Removal of heavy metal ions from aqueous solution using red loess as an adsorbent

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Abstract

The adsorption behaviors of heavy metals onto novel low-cost adsorbent, red loess, were investigated. Red loess was characterized by X-ray diffraction, scanning electron microscopy and Fourier transform infrared spectra. The results indicated that red loess mainly consisted of silicate, ferric and aluminum oxides. Solution pH, adsorbent dosage, initial metal concentration, contact time and temperature significantly influenced the efficiency of heavy metals removal. The adsorption reached equilibrium at 4 hr, and the experimental equilibrium data were fitted to Langmuir monolayer adsorption model. The adsorption of Cu(II) and Zn(II) onto red loess was endothermic, while the adsorption of Pb(II) was exothermic. The maximum adsorption capacities of red loess for Pb(II), Cu(II) and Zn(II) were estimated to be 113.6, 34.2 and 17.5 mg/g, respectively at 25°C and pH 6. The maximum removal efficiencies were 100% for Pb(II) at pH 7, 100% for Cu(II) at pH 8, and 80% for Zn(II) at pH 8. The used adsorbents were readily regenerated using dilute HCl solution, indicating that red loess has a high reusability. All the above results demonstrated that red loess could be used as a possible alternative low-cost adsorbent for the removal of heavy metals from aqueous solution.

Key words: red loess; adsorption; heavy metals

DOI: 10.1016/S1001-0742(10)60581-5

Citation: Xing S T, Zhao M Q, Ma Z C, 2011. Removal of heavy metal ions from aqueous solution using red loess as an adsorbent. Journal of Environmental Sciences, 23(9): 1497–1502.

Introduction

Heavy metal contamination is a serious problem that has attract worldwide attention. In general, heavy metals are not biodegradable and they tend to accumulate in living organisms, causing various diseases and disorders (Bailey et al., 1999). Heavy metals are often discharged by a number of industries including storage batteries, electroplating, metal finishing, mining, textile, ceramic and glass industries. Lead, copper and zinc are common contaminants of industrial wastewater. Various methods have been developed to remove heavy metals from water such as ion exchange, reverse osmosis and nanofiltration, precipitation, coagulation, solvent extraction and adsorption (Rousseau, 1987). Among them, adsorption is very popular due to its efficiency and low cost. An adsorbent must be eco-friendly, cost-effective, industrially viable and efficient for a wide range of concentration of different heavy metals. Active carbon (Srivastava et al., 2008), alumina (Vargas et al., 2004) and ferric oxides (Manceau et al., 1992) are the commonly used adsorbent in the treatment of wastewater due to their large specific surface area and high metal adsorption capacities. However, the high cost limits their use, especially in developing countries. Therefore, recent studies have focused on the search of a low-cost and efficient adsorbent.

In recent years, a wide variety of materials have been studied as low-cost adsorbents for the removal of heavy metals from water, such as fly ash (Nascimento et al., 2009), lignite (Ucurum, 2009), phosphate rock (Saxena and D'Souza, 2006), kaolinite-based clays (Hizal and Apak, 2006), red muds (Wang et al., 2008), sawdust (Sciban et al., 2007), loess soil (Wang et al., 2009), green algae (Gupta et al., 2001), and husk of wheat and rice (Aydin et al., 2008). Red loess is widely distributed in China and may be used as a low-cost adsorbent. However, the adsorption capacities of red loess towards heavy metals remain unknown.

The objective of this work is to evaluate the adsorption and desorption abilities of red loess for the removal of lead, copper and zinc from aqueous solution. The microstructure and composition of red loess were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectra (FT-IR). The effects of pH, contact time, adsorbent dosage, initial metal concentration and temperature on the removal of Pb(II), Cu(II) and Zn(II) were studied using kinetic and isothermal tests.

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1 Materials and methods

1.1 Materials

Red loess was collected from the suburban area of Shijiazhuang, China. The soil was dipped in distilled water for 10 hr, then washed several times and dried in an oven at 110°C for 10 hr. Finally, the sample was ground and sieved with a 100-mesh sieve, and then stored in a desiccator for further use. Pb(II), Cu(II) and Zn(II) stock solutions (1000 mg/L) were prepared by dissolving $Pb(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ (analytical grade) into deionized water, respectively.

