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Adsorption properties and mechanism for Fe(III) with solvent impregnated resins containing HEHEHP

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ABSTRACT

Three solvent impregnated resins (SIRs) were first prepared using two types of nonreactive polystyrene-divinylbenzene polymers (HZ818 and HZ830) and one type of reactive weak basic ion exchange resin (D301) as supports and HEHEHP (2-ethylhexyl phosphonic acid mono(2-ethylhexyl) ester) as the extractant. Then the first two prepared SIRs were coated by poly-vinyl alcohol (PVA)-H_3BO_3 to improve their stability. The two types of coated SIRs were called HZ818-CSIR and HZ830-CSIR, and the third type of SIR was called D301-SIR. The three adsorbents were characterized by scanning electron microscopy and infrared spectrometer. The adsorption properties of iron (III) with three adsorbents were studied by batch method from sulfuric acid medium in the range of pH 0.9–1.9. The optimal pH values of all adsorbents were found at 1.5, and the saturated adsorption capacities of HZ818-CSIR, HZ830-CSIR and D301-SIR were determined as 16.7 $mg \cdot g^{-1}$, 15.9 $mg \cdot g^{-1}$ and 25.6 $mg \cdot g^{-1}$ at 298 K, respectively. The adsorption isotherms were found to be fitted with Langmuir isotherms. The adsorption kinetic behaviors of HZ818-CSIR and HZ830-CSIR were fitted with pseudo-second-order kinetic model, while that of D301-SIR with Lagergren first-order kinetic model. The adsorption mechanisms of the three adsorbents were investigated with methods of saturation, equimolar series change and infrared adsorption spectra. It was found that the adsorption mechanism of Fe(III) with HZ818-CSIR and HZ830-CSIR could be deduced as cation exchange between Fe^{3+} and H^+ from P-OH of HEHEHP accompanied with coordination between Fe(III) ion and the phosphoryl oxygen from HEHEHP. While for the D301-SIR, only a cation exchange between Fe^{3+} and H^+ from P-OH of HEHEHP can be proposed.

1. Introduction

In most of hydrometallurgical process, the presence of iron in acidic leach liquor is a common problem (Mishra et al., 2011). Thus, the control of iron is of concern in the production of many metals facing the world's hydrometallurgical industry. In addition, the removal of iron from aqueous wastes is also required by environmental regulations (van Halem et al., 2012). Removal of iron from the acidic leach liquors is usually carried out via precipitation and solvent extraction techniques (Agrawal et al., 2011). The major drawback for precipitation is the poor selectivity and that for solvent extraction is the loss of expensive and sometimes toxic solvents (Navarro et al., 2009).

For this reason, solvent impregnated resins (SIRs) technology has been considered as an alternative process that combines the easy management of solid sorbents and the high efficiency and selectivity of readily available extractants (Marinsky and Marcus, 1997). SIRs can be prepared by a most common process, which consists in the impregnation of the resin with the extractant previously diluted in an appropriate solvent. The solvent will be removed by evaporation after complete wetting of the resin with the impregnation solution. In the last decades, a number of extractants and resins have been used for the preparation of SIRs (Juang, 1999; Kabay et al., 2010; Li et al., 2012). Amberlite XAD-7 resin impregnated with trioctylphosphine oxide (Cyanex 921) has been applied to study the extraction of Fe(III) from hydrochloric acid solutions (Navarro et al., 2009). However, less SIRs has been focused on the adsorption of Fe(III) in sulfuric acid medium. In actual non-ferrous metal hydrometallurgy process, iron as the impurity is often in sulfuric acid system.

Meanwhile, the relatively low stability is the main drawback for application of SIRs because the extractant can be leached from the supports during recycle test. The drawback limits a wide application of SIRs in hydrometallurgy and other industries (Muraviev et al., 1998; Trochimczuk et al., 2004).

Here in this work, two types of coated SIRs (CSIRs) with PVA-boric acid cross-linking technique and one type of novel adsorbent based weak basic ion exchange resin were synthesized. The stability of the first two types of CSIRs was realized through preparing a semipermeable

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coat around each bead of SIRs using poly-vinyl alcohol (PVA) to form the protective layer with porous structure and boric acid as the cross-linking agent (Yuan et al., 2010). The stability of the last adsorbent comes from the acid–base interaction between the basic functional groups of the polymeric support and acidic groups of the extractants instead of physical coating for first two types of CSIRs. Then the adsorption behaviors for Fe(III) from sulfuric acid solution with three types of adsorbents were investigated using batch method. The adsorption mechanisms for Fe(III) were also carried out with saturation adsorption method, equimolar series method and infrared spectrometer measurement. Knowing the adsorption characteristics and mechanisms of Fe(III) with the adsorbents will make possible anticipating the possibility for non-ferrous metals by hydrometallurgical processes or the removal of iron from aqueous wastes required by environmental regulations.

2. Experimental

2.1. Chemicals and reagents

EHEHHP (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) was supplied by Shanghai Rare-earth Chemical Co., Ltd, China, which is weak acid ($pK_a = 4.10$). The purity of the EHEHHP is about 95%. The structure formula was shown in Fig. 1.

