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Nano-sized Fe_2O_3/Fe_3O_4 facilitate anaerobic transformation of hexavalent chromium in soil–water systems

Yaxian Zhang[1], *Hua Li*[1], *Libo Gong*[1], *Guowen Dong*[1], *Liang Shen*[1], *Yuanpeng Wang*[1,*], *Qingbiao Li*[1,2]

1. *Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. E-mail:* zhangyaxian163@126.com

2. *College of Chemistry and Life Science, Quanzhou Normal University, Quanzhou 362000, China*

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ABSTRACT

The purpose of this study is to investigate the effects of nano-sized or submicro Fe_2O_3/Fe_3O_4 on the bioreduction of hexavalent chromium (Cr(VI)) and to evaluate the effects of nano-sized Fe_2O_3/Fe_3O_4 on the microbial communities from the anaerobic flooding soil. The results indicated that the net decreases upon Cr(VI) concentration from biotic soil samples amended with nano-sized Fe_2O_3 (317.1 ± 2.1 mg/L) and Fe_3O_4 (324.0 ± 22.2 mg/L) within 21 days, which were approximately 2-fold of Cr(VI) concentration released from blank control assays (117.1 ± 5.6 mg/L). Furthermore, the results of denaturing gradient gel electrophoresis (DGGE) and high-throughput sequencing indicated a greater variety of microbes within the microbial community in amendments with nano-sized Fe_2O_3/Fe_3O_4 than the control assays. Especially, *Proteobacteria* occupied a predominant status on the phylum level within the indigenous microbial communities from chromium-contaminated soils. Besides, some partial decrease of soluble Cr(VI) in abiotic nano-sized Fe_2O_3/Fe_3O_4 amendments was responsible for the adsorption of nano-sized Fe_2O_3/Fe_3O_4 to soluble Cr(VI). Hence, the presence of nano-sized Fe_2O_3/Fe_3O_4 could largely facilitate the mobilization and biotransformation of Cr(VI) from flooding soils by adsorption and bio-mediated processes.

Introduction

Chromium (Cr) has been listed as one of the top 20 contaminants in the superfund priority list of hazardous substances (Dhal et al., 2013). For centuries, the anthropic activities, *e.g.*, mining, processing, and smelting activities have greatly contaminated the soil and water resources, resulting in an unavoidable introduction of Cr-contaminants (Wang et al., 2007). Geochemical processes and weathering, acting upon metallurgical wastes and by-products, initiate transport of Cr from contaminated areas and redistribution to surrounding soils, streams, and groundwater. Thus, Cr will be accumulated in soils. Its presence could be regarded as one of potential largest environmental risks due to the deposit/precipitation of Cr-contaminants, especially emerged in the soils close to Cr mines areas (Desjardina et al., 2002). Therefore, there was an urgent need to pay the efforts on investigating the transformation of Cr from soil–water systems as seeking the feasible remediation on Cr pollution in the environment (Teng et al., 2013).

In general, the main species of Cr were presented with trivalent (Cr(III)) and hexavalent (Cr(VI)). Cr(VI) is highly soluble and toxic. However, the reduced form, Cr(III), is relatively in soluble and in a low toxicity (Arias and Tebo, 2003). In alkaline

* *Corresponding author*. E-mail: wypp@xmu.edu.cn (Yuanpeng Wang).

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soils, such as the soil from Cr mine, the predominant state is hexavalent Cr(VI) and existed with the form of CrO_4^{2-} and $Cr_2O_7^{2-}$ (Døssing et al., 2011). In soil–water systems, microorganisms play important roles in the transformation of Cr(VI) and Cr(III). Recently, microbial mediation on the transformation of Cr(VI) in soil–water systems has been well studied (Samuel et al., 2012; Wang and Shen, 1995). Many microorganisms could directly reduce Cr(VI), such as *Proteobacteria*, *Shewanellaalga*, *Bacillus* spp., and several new isolated bacterial (Basu et al., 1997; Garavaglia et al., 2010; Shen and Wang, 1993). Guha et al. (2001) have found that oxygen could also serve as electron acceptors and subsequently competed with Cr(VI) in the systems containing high Cr(VI) concentrations. Moreover, Cr(VI) in estuarine soils was reported to be permanently reduced to Cr(III) under anaerobic conditions (Wadhawan et al., 2013). The regarding surveys illustrated that some limited factors, such as oxygen and electron donors, affected the bio-mediated process on the speciation and mobilization of Cr(VI) from soil.