1.2 Characteristics

The morphology and composition of the product were examined by a scanning electron microscope (S-570, Hitachi, Japan) combined with X-ray energy dispersive spectrometer (PV9900, EDAX, USA). Phase identification was carried out by powder X-ray diffraction (D8-ADVANCE, Bruker, Germany) using Cu $K\alpha$ radiation. Infrared spectra were recorded using a FT-IR spectrometer (1730, PerkinElmer, USA) with KBr disks at room temperature in the range of 4000–400 cm^{-1}.

1.3 Methods

1.3.1 Effect of pH

Red loess sample (1 g/L) and heavy metal solutions (25 mg/L, 30 mL) were put into PVC tubes. The initial pH values of the solutions were adjusted from 2.0 to 8.0 by adding dilute HCl or NaOH solutions. The sample tubes were then put into a gas bath constant temperature oscillator (HZQ-F160, China) at 240 r/min, 25°C for 4 hr. The solutions were then centrifuged, and filtered through a millipore filter (pore size 0.22 μm). The heavy metal concentrations were determined by the atomic absorption spectroscopy (180-70, Hitachi, Japan).

1.3.2 Effect of adsorbent dosage

The initial heavy metal concentrations were set at 25 mg/L (30 mL) and the adsorbent dosage ranged from 10 to 200 mg. The solution pH was controlled at 6.0 ± 0.5 by adding dilute HCl or NaOH solutions. The reaction temperature was maintained constant at 25°C and the reaction duration was 4 hr. Afterwards, the solutions were centrifuged and filtered for analysis.

1.3.3 Adsorption kinetics

The adsorbent dosage was 1 g/L and the initial heavy metal concentrations (C_0) were 25 mg/L. The solution pH was controlled at 6.0 ± 0.5 and the temperature was maintained at 25°C. The equilibration times were set increasing from 2 to 240 min. Samples were withdrawn at intervals and filtered through a millipore filter for analysis.

1.3.4 Adsorption isotherms at different temperatures and pH values

The adsorption isotherms of heavy metals on red loess were studied using batch tests at different temperatures (25 and 40°C) and pH values (4.0 and 6.0). The adsorbent dosage was 1 g/L and the initial heavy metal concentrations ranged from 10 to 300 mg/L.

1.3.5 Desorption

The used red loess in adsorption kinetics experiments were desorbed using 90 mL of 0.1 mol/L HCl solution. At given time intervals, samples were withdrawn and filtered through a millipore filter (pore size 0.22 μm) for analysis.

2 Results and discussion

2.1 Adsorbent characterization

The heterogeneity of the sample was observed in the SEM image (Fig. 1). The inorganic compositions of the adsorbent obtained by EDAX are the follows: Si (60.5 wt.%); Fe (25.1 wt.%); Al (6.2 wt.%); K (4.2 wt.%); Ca (3.3 wt.%); others (0.7 wt.%). As shown in Fig. 2, the XRD pattern of the sample was similar to that of kyanite (Al_2SiO_5) (Xu et al., 2008). The FT-IR spectrum of red loess (Fig. 3 line a) shows a wide adsorption band at 1035 cm^{-1}, which is attributed to the asymmetrical stretching vibration of Si–O–Si (Kim, 1997). The adsorption bands at 466 and 518 cm^{-1} are assigned to the bending vibration of Si–O–Al (Tabak et al., 2007). The above results indicated that red loess mainly consisted of silicate, ferric and aluminum oxides.

2.2 Effect of pH

The solution pH has a great influence on the adsorption process, which can determine the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. The effects of pH on the adsorption of Pb(II), Cu(II) and Zn(II) on red loess are shown in Fig. 4. The removal efficiencies increased remarkably with increasing pH. Maximum removal efficiency reached 100% for Pb(II)
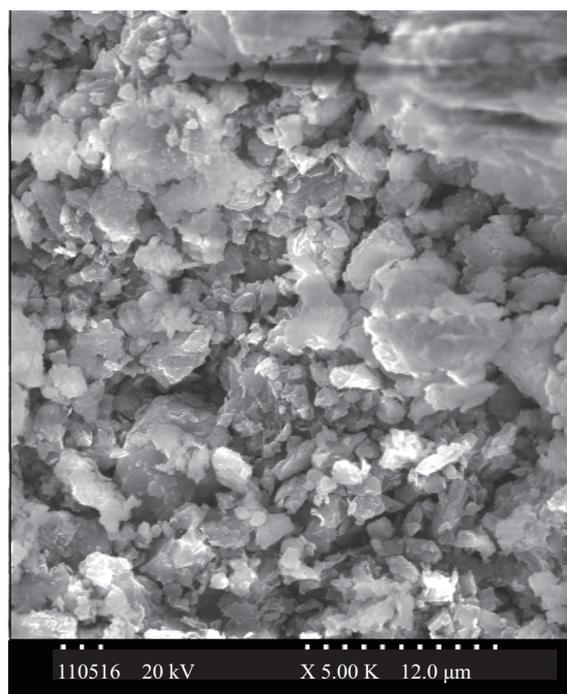

