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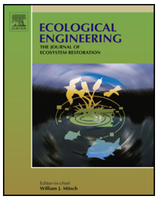

Removal of mixed contaminants Cr(VI) and Cu(II) by green synthesized iron based nanoparticles

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In this study, iron based nanoparticles (Fe NPs) synthesized by *eucalyptus* leaf extracts was used to remove mixed Cr(VI) and Cu(II), where the efficiency was 58.9% and 33.0%, respectively. In contrast, only 20.2% of Cr(VI) and 11.8% of Cu(II) were removed by adsorption using *eucalyptus* leaf extracts. In addition, the removal mechanism for mixed Cr(VI) and Cu(II) based on both adsorption and reduction by Fe NPs was confirmed by various characterization techniques, including the formations of Fe NPs, iron oxides and capping layer. Furthermore, the kinetics suggested that firstly, their sorption followed the pseudo second-order model well; and secondly, reduction of Cr(VI) and Cu(II) followed the pseudo-first-order model well. Finally, Fe NPs not only removed Cr(VI) and Cu(II), but also Pb(II) and Zn(II) in electroplating wastewater. This provides a new insights into the removal of metal ions using green Fe NPs with a low cost and environmentally friendly remediation strategy.

1. Introduction

Heavy metals have become a key environmental issue because of its toxicity, bioaccumulation and persistence (Fu and Wang, 2011). Industrial effluents discharged from extracting, leather tanning, mining, electroplating, and paper manufacturing industries contain high concentrations of Cr(VI) and Cu(II) (Ko et al., 2011). Cr(VI) as a metalloid is toxic and highly soluble and mobile in soils (Zhong et al., 2014; Carroll et al., 2013), while Cu(II) causes detrimental and dangerous outcomes (Zhong et al., 2014; Carroll et al., 2013). Hence, given the strong dependence of Cr and Cu mobility and toxicity on its redox state, developing new remediation technologies such as the removal of mixed metalloid Cr(VI) and metal Cu(II) by nanoscale zero-valent iron (nZVI) is of significant interest (Carroll et al., 2013).

In recent years, nZVI has been used in groundwater and site remediation due to its high intrinsic reactivity of its surface sites (Carroll et al., 2013). NZVI has been employed to remove metal ions such as Pb(II), Cd(II), Cu(II), Co(II), As(III) and Cr(VI) (Cai et al., 2014; Shahwan et al., 2010). To date, most work have focused on the removal of a single metal ion rather than the removal of mixed metals and metalloids. This is due to the fact that the specific removal mechanisms involved in the removal of heavy metals with nZVI depend on the standard redox potential of the metals(Carroll et al., 2013). However, the simultaneous removal of contaminants such as metalloid Cr(VI) and metal Cu(II) ion by nZVI in aqueous solution is a challenge due to the different physical and chemical properties of Cr(VI) and Cu(II) (Zhong et al., 2014; Carroll et al., 2013). Understanding the influence of Cr(VI) on the removal of Cu(II) by nZVI is important since heavy metals are often found as mixed waste at hazardous sites. The metal co-contaminants undergoing redox reactions may enhance or hinder the removal of another metal ion by nZVI. Furthermore, while nZVI can be readily synthesized with chemical and physical methods, the drawbacks of these methods include consumption of large amounts of energy, use and high cost of toxic chemicals, and the aggregation of iron nanoparticles (Fe NPs) into chain-like structures, which is one of their well-known characteristics (Weng et al., 2013).

These issues can be addressed by green synthesis of Fe NPs using plant extracts (Mittal et al., 2013), where biomolecules in plant extracts such as polyphenols serve as reducing and capping agents to prepare well-dispersed Fe NPs (Huang et al., 2014; Wang et al., 2014). The *eucalyptus* leaf extracts for the preparation Fe NPs have been investigated by previous studies since *eucalyptus* leaf extracts contain aldehydes, phenols, amines and alkanes which serve as reducing and capping agents (Machado et al., 2013). In our previous work, Fe NPs were successfully synthesized using

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tea extracts and have been employed to degrade malachite and monochlorobenzene in aqueous solution (Huang et al., 2015; Kuang et al., 2013). Furthermore, green synthesis of Fe NPs using eucalyptus leaf extracts was utilized for the treatment of eutrophic wastewater and Direct black G in aqueous solution (Wang et al., 2014; Zhuang et al., 2015). To date, most of green synthesis of Fe NPs has been used for the removal of a single metal ion rather than the removal of mixed heavy metal despite the removal of As(III) and Cr(VI) from aqueous solutions using "green" zero-valent iron nanoparticles produced by oak, mulberry and cherry leaf extracts have been reported recently. In addition, the green synthesis of Fe NPs using eucalyptus extracts provides a simple, cost-effective, and eco-friendly solution to environmental remediation. For these reasons, the removal of mixed Cr(VI) and Cu(II) using Fe NPs synthesized by eucalyptus extracts could be a potential technique for site remediation as it is simple, cost-effective, eco-friendly and sustainable. To achieve the aims, the following aspects are included (1) the characterization of Fe NPs before and after removal of Cr(VI) and Cu(II); (2) the investigation of impacting factor on the removal efficiency such as pH and temperature; and (3) the corresponding kinetics and isotherms for removal of Cr(VI) and Cu(II) by Fe NPs.

