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Feasibility of nanoscale zero-valent iron to enhance the removal efficiencies of heavy metals from polluted soils by organic acids

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ABSTRACT

Soil washing with natural chelators to remediate metal-contaminated soils has been gained attention by researchers. However, the abilities of the chelators to remediate the multiple metal polluted soils are less effective. This study employed zero-valent iron nanoparticle (nZVI) to enhance the removal efficiencies of citric (CA), tartaric (TA) and oxalic acids (OA), and evaluate their feasibility. Results showed that metal removal efficiencies increased with the increasing concentration of nZVI and soil-liquid ratio, decreased with the increasing solution pH. The kinetic simulation indicated that pseudo-first-order and pseudo-second-order models could be used for describing the washing processes. Additionally, metal removals were significantly improved by addition of nZVI ($p < 0.05$). The highest enhancements of soil Cd, Pb and Zn removals under solution pH of 4.0, soil-liquid ratio of 1:20 and washing time of 120 min reached 12.83% (OA- nZVI), 24.92% (CA-nZVI) and 11.64% (OA- nZVI) for mine soil, and 19.24% (TA- nZVI), 18.16% (CA-nZVI) and 8.93% (OA- nZVI) for farmland soil, respectively. After soil washing, the exchangeable forms and the environmental risks of residual metals were markedly diminished in soils. Therefore, the combinations of the organic acids and nZVI are the feasible practices to repair the soils contaminated by heavy metals.

1. Introduction

Environmental problems with increasing organic pollutants and heavy metals have become more frequent and complex in recent decades (Mukhopadhyay et al., 2016; Rizwan et al., 2016; Cao et al., 2017), which are toxicity and constitute with deleterious effects to human health (Jean-Soro et al., 2012; Udovic and Lestan, 2012; Freitas et al., 2013; Egorova and Ananikov, 2017). Available treatment processes for the removal of these contaminants from water or soil include adsorption (Pu et al., 2017a, 2017b; Suzaki et al., 2017), microbial remediation (Pu et al., 2014), stabilization (Mignardi et al., 2012), soil washing (Yan and Lo, 2012) and phytoremediation (Zhang et al., 2013). Among them, soil washing is often an alternate available for the permanent removal of soil metals by physical and/or chemical procedures (Dermont et al., 2008; Sierra et al., 2014; Xu et al., 2014), particularly highly contaminated soils with multiple heavy metals (Hu et al., 2014; Kulikowska et al., 2015; Yi and Sung, 2015).

Aminopolycarboxylate chelants such as EDTA have been commonly tested in the soil washing process due to its strong ability to form metal-ligand coordination compounds (Hasegawa et al., 2010; Finzgar et al., 2014; Qiao et al., 2017). However, EDTA is poorly photo-, chemo- and biodegradable (Bucheli-Witschel and Egli, 2001; Wen et al., 2009), and can form stable complexes with metals (Nowack, 2002; Guo et al., 2016), as it may persist for a longer period in soil environment (Jez and Lestan, 2016). Therefore, searching for the eco-friendly alternatives instead of traditional aminopolycarboxylate chelants is highly recommended.

Organic acids, including citric, tartaric and oxalic acids, are natural chelators (Ettler et al., 2009; Ren et al., 2015; Yoo et al., 2018). They are easily biodegradable in soil suspension (Wang et al., 2014) owing to their possible origin from the degradation of organic matter, microbial metabolism and plant root exudates (An et al., 2011; Yin et al., 2018). Thus, some researchers have employed the organic acids to substitute aminopolycarboxylate chelants to repair heavy metal contaminated soil (Astuti et al., 2016). However, their abilities to remove soil heavy metals are less effective (Wen et al., 2009; Chen et al., 2016). Therefore, it is of importance to improve the removal efficiency of heavy metal by organic acids.

Nanomaterials such as zero-valent iron nanoparticle (nZVI) have larger specific surface area and high reactivity (Su et al., 2012;