Some materials, such as carbon sources, electron shuttles, and iron minerals affect Cr(VI) transformation under anaerobic conditions (Field et al., 2013). Further, given the extensive use of nanoparticles (Xu et al., 2012) recently, large amounts of nanoparticles have now been released into aquatic environments and soil systems. It will lead to an unexpected ecological and environmental outcome because of the unique physical and chemical properties of nanoparticles (Jiang et al., 2013; Zhu et al., 2016). Therefore, it is critical to explore how nanoparticles affect soil microbial communities, and the potential effects on Cr(VI) transformation. Additionally, the recent studies have demonstrated that nanoparticles facilitated extracellular electron transfer in microbial fuel cells and soil systems. The addition of magnetite nanoparticles into soils seemed to increase the activity of methanogens through shifting the microbial abundances of acetate-oxidizing bacteria, propionate-oxidizing bacteria, and methanogenic archaea (Yamada et al., 2015; Cutting et al., 2010). Because nanoparticles might potentially influence the microbes directly (*e.g.*, *via* serving as electron shuttles to transport electrons), the possible mediating effects derived from of iron oxide nanoparticles on Cr(VI) reduction should deserve to be studied. For instance, Rao et al. (2013) has demonstrated that a more significant modification to the yeast cells in presence of phyto-inspired Fe^0/Fe_3O_4 nanoparticles during Cr(VI) reduction than in absence of Fe^0/Fe_3O_4 nanoparticles. In addition, nanoscale zero-valent iron and biogenetic nano-magnetite were capable of removing aqueous Cr(VI) from alkaline groundwater (Watts et al., 2015; Liu et al., 2010; Li et al., 2011). Although there have been studies showing that iron oxide nanoparticles mostly affected Cr(VI) reduction process, there was no clear evidence regarding roles of nanoparticles during Cr(VI) reduction in soil (Singh et al., 2012). Exactly, our previous study demonstrated that the addition of nano-sized Fe_2O_3, Fe_3O_4 and SiO_2 could potentially stimulate bacterial growth, and then changed the arsenic transformation in soil (Dong et al., 2014). Furthermore, Kato et al. (2010) reported that nano-sized Fe_3O_4 and nano zero valent iron oxide could also be used as electron conduits to dramatically improve microbial extracellular electron transfer in soil. Therefore, iron oxide nanoparticles, for example nano-sized Fe_3O_4, may influence microbial respiratory of Cr(VI) in soil–water systems. However, there was severely poor studies could powerfully illustrate how nano-sized Fe_2O_3/Fe_3O_4 shift the microbial community composition during the process of Cr(VI) transformation.

Hence, the study presented the aims to investigate Cr(VI) transformation from Cr-contaminated soil–water systems in presence of nano-sized or submicro Fe_2O_3/Fe_3O_4, particularly emphasizing on the role of nano-sized Fe_2O_3/Fe_3O_4. Additionally, microbiota in soil sample was analyzed by denaturing gradient gel electrophoresis (DGGE) and using pyrosequencing after treatment of nano-sized Fe_2O_3/Fe_3O_4. Finally, the involving mechanisms regarding nano-sized Fe_2O_3/Fe_3O_4 affecting Cr(VI) transformation and microbial communities in soil were committed to be illuminated.

1. Experimental

1.1. Test site

Cr-contaminated soil samples were collected from a tailings at a Cr-enriched mine area in Qujing, Yunnan Province, China. The total Cr content in the experimental samples used was 12,202.5 mg/kg (Granadlllo et al., 1994). The initial water-extraction Cr(VI) concentration in soil was 750 mg/kg and the initial water-extraction Cr(VI) concentration of each reactor was 325 mg/kg (Padarauskas et al., 1998). Content of other elements were negligible in soil. The pH of the soil was 8.9.

Soil samples from tailings were carefully collected and stored in sterile polyethylene bags and transported to the laboratory. Those not-dried samples to permitted for the microbiological analysis and used for the batches of soil microcosms culture incubation. The remained moist soil samples from tailings were stored in polyethylene vinyl containers at 4°C to maintain the original environment and survival of indigenous bacteria.

1.2. Sample preparation and treatment

Nano-sized Fe_2O_3 (30 nm)/Fe_3O_4 (20 nm) and submicro Fe_2O_3/Fe_3O_4 were purchased from Aladin company. The morphology of the above particles was characterized by scanning electron microscopy (SEM) (Appendix A Fig. S1). The specific surface area of nano-sized Fe_2O_3, nano-sized Fe_3O_4 submicro Fe_2O_3 and submicro Fe_3O_4 were 108.44m^2/g, 8.92m^2/g, 1.05m^2/g and 0.04m^2/g, respectively. All experimental operations were conducted under obligate anaerobic conditions. The treatment conditions were set up as follows: (1) anaerobic, 20 ± 1 g soil, treated with 0.2 g of submicro Fe_2O_3/Fe_3O_4 and 24 mL deionized water; (2) anaerobic, 20 ± 1 g soil, treated with 0.2 g of nano-sized Fe_2O_3/Fe_3O_4 and 24 mL deionized water; and (3) anaerobic, 20 ± 1 g soil, treated with 24 mL deionized water. In order to clarify if Cr(VI) could be abiotically reduced, another triplicate anaerobic samples with same amendments were incubated under the abiotic condition. The sterile treatments were autoclaved at 120°C for 20 min. The mixture of soil/water slurries were placed in 105 mL serum bottles, bubbled with N_2 for 30 min, fitted with a butyl rubber stopper, sealed with an aluminum clamp under an N_2 atmosphere, and finally incubated at 30°C in the dark. Soil microcosms were subsampled at discrete time points.

In the other experiments exploring the adsorption of Cr(VI) to nano-sized or submicro Fe_2O_3/Fe_3O_4, 100 mg/L Cr(VI)(K_2CrO_4)

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