Poly(vinyl alcohol) (PVA) with polymerization degree of 1750 ± 50 was purchased from Shanghai Aibi Chemical Co., Ltd, China. Three types of supports (HZ818, HZ830 and D301) were obtained from Shanghai Huazhen Polymer Co., Ltd, China. The chemical and physical properties of adsorbents were shown in Table 1. All other chemicals used in this work were of analytical grade and used without further purification.

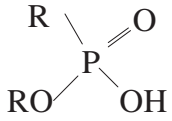
The shapes and surface morphology of the samples were examined on a scanning electron microscope (SEM), JSF5600LV, JEOL, Japan. Infrared spectra were recorded on a Nicolet MAGNAIR 550 (series II) spectrophotometer, test conditions: potassium bromide pellets, scanning 32 times, resolution are 4 cm^{-1}. The data were treated with Thermo Nicolet Corporation OMNIC32 software of version 6.0a.

2.2. Preparation of adsorbents

2.2.1. Preparation of HZ818-CSIRs and HZ830-CSIRs

Before impregnation, HZ818 and HZ830 supports were kept in ethanol for 4 h, and washed with 5% hydrochloric acid solution to remove inorganic impurities and monomeric material. Then the supports were rinsed thoroughly with distilled water to eliminate chloride ions.

HZ818-SIRs were first prepared using a dry impregnation method. Five grams of HZ818 support was placed in 50 mL of HEHEHP–*n*-hexane solution (preliminary experiment showed that *n*-hexane was better than ethanol). The mixtures were shaken at 298 K for 48 h. Then SIRs were separated from mixed solution and evaporated at 323 K in a vacuum oven. For the fabrication of HZ818-CSIRs, a known amount of HZ818-SIRs was immersed in 50 mL of 3% PVA–0.06% sodium alginate



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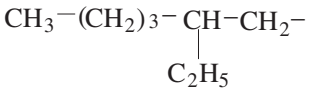

Fig. 1. Structure diagram for HEHEHP.

Table 1
Chemical and physical properties of adsorbents.

Macroporous resin	HZ818	HZ830	D301
Chemical structure	Styrene-DVB	Styrene-DVB	Styrene-DVB-N$(CH_3)_2$
Particle size/mm	0.3–0.6	0.3–1.2	0.3–1.2
Wet real density/g/mL	1.00–1.10	1.00–1.10	1.03–1.06
Wet apparent density/g/mL	0.60–0.70	0.60–0.70	0.65–0.72
Moisture content/%	60–70	62–72	48–58

(w/w) solution and shaken for 22 h at 323 K. After that, the resins were separated from the solution. Then the beads were re-immersed in solution consisting saturated boric acid and shaken for 8 h, and HZ818-CSIRs were obtained by cross-linking reaction of PVA and boric acid. The adsorbents were separated and washed with distilled water subsequently. Finally, the adsorbents were evaporated at 323 K to remove the solvent completely.

The preparation of HZ830-CSIRs was the same as that of HZ818-CSIRs except that support HZ818 was displaced by HZ830.

Considering the extractant impregnated in HZ818-CSIRs or HZ830-CSIRs is acidic type, the content of extractant was determined by NaOH solution titration. First, 0.5 g of HEHEHP impregnated resins was shaken with 25 mL of ethanol to elute the extractant completely, and then the elution was titrated with 14.84 $mmol \cdot L^{-1}$ of NaOH solution. Hence, the amount of HEHEHP adsorbed by HZ818-CSIRs and HZ830-CSIRs was determined as 1.45 $mmol \cdot g^{-1}$,1.42 $mmol \cdot g^{-1}$, respectively.

2.2.2. Preparation of D301-SIRs

The preparation operation of D301-SIRs was shown as follow. Five grams of D301 resin was impregnated in 50 mL of HEHEHP–*n*-hexane solution. The mixtures were shaken at 298 K for 48 h. Then D301-SIRs were separated from mixed solution and evaporated at 323 K in a vacuum oven, and 8.730 g of the dry adsorbent was obtained. The amount of HEHEHP adsorbed by D301-SIRs was determined by mass balance before and after impregnated as 1.40 $mmol \cdot g^{-1}$.

2.3. Batch method

In the batch method, 25 mL of Fe(III) solution with known concentration was taken in 100 mL glass-stoppered flask, and pH was adjusted to the desired value. Then a known amount of adsorbents was introduced. The suspension in flask was shaken for equilibrium in a thermostatic bath. After phase separation, the concentration of Fe(III) ion in the aqueous phase was analyzed by UV-2550 spectrophotometer (Shimadzu, Japan) using orthophenanthroline method (Smelter, 1979). The amount of metal ions adsorbed by the adsorbent was determined by mass balance. The adsorption capacity, Q (mg/g), was calculated with the following equation:

$$Q = \frac{(C_0 - C_e)V}{M} \quad (1)$$

In this equation, C_0 and C_e are the initial and equilibrium concentrations ($mg \cdot L^{-1}$) of metal ions in solution, respectively. V is the volume of solution (mL) and M is the weight of the adsorbents used (mg).

3. Results and discussion

3.1. Characterization of adsorbents

3.1.1. Microscopic study

The appearance and morphology of different adsorbents were examined using scanning electron microscopy. The representative SEM photographs of HZ818-CSIRs were shown in Fig. 2(a–c). Fig. 2(d) was that of HZ818-SIRs. It was shown that the surface morphology