Journal of Contaminant Hydrology 199 (2017) 50–57

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

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

In situ reactive zone with modified $Mg(OH)_2$ for remediation of heavy metal polluted groundwater: Immobilization and interaction of Cr(III), Pb(II) and Cd(II)

Jun Dong, Bowen Li, Qiburi Bao *

Key Lab of Groundwater Resources and Environment Ministry of Education, Jilin University, Changchun 130026, China

ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form 4 February 2017
Accepted 22 February 2017
Available online 24 February 2017

Keywords:
Modified $Mg(OH)_2$
Heavy metal
Groundwater
Precipitate
Transport

ABSTRACT

$Mg(OH)_2$ dissolves slowly and can provide a long-term source of alkalinity, thus a promising alternative reagent for the in situ remediation of heavy metal polluted groundwater. However, the application of $Mg(OH)_2$ on in situ reactive zone (IRZ) for heavy metal polluted groundwater has never been investigated. In this study, the behaviors of heavy metals in a $Mg(OH)_2$ IRZ were monitored for 45 d. The heavy metals show a sequential precipitation by modified $Mg(OH)_2$ due to the difference of K_{sp}. Column tests were conducted to investigate the temporal and spatial distribution of heavy metals in $Mg(OH)_2$ IRZ and evaluate the stabilization effect for multi-heavy metal polluted groundwater. Experimental results indicate that there exist interactions between different heavy metals, and their zoning distribution is attributed either to the competitive adsorption onto porous media (control column) or to the sequential precipitation of heavy metal ions (IRZ column). In contrast with the control column, heavy metal contaminated area in $Mg(OH)_2$ IRZ significantly shrinks. According to the chemical speciation analysis, when water containing Pb(II), Cd(II) and Cr(III) flows through $Mg(OH)_2$ IRZ, exchangeable fraction of total concentration significantly reduce and the proportion of carbonate and Fe/Mn oxides fraction increase, indicating the decrease of their mobility and toxicity.

1. Introduction

With the development of industry, the release of heavy metals into environment is accelerating annually, causing serious environmental pollution and threat to the human health (Albuquerque and Labrincha, 2008; Moghaddam and Mulligan, 2008; Rheinheimer dos Santos et al., 2013; Satyawali et al., 2011; Vermeul et al., 2003; Wang et al., 2016b). Mining activities, as an important source of heavy metal pollution, give rise to acid drainage containing several hazardous heavy metals, such as lead, cadmium and chromium that easily infiltrate to groundwater (Chotpantarat et al., 2015; Kim et al., 2014; Obiri-Nyarko et al., 2015; Wikiniyadhanee et al., 2015). Unlike hazardous organics, heavy metals cannot be degraded. For this reason, in situ immobilization by means of chemical precipitation is the major method for heavy metal pollution control (Brown et al., 2005; Cao et al., 2003; Cao et al., 2004; Chen et al., 2003; McGowen et al., 2001; Melamed et al., 2003). Chemical precipitation involves use of reactive chemical reagents to modify the aquifer pH, converting mobile heavy metals into their insoluble state.

Conventionally, soluble hydroxides (NaOH and KOH) are used for subsurface pH modification. However, excessive injection of soluble hydroxides into a poorly buffered aquifer will lead to an unacceptable high pH, resulting in secondary pollution and failure of immobilization due to the dissolution of heavy metal hydroxides. Unlike the soluble hydroxides, $Mg(OH)_2$ with a lower aqueous solubility, slowly dissolves and releases OH^- over time (Pishtshev et al., 2014; Rötting et al., 2006).

Thus, $Mg(OH)_2$ is capable to limit the drastic pH rise of groundwater and to provide a long-term source of alkalinity for heavy metal precipitation (Hiortdahl and Borden, 2014; Kameda et al., 2009; Liu et al., 2015; Wang et al., 2016a). Permeable reactive barrier (PRB) with caustic magnesia (mainly MgO, could react with water to form $Mg(OH)_2$) has been demonstrated to be effective for the treatment of groundwater contaminated by Cu, Zn and Pb (Cortina et al., 2003). Such a PRB system could maintain the pH around 9 for a long time (over 20 years when the barrier is 2 m thick and the groundwater velocity is lower than 60 m/a).