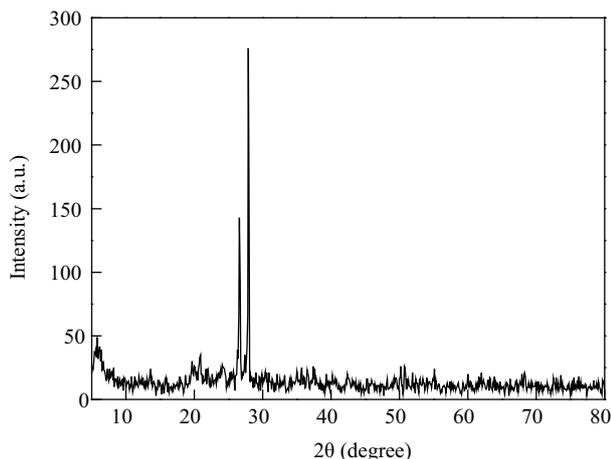**Fig. 1**　SEM image of the adsorbent.

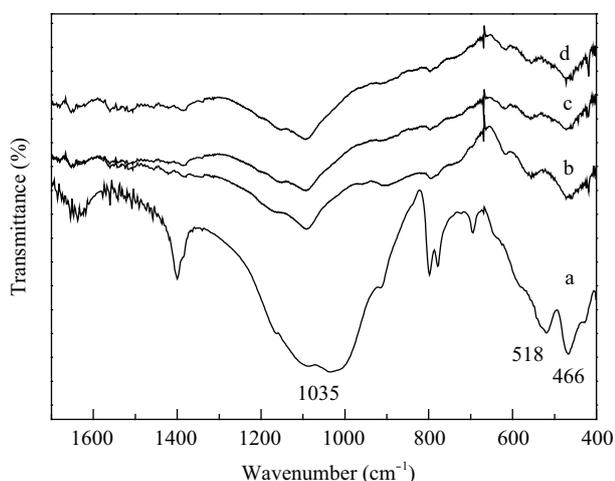**Fig. 2**   XRD pattern of the adsorbent.

Fig. 3   FT-IR spectra of the adsorbent before (line a) and after adsorption of Zn(II) (line b), Cu(II) (line c), and Pb(II) (line d).
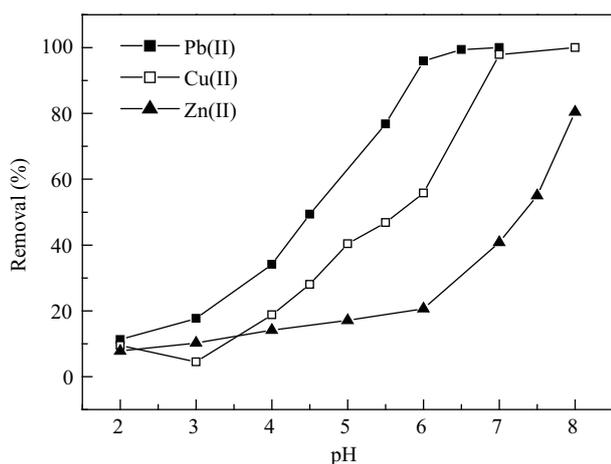

Fig. 4   Effect of pH on heavy metals adsorption on red loess.

at pH 7, 100% for Cu(II) at pH 8, and 80% for Zn(II) at pH 8. The analysis result indicated that the affinity of heavy metals towards adsorbent at pH 4–7 followed the order of Pb(II) > Cu(II) > Zn(II).

