Journal of Hazardous Materials 196 (2011) 101–108

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

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

# Water-soluble organo-building blocks of aminoclay as a soil-flushing agent for heavy metal contaminated soil

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ARTICLE INFO

*Article history:*
Received 12 April 2011
Received in revised form 28 August 2011
Accepted 31 August 2011
Available online 6 September 2011

*Keywords:*
Heavy metals
Soil flushing
Water-soluble clay
Phyllosilicate
Remediation

ABSTRACT

We demonstrated that water-soluble aminopropyl magnesium functionalized phyllosilicate could be used as a soil-flushing agent for heavy metal contaminated soils. Soil flushing has been an attractive means to remediate heavy metal contamination because it is less disruptive to the soil environment after the treatment was performed. However, development of efficient and non-toxic soil-flushing agents is still required. We have synthesized aminoclays with three different central metal ions such as magnesium, aluminum, and ferric ions and investigated applicability of aminoclays as soil flushing agents. Among them, magnesium (Mg)-centered aminoclay showed the smallest size distribution and superior water solubility, up to 100 mg/mL. Mg aminoclay exhibited cadmium and lead binding capacity of 26.50 and 91.31 mg/g of Mg clay, respectively, at near neutral pH, but it showed negligible binding affinity to metals in acidic conditions. For soil flushing with Mg clay at neutral pH showed cadmium and lead were efficiently extracted from soils by Mg clay, suggesting strong binding ability of Mg clay with cadmium and lead. As the organic matter and clay compositions increased in the soil, the removal efficiency by Mg clay decreased and the operation time increased.

## 1. Introduction

Soil contamination with toxic heavy metals such as copper, zinc, chromium, cadmium, and lead, has been a big concern in many countries due to their adverse health effects [1]. Thousands of sites contaminated with heavy metals need to be remediated in the United States and other countries, which requires new development of effective soil treatment technologies [2–4]. Currently, various soil treatment technologies, including excavation and landfill, isolation, containment, electrokinetics (EK), biological treatment, and soil flushing (washing) have been applied to remediate heavy metal contaminated sites [3–6]. Among them, soil flushing has shown several advantages such as relatively low cost and less environmentally disruptive consequences compared to the conventional excavation and landfill methods [3,4]. Therefore, it has been widely applied to remove heavy metals from contaminated soils. During soil flushing, acids and other solvents have been applied to enhance the performance, which have caused disruption in the soil environment after treatment [7,8]. Thus, chelating agents such as pyridine-2,6-dicarboxylic acid (PDA), *N*-(2-acetamido) iminodiacetic acid (AIA), and ethylenediaminetetraacetic acid (EDTA), or surfactants [9–14] have been widely employed in place of acids and other solvent to extract heavy metals from soils. However, these chelating agents also resulted in problems because of their recalcitrance and the difficulties separating them from the heavy metal cations, which required additional processes for disposal treatment. Recently, a new class of nanoscale water-soluble chelants of poly(amidoamine) (PAMAM) dendrimer in environmental applications was explored in aqueous solutions [15,16] and soils [1,17]. However, these chelants are expensive and need an additional nanofiltration process to recover them. Therefore, development of alternative chelating agents is still required for an environmentally non-destructive and cost-effective remediation process.

Organic–inorganic hybrid nanomaterials have been getting attractions because of their wide applications. Mann et al. have developed 3-aminopropyl functionalized phyllosilicates (aminoclay) by covalent bonding with a central metal ion and sandwiched organo-functionalities via Si–C bonds [18,19] and reported nanocomposites with biomolecules [20–24]. Unfortunately, they do not have focused on environmental areas. Thus, because aminoclay has unique nano-sized and water-soluble properties with a high density of amino groups, it can lead to applications in environmental studies. In addition, its high chelating capacity with metal ions and less toxicity make the aminoclay as an excellent candidate for a soil flushing agent.

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doi:10.1016/j.jhazmat.2011.08.077

**Table 1**
Properties of Jumunjin sand, Soil A, B, and C used in this study.

| | Density (g/cm$^3$) | Bulk density (g/cm$^3$) | Porosity | pH | Organic content (%) | Soil composition (%) | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Sand (2–0.02 mm) | Silt (0.02–0.002 mm) | Clay (<0.002 mm) |
| Jumunjin sand | 2.320 | 1.500 | 0.582 | – | 0.11 | 100 | 0 | 0 |
| Soil A | 2.340 | 1.521 | 0.350 | 5.85 | 0.6 | 93.5 | 2.5 | 4.0 |
| Soil B | 2.286 | 1.136 | 0.497 | 4.00 | 3.5 | 75.0 | 15.0 | 10.0 |
| Soil C | 2.254 | 0.789 | 0.650 | 6.48 | 12.1 | 55.0 | 28.0 | 17.0 |

The objective of this study is to demonstrate that aminoclay can be applied as an alternative soil-flushing agent to remediate heavy metals from soils. We synthesized aminoclays with three different central metal ions and investigated heavy metal binding of aminoclays through batch and column experiments.