The concept of in situ reactive zones (IRZ) is based on the creation of a subsurface zone where migrating contaminants in groundwater are intercepted and permanently immobilized or degraded into harmless end products (Suthersan, 2001). Creation of IRZ involves digging wells and injecting reactive materials. As a passive in situ remediation method, IRZ has been increasingly used in recent years and is regarded as a promising alternative for the remediation of heavy metal polluted

* Corresponding author.
E-mail address: qbr_6022@126.com (Q. Bao).

http://dx.doi.org/10.1016/j.jconhyd.2017.02.005
0169-7722/

groundwater. In contrast with PRB, IRZ has several advantages. Drilling injection wells could be much cheaper than creating a treatment wall especially when the groundwater table is very deep. No excavation of contaminated soil is needed, therefore human exposure to hazardous materials is minimum. Besides, injection wells could be installed much deeper than trenches. To make sure an IRZ functions well, remediation materials should be inexpensive and durable (Gavaskar et al., 2005; Hood et al., 2008), and easily transport in porous media without interrupting the flow of groundwater. $Mg(OH)_2$ has a potential to be applied in IRZ system. However, with the PZC (point of zero charge) of 11, $Mg(OH)_2$ is positively charged (zeta potential = +9.26 mV) under typical aquifer conditions (Appel et al., 2003), thus strongly retained by negatively charged aquifer media. Therefore, modification are necessary to alter the charge of the $Mg(OH)_2$ so that it is not retained by the porous aquifer media.

The major removal mechanism of heavy metals by $Mg(OH)_2$ is assumed to be: 1) dissolution → increase in pH → precipitation: 2) adsorption by modified sorbents (Cortina et al., 2003; Kameda et al., 2009; Wang et al., 2016a). Most related studies focus on the removal ratio of heavy metals, while few consider the interaction between different heavy metals. González found that when Cu^{2+}, Pb^{2+} and Cd^{2+} coexisted in a system, they were removed sequentially by Mg-Al layered double hydroxides (González et al., 2014). However, the effect of porous media on the reaction has not been investigated nor the stability of reaction product.

To our knowledge, this is the first study giving an insight into $Mg(OH)_2$ IRZ for remediation of groundwater heavy metal pollution. In this study, $Mg(OH)_2$ is modified by polyoxyethylene sorbitan fatty acid ester (Tween 80) and sodium dodecyl sulfate (SDS), and prepared as a colloidal suspension to facilitate its transport in the subsurface. Three toxic heavy metals frequently found in groundwater, Pb(II), Cd(II) and Cr(III) are selected as target pollutants. The objectives of this work are: to evaluate the transport ability and OH^- releasing property of modified $Mg(OH)_2$; to study the interactive behavior and the temporal-spatial distribution of Cr^{3+}, Pb^{2+} and Cd^{2+} in $Mg(OH)_2$ reactive zone; and to analyze the stabilization effect of $Mg(OH)_2$ reactive zone on groundwater contaminated by heavy metals.

2. Materials and methods

2.1. Chemicals and reagents

Chemicals used in experiments were reagent grade and solutions were prepared with distilled water. The stock solutions of Pb(II), Cd(II) and Cr(III) were prepared weekly by $Pb(NO_3)_2$, $CdCl_2$ and $Cr(NO_3)_3$ respectively. $Mg(OH)_2$ suspension used was modified by Tween-80 (nonionic) and SDS (anionic), which can act synergistically on the stability of $Mg(OH)_2$.Tween 80: SDS: $Mg(OH)_2$ = 1:1:100. Zeta potential and particle size of modified $Mg(OH)_2$ were measured by a Zeta potential and particle size analyzer (Malvern, NanoPlus).