At low pH, the surface of the adsorbent was surrounded by H$^+$ ions, which prevented the metal ions from approaching the adsorptive sites of the adsorbent. However,
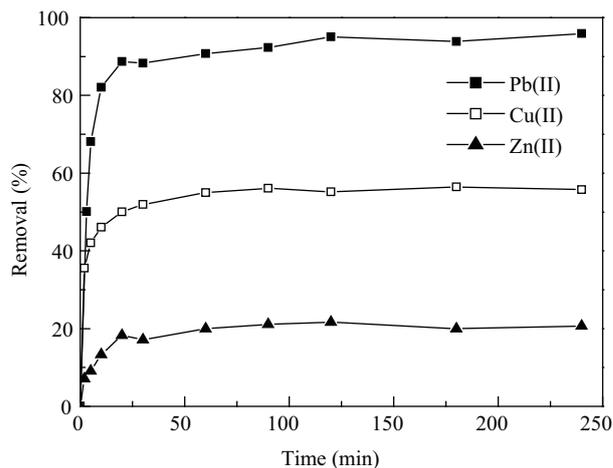

Fig. 5   Effect of contact time on heavy metals adsorption on red loess.

with increasing pH value, the competitive adsorption of H$^+$ ions decreased and the red loess surface became more negatively charged. Thus, the positively charged metal ions can be readily adsorbed onto the negatively charged sites of the adsorbent.

2.3 Adsorption kinetic studies

The equilibration time is an important parameter for economical wastewater treatment plant applications (Lin et al., 1998). Figure 5 shows the effects of contact time on the removal of Pb(II), Cu(II) and Zn(II). The adsorption of Cu(II) and Zn(II) sharply increased as a function of time up to 30 min at initial concentration of 25 mg/L and kept slowly increasing thereafter. The rate of adsorption of Pb(II) on red loess was more rapid than the others. About 89% of Pb(II) adsorption occurred within 20 min and reached equilibrium after 60 min. This result suggested that adsorption took place rapidly on the external surface of the adsorbent at the initial stage, followed by a slower internal diffusion process, which may be the rate determining step. Based on these results, the contact time was fixed at 4 hr to ensure the reaction equilibrium can be reached.

2.4 Effect of adsorbent dosage

The effects of adsorbent dosage on the removal of Pb(II), Cu(II) and Zn(II) are presented in Fig. 6. The maximum adsorption of Pb(II) was obtained for the adsorbent dosage of 30 mg (1 g/L). However, the adsorption of Cu(II) and Zn(II) on red loess kept slowly increasing with an increase in the adsorbent dosage. The removal efficiency increased by 23.3% for Pb(II), 50.1% for Cu(II) and 38.8% for Zn(II) (Fig. 6a), but the adsorption density decreased dramatically (Fig. 6b). The reason is that the number of available adsorption sites increased by increasing adsorbent dosage. While the decrease in adsorption density with increasing adsorbent dosage is mainly due to unsaturated adsorption sites through the adsorption reaction (Kadirveli and Namasivayam, 2003). Another reason may be owing to the particle interactions, such as aggregation, caused by high adsorbent concentration. Such aggregation would lead to a decrease in the total surface area of the adsorbent (Ramesh et al., 2007).
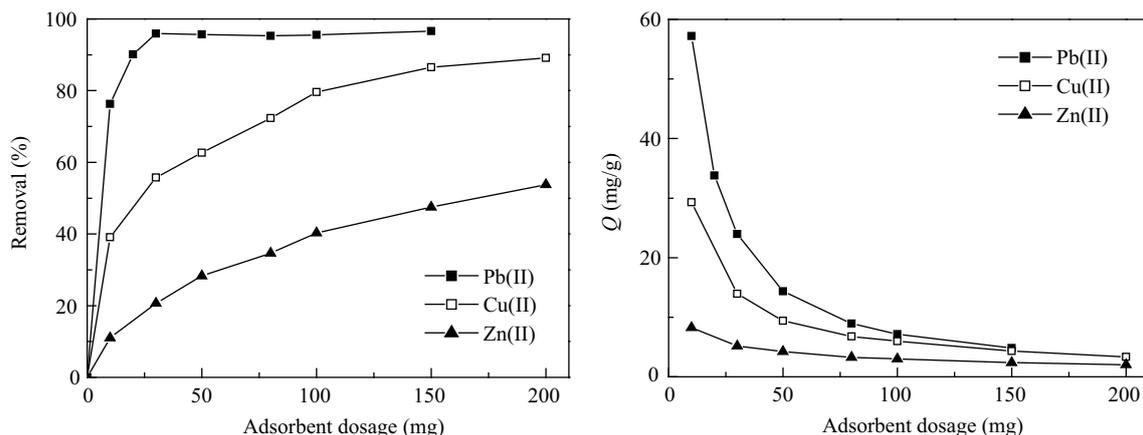
Fig. 6   Effect of adsorbent dosage on heavy metals adsorption on red loess.

