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Combined modification of clay with sulfhydryl and iron: Toxicity alleviation in Cr-contaminated soils for mustard (*Brassica juncea*) growth

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ABSTRACT

Clays are promising adsorbents for heavy metal removal from the environment because they are economical, naturally abundant and environmentally stable. Application of natural clays, however, are typically limited due to their adsorption capacity and because they usually possess little redox potential except for some specific clays with special functional groups, restricting their application in the removal and detoxification of oxidized metal ions, such as Cr(VI). In the present study, natural bentonite was modified with thiol and iron functional groups to improve both its adsorption performance and reduction ability. Material characterization techniques confirmed the success of grafting the thiol group and pillaring the reduced Fe in the clay. Batch adsorption tests demonstrated an enhanced Cr-adsorption capability of the functionalized bentonite. Moreover, the reduced product, Cr(III),was accumulated in the reaction system, indicating a decrease in Cr(VI) toxicity due to its reduction to Cr(III)by the reduced iron functional group in the modified clay. Pot experiments, using mustard as the target seedling, further demonstrated that the thiol/Fe-modified clay could efficiently stabilize and detoxify Cr(VI) in the soil, therefore inhibiting its accumulation in the crop tissues and ultimately improving plant growth. The results suggested that this novel clay modified with sulfhydryl and iron might be a promising material for the stabilization and toxicity alleviation of Cr(VI)-contaminated soils.

1. Introduction

Clay minerals have historically been used as adsorbents for heavy metal in removal processes because of their advantageous characteristics, including high specific surface area, ion exchange properties, low cost, natural abundance and environmental stability (Celis et al., 2000; Sarkar et al., 2013; Vasilyeva et al., 2014). Since natural clay usually suffers from poor binding strength and low metal selectivity, it typically requires functional modifications (Celis et al., 2000; Milićević et al., 2013; Sarkar et al., 2013). For example, the introduction of the thiol group (—SH)into clay minerals was explored to improve their specific binding capability toward various highly toxic heavy metal ions, such as Hg^{2+}, Pb^{2+}, and Cd^{2+} (Lagadic et al., 2001; Lee and Tiwari, 2012). Moreover, the incorporation of functional metal groups, such as iron (Fe(II)), might contribute to adding new characteristics to clay, enhancing sorptive capacity (Dousova et al., 2014) and reducing reactivity (Bhattacharyya and Sen Gupta, 2008; Bishop et al., 2014). These modifications would be highly beneficial for the remediation of soils contaminated by oxidative pollutants, such as hexavalent chromium (Cr(VI)).

Chromium (Cr) is one of the most common pollutants in groundwater, soil and sediments, and it presents one of the leading threats to human health (Dhal et al., 2013; Sarkar et al., 2013; Albanese et al., 2007). Trivalent chromium, Cr(III), and hexavalent chromium, Cr(VI), are two of the most stable and common forms of Cr in the environment. Compared to Cr (III), Cr(VI) is a more toxic and carcinogenic form, with a high mobility due to higher water solubility over the full pH range. In contrast, Cr(III) tends to readily precipitates and adsorbs on the soil surface (Barrera-Diaz et al., 2012; Dhal et al., 2013). The environmental contamination of Cr primarily arises from solid or liquid wastes from industrial activities, such as mining, electroplating, leather tanning, metal processing, as well as pigment and dye production (Albanese et al., 2013; Dhal et al., 2013). Soils in agricultural land close to industrial areas would be affected first and would result in severe heavy metals contamination (Krishna and Govil, 2004; Shao et al., 2014). As a non-essential element, Cr is significantly toxic to microorganisms and plants. This toxicity inhibits germination, obstructs root and seedling growth and development, induces leaf chlorosis and necrosis, and alters physiological and biochemical processes of plants (Singh et al., 2013).

Various techniques have been employed to detoxify and remove Cr from soils and ground water, including precipitation, reduction, extraction, and adsorption through chemical, electrochemical, or biological means (Barrera-Diaz et al., 2012; Dhal et al., 2013). Among these

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treatments, adsorption is a widely applied method due to its low cost and simplicity (Bhattacharyya and Gupta, 2006; Ghorbel-Abid et al., 2009). Additionally, natural clay minerals, with modified functional groups, have shown great potential in this application (e.g. Gladysz-Plaska et al., 2012; Li et al., 2016; Sarkar et al., 2013). Examples of these functional groups include sulfur and iron compounds, which have been shown to be active in the reduction of toxic Cr(VI) to the less toxic Cr(III) form (Barrera-Diaz et al., 2012). The combined modification of clay with sulfhydryl and iron groups, therefore, might result in an efficient alleviation of the Cr(VI) contamination problem. However, only few reports on the single modification of clay with a thiol or iron group to improve the adsorption performance have been published (Lee and Tiwari, 2012; Sarkar et al., 2013). Studies focusing on the combined modification or on the functionalization of clay for Cr(VI) reduction in contaminated soils have not been reported.

In this study, therefore, a novel functional clay modified with a thiol group and iron was developed and was used for the remediation of Cr(VI)-contaminated soils for mustard growth through the following processes: (i) the reduction and subsequent detoxification of Cr(VI) to Cr(III), and (ii) the adsorption of Cr(VI) and Cr(III) to stabilize the soils. The results are of great importance for safe agricultural production from Cr(VI)-contaminated soils.

