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Selective adsorption of $CuSO_4$ from mixed sulfate solutions by Cu(II) ion-imprinted polymers containing salicylaldoximes, ammonium cations, and tertiary amino groups

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ABSTRACT

A polymerizable complex of copper(II) ion with unsaturated quaternary ammonium cation-modified salicylaldoxime ligand was prepared and used to synthesize a novel copper(II) ion imprinted polymers (Cu(II)-IIPs). Elemental analysis (EA), Fourier transform infrared spectroscopy (FTIR), and NMR spectroscopy confirmed the structures of the polymerizable complex and Cu(II)-IIPs. Thermogravimetric analysis (TGA), Brunauer–Emmett–Teller surface area analysis (BET), and scanning electron microscopy (SEM) characterized physical properties and morphologies of synthesized metal complex and corresponding polymers. The effect of pH, contact time, and initial Cu^{2+} and SO_4^{2-} concentration on the simultaneous adsorption of Cu^{2+} and SO_4^{2-} ions of Cu(II)-IIPs were investigated. Cu(II)-IIPs showed high hydrophilicity and simultaneously rapid adsorption of Cu^{2+} and SO_4^{2-} from solution. Moreover, Cu(II)-IIPs displayed highest adsorption capacity in the pH range of 5.0–6.5, the separation factor (β) between Cu^{2+} with respect to Fe^{3+} was 1866, the equilibrium adsorption capacities for Cu^{2+} and SO_4^{2-} were almost the same and close to 0.13 mmol g^{-1} at 25 °C. Stripping experiments revealed that 1.5 mol L^{-1} H_2SO_4 was an effective eluent for desorbing copper (II) ions from Cu(II)-IIPs. In additional, Cu(II)-IIPs exhibited good recyclability and reusability for 5 cycles without deterioration of its selective ion-absorbing capacity.

1. Introduction

The production of copper, one of the most important metals, comes from metallurgical industry. Hydrometallurgical methods feature simplicity, rapid mass transfer kinetics, capability for scale-up, and facile recovery of the solvent extractant [1]. Now a quarter of the worldwide production of copper using alkylsalicyloximes is applied in solvent extraction during the hydrometallurgical process. These alkylsalicyloximes, used as the solvent extractants, are capable of selectively transferring Cu^{2+} from acidic sulfate media that contains a high concentration of Fe^{3+}. The crucial step during solvent extraction involves the formation of square-planar complexes [2,3], which are stabilized by interligand hydrogen bonding between alkylsalicyloximes and Cu^{2+}. However, inherent limitations, such as organic solvents usage, low enrichment factors, third phase formation, tedious back extraction, and anionic pollutions, still go with current hydrometallurgical technique [4–7].

Solid phase extraction (SPE) emerges as an alternative method for copper production to address the issues in hydrometallurgy [8–11]. SPE can effectively preconcentrate and separate heavy metal ions from the aqueous solutions, and can attain a high concentration factor rapidly. So far, numerous substances have been used as solid-phase extractants, such as ion-exchange resins, [12] chelating resins, [13] activated carbon, [14] and silica gel [15]. However, the main problem of SPE pertains to poor selectivity among different heavy metal ions. In the literature, ion imprinted polymers (IIPs), which were prepared using polymerizable ligands as functional monomers and metal ions as ion templates, have selectivity for a specific ion in metal extraction [16–18]. A polymerizable ligand is crucial as it directly influences the selectivity adsorption of IIPs. In addition, coordination geometries, coordination numbers, charges, and sizes of metal ions play important roles in the selectivity of IIPs [15].