2. Experimental

2.1. Materials and chemicals

Ferrous sulfate ($FeSO_4{\cdot}7H_2O$), potassium dichromate ($K_2Cr_2O_7$) and copper chloride dehydrate ($CuCl_2{\cdot}2H_2O$) were obtained from Tianjin Chemical Reagent Co. (China). They were all of analytical reagent grade and used in this study without further purification. Eucalyptus leaves were obtained from a local farm in Fuqing, China. All aqueous solutions were created using distilled water.

2.2. Green synthesis of Fe NPs

The green synthesis of Fe NPs using eucalyptus leaf extracts has been described previously (Wang et al., 2014). In this work, eucalyptus leaf extract (ELE) was prepared by heating 50 g/L eucalyptus leaves at 80 °C for 2 h. After cooling to room temperature, the extract was vacuum-filtered. Fe NPs were synthesized by adding 0.05 M $FeSO_4$ solution to the ELE in a 1:2 volume ratio at room temperature. The formation of Fe NPs was marked by the appearance of black precipitate which indicated the reduction of Fe^{2+} ions.

2.3. Characterizations and methods

SEM images of Fe NPs before and after removal of Cr(VI) and Cu(II) were determined using JSM-7500F SEM instrument (JEOL Ltd. Co., Tokyo, Japan) with an accelerating voltage of 5 kV. The elemental composition of Fe NPs before and after removal of Cr(VI) and Cu(II) was carried out with spectroscope (Oxford Instruments, UK) attached to SEM.

XRD patterns of Fe NPs before and after removal of Cr(VI) and Cu(II) were conducted in ambient air with Cu-Kα using a Philips-X'Pert Pro MPD (Netherlands) operated at 40 kV and 40 mA; continuous scans from 5° to 70° 2θ were done with 3° 2θ per minute.

XPS measuring the surface composition and chemical oxidation state of Fe NPs after removal of Cr(VI) and Cu(II) within a depth of <10 nm was carried out on a Thermo Scientific (ESCALAB 250, X-ray photoelectron spectrometer). All binding energies were referenced to the neutral C 1s peak at 284.6 eV to compensate for the surface charging effects.

FTIR spectra of ELE, Fe NPs before and after removal of Cr(VI) and Cu(II) were determined by a Fourier transform infrared spectroscope (FTIR Nicolet 5700, Thermo Corp., U.S.A.). Samples for FTIR measurement were prepared by mixing 1% (w/w) specimen with 500 mg of KBr powder and pressed into a sheer slice. A spectral resolution of 2 cm^{-1} and an average of 32 scans was used for each measurement.

2.4. Batch experiments

The simultaneous removal of Cr(VI) and Cu(II) from the aqueous using functional Fe NPs was investigated in batch removal experiments. Batch experiments were carried out with ELE and Fe NPs samples (both 0.5 g/L of dry matter) with Cr(VI) and Cu(II) concentration of 15 mg/L at 298 K in shake flasks on a rotary shaker at 250 rpm under the initial pH 5.0 with the pre-selected time intervals. The influence of the initial solution pH value was investigated using the pH value range 3.0-7.0 while the influence of temperature was analyzed with the temperature range 288–308 K. Adsorption isotherms were obtained by adding 0.5 g Fe NPs to aqueous solutions with different initial Cr(VI) and Cu(II) concentrations in range of 3.75–30 mg/L under the temperature range 288–308 K and the reaction time was 60 min. The volume of all reaction mixtures were 25 mL and all these experiments were carried out in duplicate. Samples were taken at certain time intervals, filtered with a 0.45 μm filter paper. The residual Cr(VI) in solution was determined using the 1,5-diphenylcarbazide method with a 722 N visible spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd) at wavelength of 540 nm and the residual Cu(II) concentrations using atomic absorption spectrometer (AAS, VARIAN AA240, U.S.A.) (Shi et al., 2011; Üzüm et al., 2009).

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

Where C_0 and C_t are the initial and after t min treatment of the concentration of metal ions, respectively. The removal efficiency ($R(\%)$) of metal ions was calculated using Eq. (1). The amount of metal ions adsorbed per unit mass of the adsorbent, q (mg/g), was computed using the expression: $q = (C_0 - C_t)/m$, where C_0 was the initial concentration of metal ions and C_t (mg/L) represented the concentration of metal ions after t min treatment, and m (g) is the amount of adsorbents in 1 L of co-existing Cr(VI) and Cu(II) solution. The removal efficiency ($R(\%)$) of co-existing Cr(VI) and Cu(II) was calculated using Eq. (1).

The electroplating wastewater was supplied by an electroplating factory's sewage outfall (Fuzhou, China). The initial concentrations of the total Cr, Cu(II), Pb(II) and Zn(II) in the electroplating wastewater recorded 10.5, 12.1, 3.5, and 18.5 mg/L, respectively. A batch of 50 mL shake flasks containing 25 mL electroplating wastewater and 0.0125 g Fe NPs were mixed on a rotary shaker at 250 rpm under 298 K for 12 h. Samples were then filtered using a 0.45 μm filter paper and analyzed for residual metal ion concentrations.

2.5. Adsorption kinetics

Parameters from two kinetic models, including pseudo first-order and pseudo second-order, have generally been employed to describe adsorption kinetics in solid-liquid systems. The adsorption rate can be described using the pseudo first-order model, and is expressed as follows (Boparai et al., 2011; Poguberović et al., 2016):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

Where q_e and q_t (mg/g) represent adsorption value of Cr(VI) and Cu(II) ions in aqueous solutions at equilibrium and at time t (min), respectively, and k_1 is the first-order equilibrium constant which calculated the plot of $ln(q_e\text{-}q_t)$ against t.