2. Materials and methods

2.1. Materials

The clay used in the present study was Na-bentonite and was collected from Lin'an, Zhejiang, China. All of the chemicals for the clay modification and adsorption tests, including potassium dichromate ($K_2Cr_2O_7$), hydrochloric acid (HCl), cysteamine hydrochloride, sodium carbonate anhydrous (Na_2CO_3), ferrous sulfate ($FeSO_4$), etc., were of analytical grade and were obtained from Sigma-Aldrich Company, unless otherwise stated. A fresh stock solution of Cr(VI) was prepared by dissolving 1.47 g $K_2Cr_2O_7$ into 1 L deionized water (DI water) to yield an accurate concentration of 10 mmol/L Cr. The pH was adjusted to approximately 5.0 by HCl. As a control test, non-polluted soil was collected from a vegetable base site in the Baiyun District, Guangzhou, China. No Cr was detected in the soil by atomic absorption spectrometry after thoroughly digested in the HCl-HNO_3-HF-$HClO_4$ system. This soil was artificially contaminated in the laboratory by spiking with the prepared Cr(VI) solution to obtain a contamination level of 300 mg/kg.

2.2. Clay functionalization

The clay was first functionalized with mercaptamine to obtain thiol-modified clay using the following procedure. Na-bentonite was mixed with 20% HCl in a ratio of 1:10 (w:v) and then stirred at 80 °C for 4 h before being filtered by quantitative filter paper, dried and ground. Next, the bentonite powder was dispersed in DI water to yield a 2% suspension, which was then mixed with 10 g/L cysteamine hydrochloride in a ratio of 10:1 (v:v) and stirred for 4 h. After centrifugation at 8000 rpm for 10 min and washing with DI water several times, the modified clay was dried at 60 °C and ground to pass through a 200-mesh sieve.

To prepare the combined thiol/Fe-modified clay, a poly-hydroxyl iron solution was firstly prepared by the addition of 16 g Na_2CO_3 to 1.0 L of 0.1 mol/L $FeSO_4$. The mixture was stirred for 2 h and aged for 24 h at 60°C. The freshly prepared poly-hydroxyl iron solution was then added to a 2.0% thiol-modified clay suspension at a ratio of 2:1 (v:v). The mixture was then stirred for 2 h and aged for 24 h at 60°C. After centrifugation at 8000 rpm for 10 min, the sample was washed several times with DI water. After drying at 60°C, the sample was ground to pass through a 200-mesh sieve, thus obtaining the combined thiol/Fe-modified clay.

2.3. Characterization of clays

In order to characterize the clay samples, the natural and modified clays were homogeneously ground into powder. The powder samples were characterized by scanning electron microscopy/energy dispersive spectroscopy (SEM-EDS), Fourier Transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The morphology and chemical compositions of the clay were investigated using SEM-EDS (Leica Stereo scan 400i series, USA), operating at 20 kV. For FTIR characterization, the powder samples were mixed with KBr powder and pressed into pellets. Each FTIR measurement (Bruker Vector 33, Germany) was recorded with 64 scans at a resolution of 4 cm^{-1} over a range of 4000 to 400 cm^{-1}. XPS analyses were performed on a Kratos Axis spectrometer (SHIMADZU, Japan) with Mg $K\alpha$ radiation ($h\gamma =$ 1250.6 eV). The pressure in the analysis chamber was $<1 \times 10^{-9}$ mbar, and the binding energies of the samples were calibrated by taking the carbon 1 s peak as a reference (284.8 eV).

2.4. Cr(VI) adsorption and reduction experiments

The adsorptive capacities of the modified clays for Cr(VI) were investigated through batch experiments. During the adsorption experiments, clays were added to the prepared working solutions at initial Cr(VI) concentrations of 2.0 mmol/L, thereby obtaining clay dosages of 3.0 g/L. Then, the pH of the suspension was adjusted with 0.5 M NaOH or HCl to reach the target pH values. After allowing adsorption equilibration at 150 rpm shaking for 24 h or at regular time intervals, the clays were separated from the solution via centrifugation at 4500 rpm for 5 min, and the supernatant was filtered through 0.45-μm hydrophilic PTFE filters (Millipore, MA, USA) to determine the Cr concentrations. All of the experiments were conducted in triplicate, and the results are provided with standard deviation values.

2.5. Mustard seed germination experiments

To investigate the primary ecotoxicological effect of Cr stress on mustard seed germination (Dell'Aquila, 2009; Bae et al., 2014), seeds of *Brassica juncea* in uniform size were placed in petri dishes lined with three layers of qualitative filter paper (Wet Strengthened Grades, Whatman, UK). The filter paper layers were previously moistened with 15 mL of a Cr(VI) solution at concentrations of 0, 90, 300, and 600 mg/L. Triplicate experiments were conducted for each treatment. All of the petri dishes were incubated in a climate incubator (MGC-300H, Shanghai, China) at 25 °C for 7 days, with a 16/8-h photoperiod and a humidity of 75%. The germination ratio, root length, and root dry weight were measured at the end of the experiments.

2.6. Experimental remediation of Cr(VI)-contaminated soil with clays for mustard growth

Pot experiments for mustard growth were performed to evaluate the ability of the clays to remediate Cr(VI)-contaminated soil. The thiol/Fe-modified clay was dosed and homogeneously mixed into the Cr-contaminated soil at treatment levels of 0, 1.0, 5.0, 10, 20 g/kg. The treated soils were then mixed with DI water in a ratio of 1:2.5 (w:v) and equilibrated for 30 days before use.

When the treated soils were ready and no water logging was found on the surface, selected plump mustard seeds of uniform size which looked healthy and vigorous were sown. Twelve seeds were placed in each pot, and the seeds were covered with the homogeneous soils up to a thickness of 1–2 times the seed size (~5 mm). The pots were covered with plastic film to preserve the humidity for seed germination until the second euphylla started to expand. After the fourth euphylla developed, the seedlings were removed, and only 6 strains demonstrating positive and similar growth conditions were retained in each pot. Soils were watered every day to maintain the water content at

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