal refining and smelting (Filiplč, 2012). Cadmium has been categorized as a potential carcinogen in humans by the U.S. national Toxicology program and International Agency for Research on Cancer (IARC, International Agency for Research on Cancer, 1993; Nordberg et al., 2000; IARC, International Agency for Research on Cancer, 2012). Some evidence indicates that genomic instability can be induced by exposure to Cd (Filiplč, 2012). Additionally, Cd is a cumulative toxin because of its long biological half-life about 10–30 years in a human body (Nordberg et al., 2007). Unfortunately, there have not been effective therapies for treating Cd intoxication (Nordberg et al., 2007; Candan et al., 2009).

Previous studies about the Cd^{2+} transport have focused on solute transport without colloidal particles and investigated effects of pH and pore-water velocity. Pang et al. (2002) investigated the effects of pore-water velocity on chemical nonequilibrium during transport of Cd^{2+} through alluvial gravel columns and found that pore-water velocity was positively correlated with the partitioning coefficient, forward rate and backward rate, but was inversely correlated with the retardation factor, mass transfer coefficient and ratio of forward and backward rates. In addition, Moradi et al. (2005) applied HYDRUS-1D and MACRO to describe Cd^{2+} transport below the root zone of a multilayer field soil in an arid region. They found that the sorption of Cd^{2+} could be described using Freundlich isotherm and Cd^{2+} moved to depths of 60 and 70 cm from soil surface for enriched sewage sludge by 38 and 80 mg Cadmium per a kilogram of sewage and the results showed that equilibrium CDE model generated far better simulation but the sorption constants of Freundlich isotherm were lower than the measured values. Recently, Zhi-Ming et al. (2012) studied about Cd^{2+} transport in neutral and alkaline soil columns at various depths. The results revealed that the equilibrium CDE model was sufficient for modeling Cd transport and the dispersion coefficient were between 0.78 and 10.70 $cm^2\ h^{-1}$ retardation factors were between 25.4 and 54.7. However, there are many studies on the influence of colloids on the transport of Cd^{2+} in groundwater but not many on the fate and transport of natural colloids (Zhou et al., 2011), and the effects of ionic strength on co-transport of colloidal particles and Cd^{2+}.

Many computer programs, for example HYDRUS-1D (Šimunek et al., 2008) and CXTFIT (Toride et al., 1999), have been used to model the water and solute transports. However, CXTFIT is frequently applied to describe breakthrough curves of tracer in steady state one dimensional flow (Toride et al., 1999). HYDRUS-1D was chosen in this study because it is a freeware and its window interface is similar to CXTFIT making this program easy to use and HYDRUS-1D has many options to estimate parameters. Moreover, HYDRUS-1D has been developed and used in many studies to carry out new modules (Chotpantarat et al., 2012). Mathematical models were used to analyze the experimental data to obtain numerical parameters which may be used to describe the behavior of metal transport and metal co-transport with colloidal particles. Consequently, the estimation of Cd^{2+} transport in a geological aquifer can be more accurate and reliable by applying mathematical models. However, a few research, especially mathematical models, are available on effects of kaolinite colloids under different ionic strengths on the Cd^{2+} transport in subsurface environment.

As mentioned above, therefore, in this study, we investigated the influence of ionic strength and kaolinite colloids on the migration of Cd^{2+} in columns packed with quartz sand. The objectives of this study were to (1) evaluate the effects of ionic strength on the co-transport of Cd^{2+} with kaolinite colloids in saturated sand columns and (2) investigate the effects of mobile kaolinite colloids on the Cd^{2+} transport in saturated sand columns and to model the effects of ionic strength and kaolinite colloids on Cd^{2+} sorption and transport in saturated sand columns by HYDRUS-1D.

2. Materials and methods

2.1. Quartz sand

Ottawa sand (quartz sand) purchased from Fisher Chemical (England) had a grain size of 0.6–0.8 mm in diameter. The sand was cleaned according to the procedure described by Zhou et al. (2011) to remove metal oxides and adsorbed particles from the sand surface. The cleaned sand was then analyzed for its mineral compositions using X-ray diffraction (XRD) (AXS D8, Bruker, Germany).