2.5 Adsorption isotherms

Figure 7 shows adsorption isotherms of heavy metals on red loess at different pH and temperatures. The adsorption of heavy metals on red loess showed a gradual ascending trend and finally achieved a maximum adsorption amount with an increase in equilibrium solute concentration. The Langmuir isothermal equation was applied to evaluate the test data, and the results are listed in Table 1. At pH 6.0, the saturated adsorption amounts of Pb(II), Cu(II) and Zn(II) at 40°C were 0.96, 3.21 and 2.95 times as much as those at 25°C, respectively. The result demonstrated that the adsorption of Cu(II) and Zn(II) was endothermic, whereas the adsorption of Pb(II) was exothermic, which was consistent with the previous reports (Ho, 2003; Guo et al., 2009; Gupta et al., 2009). At 40°C, the adsorption capacities of Pb(II), Cu(II) and Zn(II) at pH 6.0 were 1.40, 6.78 and 1.04 times as much as those at pH 4.0. The result showed that the effect of temperature was less than that of pH for Pb(II) and Cu(II) in these experiments, whereas it was opposite for Zn(II).

2.6 Desorption study

The regeneration of adsorbent is an important step to make the adsorption process more economical. As shown in Fig. 8, the desorption of heavy metals was very fast and the equilibrium could be reached after 10 min. The desorption rates for Pb(II), Cu(II) and Zn(II) were 64.9%, 99.6% and 68.5%, respectively. Cu(II) was more readily desorbed and the desorption rate was above 99% when

Table 1   Predicted isothermal constants for Pb(II), Cu(II) and Zn(II).

Adsorbate	Temperature (°C)	pH	K (L/mg)	Q_{max} (mg/g)	r^2
Pb(II)	25	6.0	0.410	113.6	0.999
	40	6.0	0.094	108.7	0.986
	40	4.0	0.018	77.5	0.990
Cu(II)	25	6.0	0.040	34.2	0.950
	40	6.0	0.024	109.9	0.975
	40	4.0	0.038	16.2	0.915
Zn(II)	25	6.0	0.022	17.5	0.988
	40	6.0	0.018	51.5	0.952
	40	4.0	0.008	49.8	0.833

K (L/mg) is the equilibrium constant, Q_{max} (mg/g) is the maximum adsorption capacity of adsorbent, r^2 is the coefficient of determination.
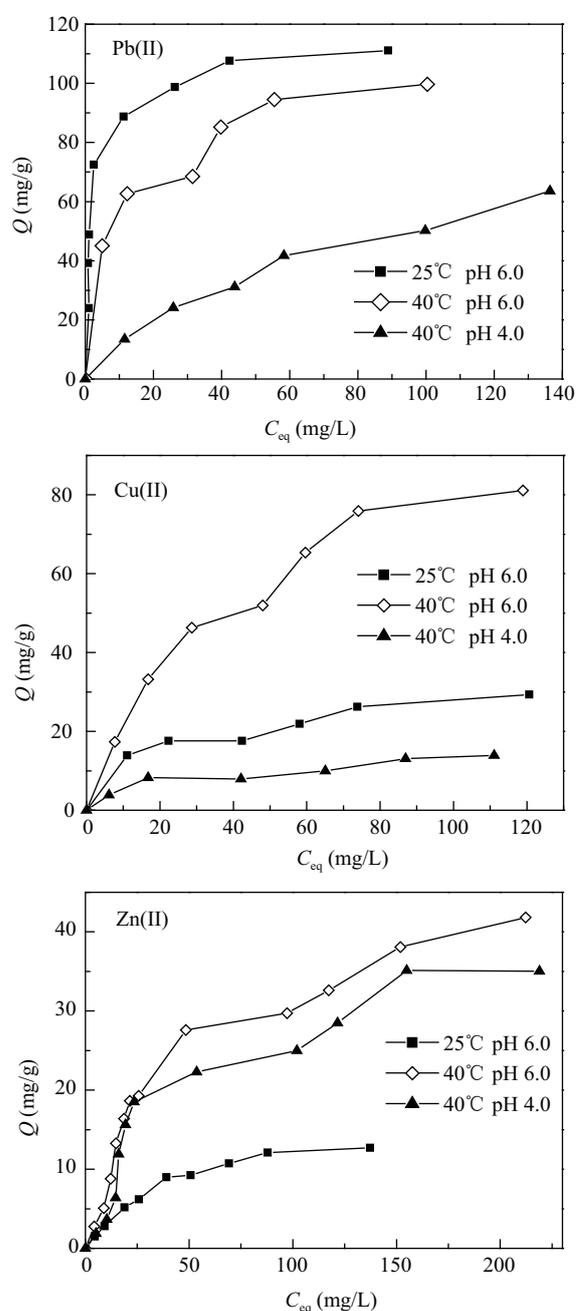