## 2. Experimental

### 2.1. Materials

All chemical used in this study were reagent grade or higher grade and used without further purification. 3-Aminopropyltriethoxysilane (APTES, 99%), ferric chloride hexahydrate, and aluminum chloride hexahydrate were purchased from Sigma–Aldrich (St. Louis, MO, USA) and magnesium chloride hexahydrate (98.0%) was obtained from Junsei Chemical Co., Ltd. (Tokyo, Japan). Cadmium and lead sources were used as chloride counterions (>99%, A.C.S. reagent). The 1000 mg/L standard solutions of cadmium, lead, and magnesium were obtained from Fluka. Ethanol (>99.9%) was purchased from Merck KGaA (Darmstadt, Germany). Centrifugal filters (Amicon® Ultra, 3 kDa) were bought from Millipore. HCl or NaOH standard solutions (1 N or 0.1 N) were used from DAE JUNG (Shiheung, Korea) to adjust the pH of the samples. Double-distilled deionized water (>18 mΩ, DI water) was used through all of the experiments.

### 2.2. Preparation of hydrophilic aminoclays

An aminopropyl functionalized magnesium phyllosilicate clay was prepared as previously reported [18–24]. The APTES (1.3 mL, 5.63 mmol) was added in a drop-wise manner to a magnesium chloride (0.84 g, 8.82 mmol) in ethanol (40 mL) at room temperature. The molar ratio of Mg to Si was approximately 0.75. The white slurry was formed after 5 min, which was stirred overnight. The precipitate was isolated by centrifugation, washed with ethanol (50 mL) to remove excess magnesium chloride, and dried at 40 °C. Aminoclays with backbones of Fe and Al were also synthesized using the same procedure described above. For brevity, Mg, Al, and Fe backboned aminoclays will be referred to as Mg clay, Al clay, and Fe clay respectively.

### 2.3. Cadmium and lead binding of Mg clay in batch system

Batch experiments were conducted to determine the maximum binding capacity of the heavy metal cations in Mg clay solution as a function of pH. The Mg clay solution (0.5 g/L) was reacted with 50 mg/L of cadmium or lead solution at various pH values for 1 day where adsorption equilibrium time was confirmed <1 h. Samples were agitated with magnetic stirrer during the reaction. After reactions, all samples were filtered by an Amicon® centrifugal filter (3 kDa) and then analyzed by atomic absorption spectrometry (AAS, Perkin–Elmer). The removal capacity ($q$) was calculated by

$$\frac{(C_o - C_{\text{filtered}}) \times V}{W} = q\,(\text{mg/g})$$

where $C_0$ and $C_{\text{filtered}}$ were the initial and filtered concentrations after centrifugation (mg/L), $V$ (L) was the sample volume, and $W$ was the mass (g) of the Mg clay. The experiments were conducted in triplicate to get a reliable result.

### 2.4. Mg clay flushing for cadmium or lead contaminated soils

Column flushing experiments were performed with a 30 mm × 160 mm column (Kontes, USA) containing 110 g of Jumunjin sand (20–30 mesh), and Soil A, B, and C. Jumunjin sand was obtained from seashore of east coast of Korea (Jumunjin, Korea) and Soil A, B, and C were collected on a hill site inside of the university (Daejeon, Korea) and their physical properties were artificially controlled to have different sand, silt, and clay contents. The clay and silt contents increased in the order of Soil A < B < C (Table 2). The elemental compositions observed by X-ray fluorescence (XRF) and physical properties of the soils are summarized in Tables 1 and 2, respectively. X-ray diffraction analysis showed that quartz, illite, and albite are the major mineral composition of Soil A, B, and C. Approximately the same loading of each soil was packed in the column by small incremental actions to obtain homogeneous condition with uniform bulk density [25]. And soil column experiment was The schematic diagram of the column experiment in detail was depicted in Fig. 1. The pore volume of the sand in the column was 30 mL. Initially, 20 pore volumes of DI water were pushed through the column in an upward direction at a flow rate of 2 mL/min. Next, the column was contaminated by circulating an initial concentration of approximately 300 mg/L of divalent cadmium and lead, individually, at a flow rate of 1 mL/min to achieve an equilibrium state for 6 h (at pH 7). Then, more than 30 pore volumes of DI water was introduced in an upward direction in order to remove slightly bounded heavy metals from the soil surfaces. As a result, complete saturation with water for the column was achieved. The preloaded $Cd^{2+}$ and $Pb^{2+}$ uptakes for the Jumunjin sand soil were 120 ± 10 and 180 ± 20 mg/kg, respectively. In cases of Soils A, B, and C (order of clay contents: A < B < C), the preloaded concentrations of $Pb^{2+}$ were 1016, 1216, and 1446 mg/kg, respectively, reflecting sorption of heavy metals on soils were highly affected by the characteristics of the soils. This will be further discussed in Section 3.5. For the flushing of

**Table 2**
Elemental compositions (%) of Jumunjin sand, Soil A, B, and C observed by X-ray fluorescence (XRF) spectrometer in this study.

| | Si | Al | K | Fe | Ca | Ti | Cu | S | Mn | Na |
|---|---|---|---|---|---|---|---|---|---|---|
| Jumunjin | 68.4 | 8.9 | 12.7 | 0.992 | 0.36 | 0.12 | 0.065 | 0.23 | – | 6.6 |
| Soil A | 67.3 | 13.9 | 8.95 | 5.43 | 2.34 | 0.936 | 0.11 | 0.51 | 0.11 | – |
| Soil B | 42.7 | 23 | 9.15 | 15 | 3.86 | 1.39 | 0.079 | 0.36 | 0.34 | – |
| Soil C | 46.4 | 19.2 | 7.47 | 18.2 | 1.2 | 1.74 | 0.11 | 0.66 | 0.53 | – |