It was noted that the Tasker group [19–21] and some researchers [22,23] utilized alkylsalicyloximes as ditopic extractants and the tertiary amino groups are ortho to the phenolic OH-groups to improve the adsorption selectivity and achieve the simultaneous adsorption of Cu^{2+} and SO_4^{2-}. Wang group [24] attempted to anchor a ditopic zwitterionic salicylaldimine on silica gel to have good adsorption efficiency and no

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selectivity for Cu^{2+} and SO_4^{2-} from the mixed sulfate solutions. In this study, a polymerizable complex of copper (II) ion with salicylaldoxime ligands modified by unsaturated quaternary ammonium cations was designed and prepared as the functional monomers to fabricate the novel multifunctional copper(II) ion imprinted polymers (Cu(II)-IIPs). Here salicylaldoxime, a common complexing ligand, was used to capture copper (II) cations as well as the alkylsalicyloxime, and simultaneously to form stabilized square-planar complexes contributing significantly to the selectivity of copper(II) cations. In this manuscript, *N*,*N*-diallyl methylamine as the skeleton monomer was copolymerized with the polymerizable copper (II) ion complex to attain the new kind of (Cu(II)-IIPs), and to anchor the tertiary amino groups on the network of the polymers. Upon the complexation of salicylaldoximes with Cu^{2+}, the phenolic protons from Cu^{2+} binding site transferred to the pendant tertiary amino groups to yield new ammonium cations and create a positive cavity wherein SO_4^{2-} was bound by both electrostatic interactions and H-bond. Moreover, covalently linked quaternary ammonium cations and phenolates in the network of Cu(II)-IIPs formed zwitterionic extractants, [25] which contributed to efficient desorption of Cu^{2+} to facilitate regeneration of Cu(II)-IIPs. These zwitterionic groups also allowed pH value equilibrium during the recovery of Cu^{2+} and SO_4^{2-} from the aqueous media, and maintained the interspace of Cu(II)-IIPs with relatively high hydrophilicity, and gave Cu(II)-IIPs anionic exchanging capability [26].

2. Experiments

2.1. Instrumentation

Elemental analysis was carried out on a Carlo Erba-EA1108 elemental analyzer (PerkinElmer, Fremont, USA). The Fourier transform infrared (FTIR) (Bruker, Karlsruhe, Germany) spectra of the synthesized monomers, polymerizable copper (II) complex, imprinted and non-imprinted polymers were recorded using a Bruker FTIR-Tensor 27 Spectrometer in KBr pellets. The proton nuclear magnetic resonance (^{1}H NMR) (Bruker, Karlsruhe, Germany) spectra of the monomers and the corresponding polymerizable copper(II) complex were recorded on Bruker DPX300 MHz spectrometer using deuterated dimethylsulfoxide (DMSO-d_6) as solvent and tetramethylsilane (TMS) as internal standard. The concentrations of Cu(II), Ni(II), Co(II) and Fe(III) were determined using a TAS-990 flame atomic adsorption spectrometry (FAAS) (Beijing's General Instrument Co., LTD, Beijing, China)with an air acetylene flame. SO_4^{2-} concentration was carried out by using ion chromatography (Dionex, Sunnyvale, USA). Thermal stability of the polymers was measured using a Shimadzu TGA-50H thermogravimetric analyzer (Netzsch, Selb, Germany). The scanning electron microscopy (SEM) (JEOL Ltd., Tokyo, Japan) images of the imprinted and non-imprinted polymers were recorded on a JEOL-6390LA scanning electron microscope. A Pengshun Scientific Instruments Research pHs-10C digital pH meter was used for the pH adjustments.

2.2. Reagents and materials

N,*N*-diallyl methylamine (DAMA, 98%), Divinylbenzene (DVB, 85%), Ethylene glycol dimethacrylate (EGDMA), Azobisisobutyronitrile (AIBN, 98%), *N*,*N*-dimethylformamide (DMF, 99%), copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), cobalt sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), and Ferric ammonium sulfate dodecahydrate ($FeNH_4(SO_4)_2 \cdot 12H_2O$) were obtained from Aladdin (Shanghai, China). Hydroxylamine sulfate (HAS, 98%) was purchased from Jinan Tianyuan chemical Co., Ltd. (Jinan, China). *N*,*N*-diallyl methylaminium sulfate (DAMAS) was prepared with *N*,*N*-diallyl methylamine and sulfuric acid in ice water. 5-Chloromethylsalicylaldehyde (CMS) was synthesized according to previous work [27]. Unless otherwise stated, reagents of analytical purity were used for all experiments.

