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Investigation on the removal of Mo(VI) from Mo–Re containing wastewater by chemically modified persimmon residua

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ABSTRACT

Persimmon waste was chemically modified by crosslinking with concentrated sulfuric acid to obtain a novel kind of adsorption gel, which was termed as crosslinked persimmon tannin (CPT), hereinafter. The adsorption behaviors of Mo(VI) with other coexisting metal ions onto the CPT gel were investigated. The gel exhibited selectivity only for Mo(VI) ions evidenced by the high value of separation factor of molybdenum and rhenium ($\beta_{Mo/Re}$ = 164.37), and the adsorption mechanism of Mo(VI) as a multispecies was studied. The molybdenum adsorption behavior conforms to the Langmuir model with a remarkably high adsorption capacity of 0.56 mol/kg. A kinetic study for the adsorption of molybdenum at various temperatures confirmed that the endothermic adsorption process followed pseudo-second order kinetics. Moreover, its excellent adsorption properties and applicability for Mo(VI) were demonstrated by the removal and separation of Mo(VI) from different Mo–Re containing industrial wastewaters.

1. Introduction

Molybdenum is an important and strategic metal in human life and industry. Even though it is used in petrochemical industries as catalyst (Zeng and Cheng, 2009a) the widespread application of molybdenum is found in steel industries as an alloying agent. As a typical transition element, molybdenum is also used in electron tubes, vacuum tubes, heat-resistant materials and high-strength steel alloys (Sutulov, 1970). However, molybdenum and its compounds are highly toxic and can cause fatal deformities, for example, molybdenum of more than 10 ppm will endanger most livestock (Reddy and Hasfurther, 1989). Some evidences of liver dysfunction with hyperbilirubinemia have also been reported in workmen chronically exposed in a Soviet Mo–Cu plant. Signs of gout have also been found in factory workers exposed to occupational molybdenum exposure and among inhabitants of Mo-rich areas (Selden et al., 2005). Therefore, it is important to study the factors on the molybdenum uptake in cases where molybdenum may be transferred into surface or ground waters.

Rhenium, on the one hand, is a rare metal with high melting point and is extensively used in metallurgy, military, chemical and petrochemical industries. In addition, rhenium does not occur naturally and no mineable ore has been found either. It always exists in pegmatites, rocks altered by pneumatolysis, and especially in molybdenites. It is recovered through roasting or direct reduction of the concentrates in molybdenite (Sutulov, 1970). In general, it is difficult to separate molybdenum from rhenium in an aqueous solution, because of their similar chemical properties.

Although a number of solvent extraction reagents, ion exchange materials and sorbents have been reported in literatures and also commercially employed for separation of molybdenum and rhenium at present (Jordanov et al., 1968; Karagiozov and Vasilev, 1979; Zhang et al., 1993; Kim et al., 2004; Valverde et al., 2008; Elwakeel et al., 2009; Mashkani et al., 2009; Cao et al., 2009), the search for environmentally benign and cost effective method for rare metals recovery is in progress (Kapoor and Viraraghavan, 1995; Park et al., 2006; Ngah and Hanafiah, 2008; Beolchini et al., 2010; Zhao et al., 2010). Persimmon wastes or other type of tannin were reported to be able to adsorb metals in aqueous systems (Palma et al., 2003; Minamisawa et al., 2005; Adhikari et al., 2008). The major component of persimmon waste is tannin, which contains a large number of poly-phenolic groups in the form of catechol and pyrogallol, which have high affinity to metal ions. Nakajima et al. reported that the persimmon tannin gel can adsorb vanadium and hexavalent chromium effectively, but less effectively for trivalent chromium (Nakajima, 2002; Nakajima and Baba, 2004). Ogata and Nakano (2005) synthesized a novel tannin gel from natural tannin cross-linked by formaldehyde to adsorb gold. Formaldehyde was reported to be a cross-linking reagent to prepare tannin gels for adsorption of lead and copper (Sengil and Ozacar, 2008; Ozacar et al., 2008). In our previous

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work, dimethylamine functional group was grafted onto persimmon waste gel, and it was found that the modified persimmon waste gel exhibited high affinity for precious metals like palladium and platinum (Xiong et al., 2009). In the present work, persimmon residua, a natural biomaterial, was utilized to develop a low-cost, environment friendly, and effective adsorption gel. Its selectivity and adsorption properties for the removal and separation of Mo(VI) from rhenium in aqueous system will be studied.

2. Experimental

2.1. Materials

Chloride salts of copper, lead, calcium, iron, zinc, manganese and nickel were used to prepare test solutions of the respective metals. Rhenium and molybdenum stock solutions were prepared by dissolving NH_4ReO_4 and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, respectively, in hydrochloric acid. All reagents were of analytical grade and were used without further purification.

2.2. Preparation of cross-linked persimmon tannin gel

Persimmon residua material was kindly donated by Xinshan Biological Engineering Co. Ltd., China. Persimmon residua was dried for 24 h at 333 K and crushed to produce powder. The content of tannin in the powder was determined to be about 17.0%. The persimmon powder (9 g) was mixed with 30 mL of 96% H_2SO_4 as a cross-linking reagent and stirred for 24 h at 373 K in an oil bath to obtain a black particle product. The product was filtered, neutralized with sodium bicarbonate solution, and washed with distilled water until neutral pH. Such washing facilitates to wash out water soluble components from modified persimmon residua material. However it was dried for 24 h at 333 K and finally crushed to produce particles of 100–150 μm in diameter (hereafter abbreviated as CPT), which was used for carrying out all adsorption tests.

