



Hexavalent chromium removal by chitosan modified-bioreduced nontronite

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Received 10 June 2016; accepted in revised form 19 April 2017; available online 26 April 2017

Abstract

Recent efforts have focused on structural Fe(II) in chemically or biologically reduced clay minerals to immobilize Cr(VI) from aqueous solution, but the coulombic repulsion between the negatively charged clay surface and the polyanionic form of Cr(VI), e.g., dichromate, can hinder the effectiveness of this process. The purpose of this study was to investigate the efficiency and mechanism of Cr(VI) removal by a charge-reversed nontronite (NAu-2), an Fe-rich smectite. Chitosan, a linear polysaccharide derived from chitin found in soil and groundwater, was used to reverse the charge of NAu-2. Intercalation of chitosan into NAu-2 interlayer increased the basal d-spacing of NAu-2 from 1.23 nm to 1.83 nm and zeta potential from -27.17 to $+34.13$ mV, with the amount of increase depending on chitosan/NAu-2 ratio. Structural Fe(III) in chitosan-exchanged NAu-2 was then biologically reduced by an iron-reducing bacterium *Shewanella putrefaciens* CN32 in bicarbonate buffer with lactate as the sole electron donor, with and without electron shuttle, AQDS. Without AQDS, the extent of Fe(III) reduction increased from the lowest ($\sim 9\%$) for the chitosan-free NAu-2 to the highest ($\sim 12\%$) for the highest chitosan loaded NAu-2 (3:1 ratio). This enhancement of Fe(III) reduction was likely due to the attachment of negatively charged bacterial cells to charge-reversed (e.g., positively charged) NAu-2 surfaces, facilitating the electron transfer between cells and structural Fe(III). With AQDS, Fe(III) reduction extent doubled relative to those without AQDS, but the enhancement effect was similar across all chitosan loadings, suggesting that AQDS was more important than chitosan in enhancing Fe(III) bioreduction. Chitosan-exchanged, biologically reduced NAu-2 was then utilized for removing Cr(VI) in batch experiments with three consecutive spikes of $50 \mu\text{M}$ Cr. With the first Cr spike, the rate of Cr(VI) removal by charged-reversed NAu-2 that was bioreduced without and with AQDS was ~ 1.5 and $\sim 6 \mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. However, the capacity of these clays to remove Cr(VI) was progressively exhausted upon addition of subsequent Cr spikes. X-ray photoelectron spectroscopy (XPS) revealed that the reduction product of Cr(VI) by chitosan-exchanged-bioreduced NAu-2 was Cr(III), possibly in the form of $\text{Cr}(\text{OH})_3$. In summary, our results demonstrated that the combined effects of sorption and redox reactions by charge-reversed bioreduced nontronite may offer a feasible in-situ approach for remediating Cr(VI) polluted soil and groundwater.

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Keywords: Charge-reversed nontronite; Structural Fe(II); Chitosan; *Shewanella putrefaciens*; Cr(VI) removal

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1. INTRODUCTION

Release of chromium into the environment as a consequence of growing industrialization has been a major concern worldwide (McNeill et al., 2012). Although trivalent chromium [Cr(III)] at a trace level is an essential nutrient for plant and animal metabolism (glucose metabolism, amino- and nucleic acid synthesis), high levels of chromium, especially hexavalent chromium [Cr(VI)], can cause serious diseases such as nausea, skin ulcerations, and lung cancer (Richard and Bourg, 1991). Despite these health hazards associated with chromium exposure, its application in steelworks, electroplating, leather tanning, and production of dyes and pigments, is still extensive, which often causes major environmental problems (Dhal et al., 2013). Among the range of oxidation states (−2 to +6) of chromium, [Cr(VI)] is considered highly toxic, owing to its weak adsorption on mineral surfaces and strong oxidizing nature. This toxicity of Cr(VI) is in contrast to the less soluble Cr(III), which readily forms insoluble oxides and hydroxides at slightly acidic to alkaline pH conditions (Cervantes et al., 2001; Motzer and Engineers, 2004; McNeill et al., 2012). Due to the associated toxicity of chromium to biological systems, the United States environmental protection agency (US EPA) has set a maximum contamination level (MCL) of total chromium in drinking water to be 0.1 mg L^{-1} (Sutton, 2010).