Standard stock solutions of metal ions with concentration of 0.5–4.0 mg mL^{-1} were prepared by dissolving calculated amounts of sulfate salts in 0.1 mol L^{-1} H_2SO_4, and further diluted prior to use. The pH were adjusted using 0.1 mol L^{-1} H_2SO_4 or 0.1 mol L^{-1} NH_4OH.

2.3. Preparation of PCC (polymerizable copper (II) complex)

PCC was synthesized in three steps under optimized conditions (Fig. 1).

2.3.1. Synthesis of DAMAS

DAMA-S was named *N*,*N*-diallyl-*N*-(3-hydroxyr-4-formyl)benzyl-*N*-methyl ammonium chloride and prepared according to the previous work [28]. *N*,*N*-diallyl methylamine (1.0 mmol) was added dropwise into a solution containing ethyl acetate (100 mL) and CMS (20.0 g, 1.2 mmol), and the mixture was stirred at the room temperature for 12 h and filtered to obtain a white solid. Then the white-solid product was recrystallized from ethanol and dried under vacuum at 50 °C for 48 h to yield white needle-like crystals. The melting point of DAMA-S (93.3% yield) was 184–185 °C. Element analysis of $C_{15}H_{20}ClNO_2$ (calculated value, %): C 64.15 (63.94), H 7.00 (7.15), N 4.94 (4.97), Cl 11.37 (12.58). IR (KBr, cm^{-1}): 3426 (O—H), 2976, 2933 (CH_3, CH_2), 2724(formyl, C—H), 1578, 1476 (benzene, C═C), 1443 (ammonium salt, C—N), 1013(C—O), 744 (benzene, C—H). ^{1}H NMR (DMSO-d_6, ppm): 10.46 (s, 1H), 7.26–7.83 (m, 3H), 5.73 (d, 4H), 5.05 (s, 1H), 4.92 (t, 2H), 3.97 (d, 4H), 3.92 (s, 2H), and 3.35 (s, 3H).

2.3.2. Synthesis of DAMA-SA

DAMA-SA was named 5-[(chloride *N*,*N*-diallyl-*N*-methyl ammonium)methyl]salicylaldoxime and prepared as follows: DAMA-S (30 g, 0.106 mol) and HAS (18 g, 0.14 mol) were dissolved in 120 mL absolute ethanol, and the pH was adjusted to 6.0 with Na_2CO_3. The mixture was stirred for 5 h at 50 °C, and concentrated using a rotary evaporator. The product was precipitated from the solution, filtered, and dried in vacuum, and a light yellow solid was obtained. Then it was recrystallized in ethanol and a white powder of DAMA-SA (83.9% yield) with a melting point of 207–209 °C was yielded. Element analysis

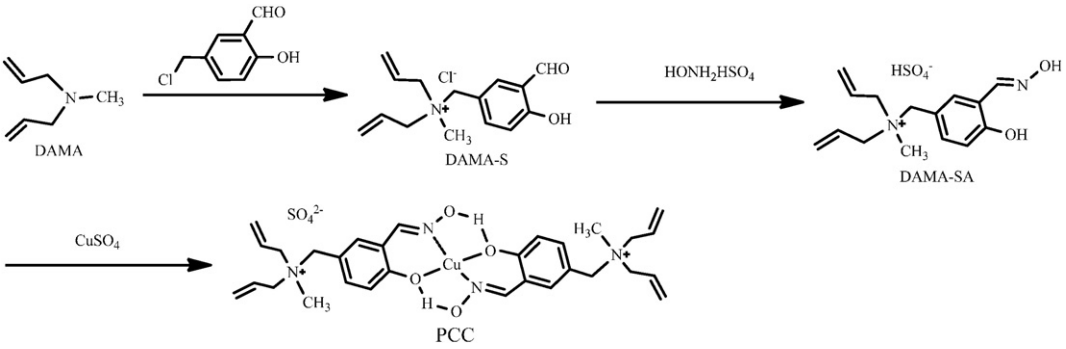

Fig. 1. The synthetic route of PCC (polymerizable copper (II) complex).