2.3. Batch adsorption studies

All equilibrium adsorption experiments were individually conducted at 303 K for Mo(VI), Re(VII), Cu(II), Pb(II), Ca(II), Fe(III), Zn(II), Mn(VII) and Ni(II) ions. Ten (10) mg of the CPT gel was mixed with 5 mL adsorbate solution (20 mg/L) at varying HCl concentrations in 25 mL flask. The flask was kept in a thermostated shaker at a speed of 180 rpm for 24 h. Adsorption kinetics for molybdenum were carried out by adding 10 mg of CPT gel in 5 mL Mo(VI) solution of concentration 20 mg/L (prepared in 1 mol/L hydrochloric acid) at varying temperature, e.g., 288, 303, 313 and 323 K. Percentage adsorption for adsorbate was calculated according to (Eq. 1):

$$\%A = \frac{(C_i - C_e)}{C_i} \times 100 \tag{1}$$

where C_i is the initial concentration of adsorbate and C_e stands for the equilibrium concentration measured after adsorption.

2.4. Analyses

The pH of the solution was measured by pH meter, while the concentrations of metal ions were measured by using PE model atomic absorption spectrophotometer and a DV 2000 ICP (Inductively Coupled Plasma) atomic emission spectrometer. FTIR spectra were recorded on a Nicolet 5700 FTIR spectrophotometer. Reproducibility of every datum was confirmed by repeating the same experiment three times and the average value was taken.

3. Results and discussion

3.1. Effect of hydrochloric acid concentration on the adsorption behavior of CPT gel

The adsorption behavior of the CPT gel for Mo(VI) along with other metal ions such as Re(VII), Cu(II), Pb(II), Ca(II), Fe(III), Zn(II), Mn(VII) and Ni(II) at varying hydrochloric acid concentrations is shown in Fig. 1a. A significant extent of adsorption of Mo(VI) over a wide range of hydrochloric acid concentration was achieved. Nearly maximum adsorption of molybdenum was found to occur at around pH 1 while the adsorption of Re(VII) was very low (0–4.6%) under the studied condition. Fig. 1a also showed that the adsorption of other metal ions such as Cu(II), Pb(II), Ca(II), Fe(III), Zn(II), Mn(VII) and Ni(II) decreased with the increase in hydrochloric acid concentration. A sharp decrease was observed at an ambient condition of 1 M hydrochloric acid. Thus, it is evident that the CPT gel has a high affinity for Mo(VI) and is selective toward its adsorption compared to Cu(II), Pb(II), Ca(II), Fe(III), Zn(II), Mn(VII) and Ni(II) at HCl concentration of 1 mol/L and higher. More importantly, rhenium and molybdenum, which have similar chemical behavior in aqueous solution and often found together in industrial effluent, could be also separated by using the CPT gel over the whole hydrochloric acid concentration region.

The separation factor, $\beta_{Mo/Re}$, is often used to evaluate the separation abilities. It is the distribution ratio of two metal ions measured under the same condition, which can be defined as $\beta_{Mo/Re} = D_{Mo}/D_{Re}$, where D_{Mo} and D_{Re} are distribution of molybde-

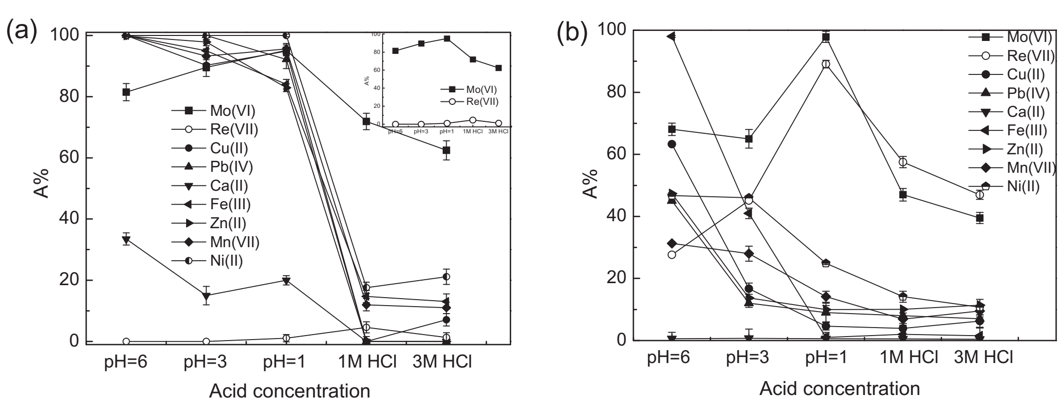

Fig. 1. Adsorption behavior of (a) the CPT gel and (b) activated carbon for various metal ions as a function of hydrochloric acid concentration. Initial concentration of metal ions = 20 mg/L, solid-to-liquid ratio = 2 g/L, temperature = 303 K.