In order to address the growing problem of chromium contamination in the environment, a considerable number of studies have used chemical, physical and biological methods to remediate this contaminant. Among these techniques, adsorption has been recognized as a popular method due to its simplicity of operation, cost effectiveness, high efficiency, easy recovery, regeneration capacity, and sludge-free operation (Zhang et al., 2016). However, adsorptive removal does not change the toxicity of Cr(VI), and this process may be partially or wholly reversible. Furthermore, high efficiency is usually achieved only at low pH, which makes it difficult to implement in-situ except for acid mine drainage areas. To overcome these problems, researchers have used structural Fe(II) in iron-bearing clay minerals such as montmorillonite, nontronite, illite, vermiculite, and kaolinite to reduce soluble and toxic Cr(VI) to insoluble and less toxic Cr(III) (Gan et al., 1996; Taylor et al., 2000; Zhuang et al., 2012; Bishop et al., 2014). Because clay minerals are ubiquitous in natural environments, redox processes involving structural Fe(II) may, therefore, play an important role in environmental remediation of heavy metals such as chromium. However, one difficulty with such approach is the inevitable coulombic repulsion between negatively charged clay surface and dichromate polyanion, which may impede the removal efficiency of anionic Cr(VI) (Taylor et al., 2000). One possible solution to this problem, especially for application in engineered system, is through charge reversal of clay surface by certain surfactants. Indeed, a number of studies have used various polymers to reverse the charge of clay minerals for various environmental applications, mostly via sorptive removal of various pollutants, including heavy metals, radionuclides, and inorganic anions (Krishna et al., 2000;

Bleiman and Mishael, 2010; Su et al., 2012; Pentrák et al., 2014), organic pollutants (Churchman, 2002), and dyes (Crini and Badot, 2008; Auta and Hameed, 2014). In addition, other aluminosilicates such as Fe(II)-modified zeolites (Kiser and Manning, 2010; Lv et al., 2014) and surfactant-modified zeolites (Li and Bowman, 1997; Li et al., 1999; Leyva-Ramos et al., 2008; Swarnkar et al., 2011; Song et al., 2015; Szala et al., 2015; Ren et al., 2016) have been successfully utilized to remove Cr(VI) from aqueous solution either by sorption or reduction mechanism.

Among various surfactants used to reverse the surface charge of clay minerals, synthetic and natural polymers such as polydiallyldimethylammonium chloride (PolyDADMAC) (Su et al., 2012) and chitosan (Pentrák et al., 2014) have been recently used. In these studies, the structural Fe(III) in charge-reversed smectites was first chemically reduced by sodium dithionite to Fe(II) and the resulting Fe(II) was subsequently used for successful removal of nitrate from aqueous solution. However, both synthetic polymers and chemical reductants may not be readily available in nature. In such case, biological reduction of structural Fe(III) in natural biopolymer-modified clay minerals may be more relevant, however, the potential of such materials for Cr(VI) removal is unknown. Moreover, due in part to abundance of microorganisms in nature, relatively low cost and environmentally friendliness, biological reduction of charge-reversed clay minerals may be achieved in-situ and may offer a more feasible approach to remediate polluted soil and groundwater.

Chitosan, a type of biopolymer (linear polysaccharide, poly-(D) glucosamine), is synthesized by living organisms (White et al., 1979; Synowiecki and Al-Khateeb, 1997; Pochanavanich and Suntornsuk, 2002; Wan Ngah et al., 2011), and is the most abundant natural biopolymer in the environment after cellulose (Rinaudo, 2006). These compounds also have applications in agriculture. Fragments from chitin and chitosan are known to have eliciting activities leading to a variety of defense mechanisms in host plants in response to microbial infections (Hadrami et al., 2010; Hafdani and Sadeghinia, 2011). As a result, interest has been growing in amending soils with chitin and chitosan to reduce the negative impacts of diseases on crop yield and quality (Hadrami et al., 2010; Hafdani and Sadeghinia, 2011; Sharp, 2013). These activities could make chitosan readily available in soil and groundwater.

Chitin and chitosan-derivatives have gained wide attention as effective sorbents due to their low-cost and high contents of amino and hydroxyl functional groups, which may serve as sites for sorbing various aqueous pollutants (Sağ and Aktay, 2002; Lito et al., 2012; Wan Ngah et al., 2012). Because these compounds possess unique properties (e.g., biodegradability, bioactivity, biocompatibility, and nontoxicity), these biosorbents are widely used for heavy metal removal (Zhang et al., 2016). However, chitosan-modified clay minerals have not been used for removing anionic pollutants such as dichromate. In addition, chitosan may be used as a model compound to understand how the surface charge of clay minerals can be reversed to enhance removal of other heavy metals. After solubilization of chitosan in acidic solution, its ionized amino groups

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