2.2. OH^- releasing property of modified $Mg(OH)_2$

Batch experiments were designed to investigate OH^- releasing properties of modified $Mg(OH)_2$. To ensure the same amount of OH^-, modified $Mg(OH)_2$ with a concentration of 0.345 mmol/L and NaOH of 0.69 mmol/L were used to precipitate Cr(III). The initial concentration of Cr(III) was 0.16 mmol/L in a 500 mL-head-space bottle. A shaking rate of 120 rpm/min was used in this experiment, solutions were collected at designed sampling times. The suspension was filtered through 0.45 μm-filter membrane and acidified with nitric acid solution prior to the chemical analyses.

2.3. Precipitation of multi-heavy metals by modified $Mg(OH)_2$

Solution, containing Pb(II), Cd(II) and Cr(III), was placed in a 500 mL-head-space bottle. The concentration of Pb(II) and Cd(II) were

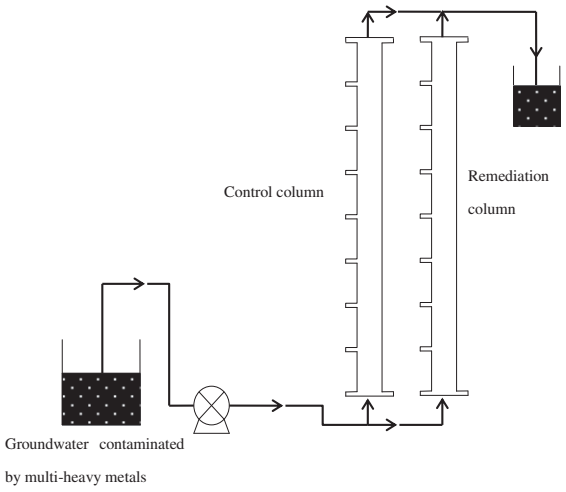

Fig. 1. Schematic of experimental facility.

0.24 mmol/L, concentration of Cr(III) was 0.16 mmol/L. Modified $Mg(OH)_2$ was added into solutions with a concentration of 200 mg/L. A shaking rate of 120 rpm/min was used in this experiment. pH of the samples was measured immediately after sampling. The suspension was filtered through 0.45 μm-filter membrane and acidified with nitric acid solution prior to the chemical analyses.

2.4. Column tests

River sand was sieved and used as aquifer porous media. Particles with the size of 0.25–0.5 mm was packed into the plexiglass column and saturated with water to simulate aquifer. The plexiglass column was 80 cm in height and 5 cm in diameter. The porosity of simulate aquifer was 0.38. At the outer flank of the column, there was a sampling port every 10 cm. One pore volume (PV) of 10 g/L modified $Mg(OH)_2$ suspension was injected to the glass column. After the injection of modified $Mg(OH)_2$ suspension, several PV distilled water was injected to the glass column. Effluent pH and modified $Mg(OH)_2$ concentration were detected. Samples were acidified to pH <7 and the concentration of Mg^{2+} was measured to represent modified $Mg(OH)_2$ concentration. Solution containing Pb(II), Cd(II) and Cr(III) with the concentration of 0.24, 0.24 and 0.16 mmol/L respectively was injected at the velocity of 1.2 m/d to the column incessantly until the 45th day. A control column with no modified $Mg(OH)_2$ and inject the same concentration of heavy metals solution were packed. Samples were collected every 2 days at

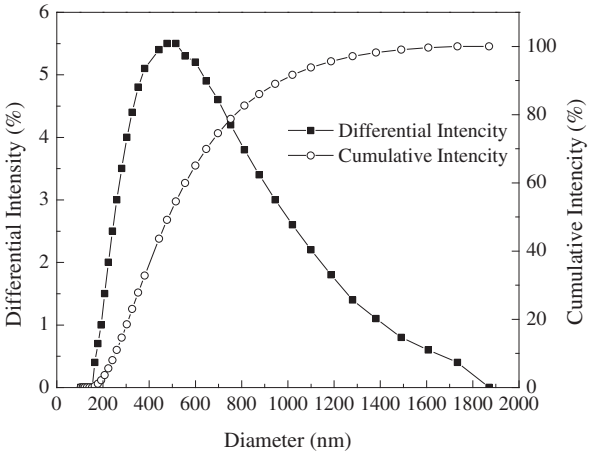

Fig. 2. Particle size distribution of colloidal $Mg(OH)_2$.