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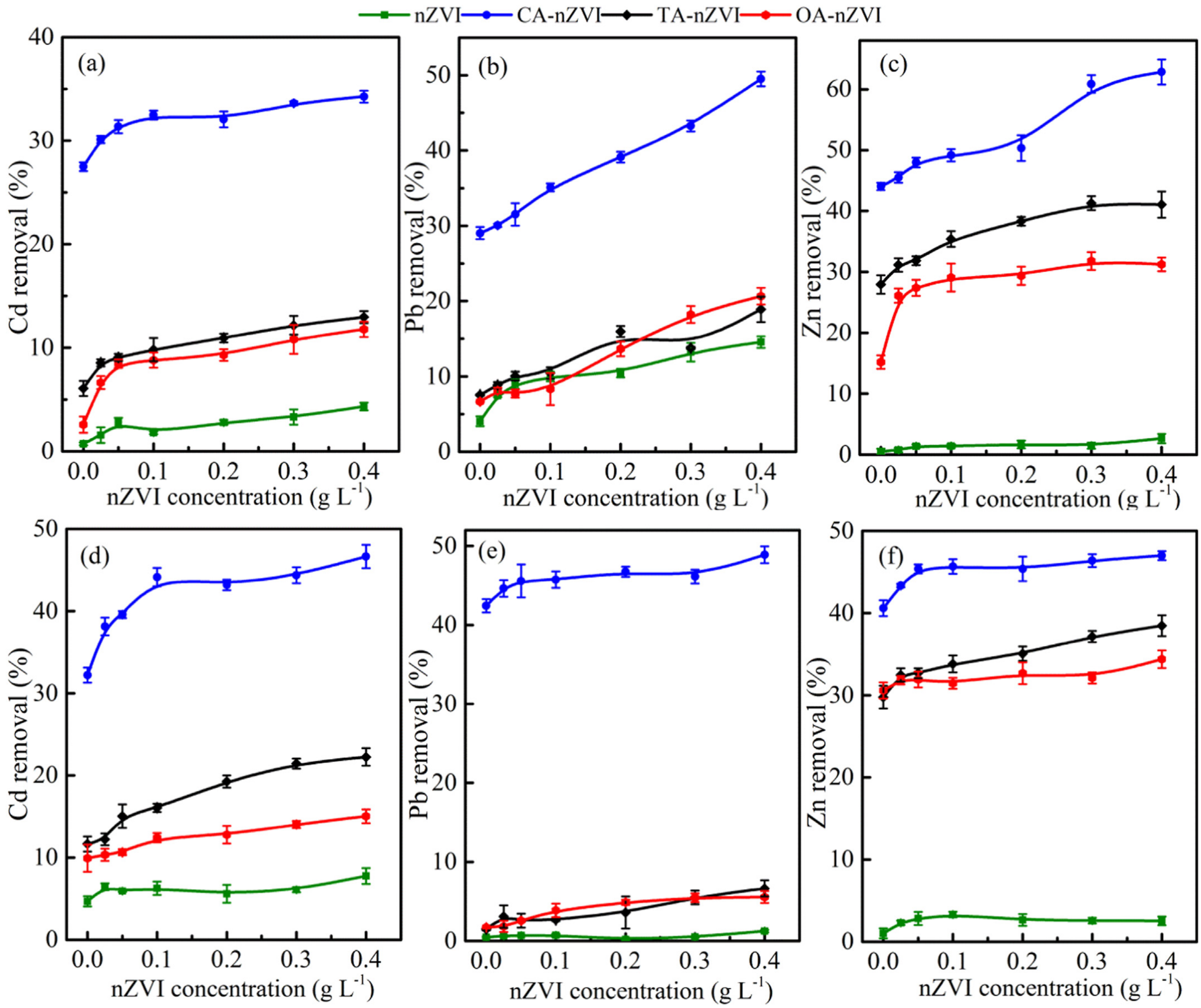

Fig. 1. Effects of nanoscale zero-valent iron (nZVI) concentration on the Cd, Pb and Zn removal efficiencies from mine (a, b and c) and farmland soils (d, e and f) combined with various organic acids. (nZVI, washing with nZVI alone; CA-nZVI, washing with mixed solution of 0.2 M citric acid and nZVI; TA-nZVI, washing with mixed solution of 0.2 M tartaric acid and nZVI; OA-nZVI, washing with mixed solution of 0.2 M oxalic acid and nZVI; Values represent mean ± standard deviation of three replicates).

Machado et al., 2013; Pu et al., 2017a, 2017b). Recently, although considerable researches have been devoted to applying nZVI to remediate organic and inorganic contaminants, especially halogenated hydrocarbons and heavy metals in surface and ground water (Wei et al., 2012; Gil-Díaz et al., 2017; Boente et al., 2018; Vítková et al., 2018), rather less attention has been paid to investigate its application to combine with organic acids for the removal of soil heavy metals. It would thus be of interest in understanding the possibility of their combination for soil washing.

This paper examined the applicability of nZVI to enhance organic acids for remediation of contaminated soil by heavy metals. Our objectives were: (i) to examine the effects of nZVI concentration, solution pH, soil-liquid ratio and washing time on the removals of soil Cd, Pb and Zn by citric, tartaric and oxalic acids; (ii) to determine the fractions of heavy metals in soils before and after washing by the organic acids with the aid of nZVI; (iii) to assess the potential ecological risk of remaining heavy metals to ecosystem.

2. Materials and methods

2.1. Soil sampling and washing agents

Two different metal-contaminated soils in Hanyuan, Sichuan, China: soil A with 18.47 mg kg^{-1} Cd, 745.06 mg kg^{-1} Pb, and 1599.17 mg kg^{-1} Zn was collected from 0 − 20 cm layer at Fuquan Pb-Zn Mine; and soil B with 11.06 mg kg^{-1} Cd, 818.42 mg kg^{-1} Pb, and 1506.25 mg kg^{-1} Zn was taken from the surface layer (0–20 cm) of a waste farmland near Tangjia Pb-Zn Mine. Soil sample was stored and homogenized in polypropylene bottle after being air-dried, ground and sieved using the 2-mm mesh. The concentrations of target heavy metals were determined by atomic absorption spectrophotometer (AAS, Thermo Solaar M6, Thermo Fisher Scientific Ltd., USA) following the *aqua regia* extraction method. In order to ensure accuracy and precision in the analysis, reagent blank and analytical duplicates were also used where appropriate.

Based on our preparation experiment, organic acid concentration in this study was chosen 0.2 M under the consideration of the removal