Fig. 7   Adsorption isotherms of Pb(II), Cu(II), and Zn(II) on red loess.
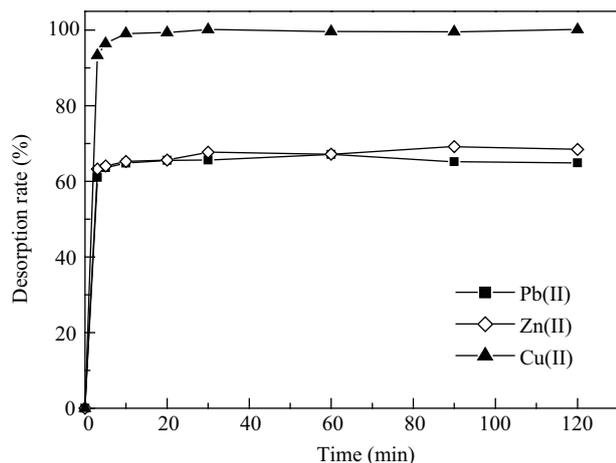
Fig. 8 Desorption kinetic curves of Pb(II), Cu(II) and Zn(II) on red loess.

the adsorbent was reused for three cycles. The desorption results indicated the red loess has a high reusability.

2.7 Adsorption mechanism

Generally, there are two basic mechanisms for heavy metals adsorption: specific adsorption, which is characterized by more selective and less reversible reactions including chemisorbed inner-sphere complexes, and non-specific adsorption (or ion exchange), which involves rather weak and less selective outer-sphere complexes. Specific adsorption occurs slowly and brings about strong and irreversible binding of heavy metal ions with adsorbent. Whereas cation exchange is a form of outer-sphere complexation with only weak covalent bonding between metals and charged soil surfaces. It is reversible in nature and occurs rather quickly as it is typical for reactions which are diffusion-controlled and of electrostatic nature (Bradl, 2004). The adsorption of heavy metals on red loess was rapid and reversible, indicating that the heavy metals were mostly removed by cation exchange.

As seen in Fig. 3b–d, the percentage transmittance of bands at 466, 518 and 1035 cm^{-1} were increased in the red loess after adsorption. This demonstrated that silica and alumina in red loess were the active sites. The removal of heavy metals can be attributed to cation exchange between heavy metals and red loess:

$$2(\equiv SOH) + Me^{2+} \longrightarrow \equiv (SO)_2Me + 2H^+$$
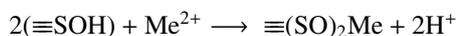
where, S represents silica and alumina in red loess.

3 Conclusions

The adsorption of Pb(II), Cu(II) and Zn(II) on red loess can be effected by solution pH, adsorbent dosage, initial metal concentration, contact time and temperature. The kinetics of adsorption was relatively fast and could reach equilibrium for about 60 min. The adsorption of heavy metals on red loess followed the order of Pb(II) > Cu(II) > Zn(II) and was fitted to Langmuir monolayer adsorption model. At 25°C and pH 6, the maximum adsorption capacities for Pb(II), Cu(II) and Zn(II) on red loess were estimated to be 113.6, 34.2 and 17.5 mg/g, respectively. Furthermore, the maximum removal efficiencies were

100% for Pb(II) at pH 7, 100% for Cu(II) at pH 8, and 80% for Zn(II) at pH 8. The used adsorbents could be regenerated using 0.1 mol/L HCl solution. In conclusion, red loess is expected to become a new cost-effective adsorbent for removing heavy metals from wastewater.

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