



Synthesis of novel copper ion-selective material based on hierarchically imprinted cross-linked poly(acrylamide-co-ethylene glycol dimethacrylate)



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ABSTRACT

A novel hierarchically imprinted cross-linked poly(acrylamide-co-ethylene glycol dimethacrylate) using a double-imprinting approach for the Cu²⁺ selective separation from aqueous medium was prepared. In the imprinting process, both Cu²⁺ ions and surfactant micelles (cetyltrimethylammonium bromide – CTAB) were employed as templates. The hierarchically imprinted organic polymer named (IIP-CTAB), single-imprinted (IIP-no CTAB) and non-imprinted (NIP-CTAB and NIP-no CTAB) polymers were characterized by SEM, FTIR, TG, elemental analysis and textural data from BET (Brunauer–Emmett–Teller) and BJH (Bartlett–Joyner–Halenda). Compared to these materials, IIP-CTAB showed higher selectivity, specific surface area and adsorption capacity toward Cu²⁺ ions. Good selectivity for Cu²⁺ was obtained for the Cu²⁺/Cd²⁺, Cu²⁺/Zn²⁺ and Cu²⁺/Co²⁺ systems when IIP-CTAB was compared to the single-imprinted (IIP-no CTAB) and non double-imprinted polymer (NIP-CTAB), thereby confirming the improvement in the polymer selectivity due to double-imprinting effect. For adsorption kinetic data, the best fit was provided with the pseudo-second-order model for the four materials, thereby indicating the chemical nature of the Cu²⁺ adsorption process. Cu²⁺ adsorption under equilibrium was found to follow dual-site Langmuir–Freundlich model isotherm, thus suggesting the existence of adsorption sites with low and high binding energy on the adsorbent surface. From column experiments 600 adsorption-desorption cycles using 1.8 mol L⁻¹ HNO₃ as eluent confirmed the great recoverability of adsorbent. The synthesis approach here investigated has been found to be very attractive for the designing of organic ion imprinted polymer and can be expanded to the other polymers to improve performance of ion imprinted polymers in the field of solid phase extraction.

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1. Introduction

Heavy metals such as mercury, cadmium, lead, chromium and copper are harmful and toxic to humans and the environment. For this reason, they should be removed from industrial wastes. Copper and its compounds play a significant role in the modern world due to excellent conductivity, ductility and frequent use in electrical, construction and plumbing materials [1]. As a result,

the presence of this metal in wastewater streams can cause gastrointestinal distresses (short-term exposure) and liver or kidney damages (long-term exposure) leading to anemia [2,3]. Thus, different environmental protection agencies have established regulations to prevent contamination of water sources for human consumption and to set priorities for removing copper ions (Cu²⁺). As examples, the Cu²⁺ levels in drinking water are limited to 4.0 and 1.3 mg L⁻¹ by the World Health Organization and the US Environmental Protection Agency, respectively [4,5].

Great efforts have been directed at developing more effective techniques for removing Cu²⁺ from aqueous streams at acceptable concentration levels. They include ion exchange, membrane

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filtration, chemical precipitation and adsorption. However, ion exchange and chemical precipitation present limitations such as low Cu^{2+} removal efficiency, high cost and absence of selectivity. Therefore, adsorption is considered to be one of the simplest, most effective and inexpensive methods for removing the metal ions from aqueous solutions [6,7]. In this regard, in recent years, adsorption methods based on ion imprinted polymers (IIPs) possessing special recognition ability toward a target substance have received significant attention [8–10]. In general, these materials has been usually synthesized from a homogeneous polymerization medium also named as bulk polymerization, which a chelating monomer form a complex with a metal ion template during growing of polymeric chain. After synthesis, the polymer is ground manually and the template is removed from the polymeric matrix giving rise to selective sites able to bind an analyte are thus created [10–12].

A survey of literature shows that IIPs for copper ions can be even prepared by using different synthesis approaches including seed emulsion polymerization [13], grafting process onto silica gel particle [14], sol–gel processing using inorganic matrices [15] and magnetic ion imprinted materials prepared by surface imprinted technique combined with a sol–gel process [16]. In comparison to these previous preparation methods, bulk polymerization has been the most widely used due to good mechanical/chemical stability of polymer, ease of preparation, low manufacturing cost and high stability in wide pH range. However, due to intrinsic polymeric structure which disfavors rapid mass transfer, these IIPs still suffers from the slow retention kinetics, low adsorption capacity, incomplete template removal and poor site accessibility [17,18]. Such limitations can be overcome by using a new preparation method of organic IIPs based on double-imprinting technology also named hierarchical imprinting technology [19]. This technology for IIPs preparation relies upon ionic and micellar imprinting combination, which permits obtain hierarchical microstructure and mesostructures in the polymeric matrix. Despite these interesting characteristics, the use of surfactant molecules acting as structure directing agent in the organic polymer preparation has been very well reported [20,21], but its combination with ionic imprinting still has been incipient. Furthermore, the majority of studies have focused on development of hierarchically imprinted polymers exploiting sol–gel process [22,23]. As an example, Wu and co-workers [24] assessed adsorption properties of hierarchical organic–inorganic hybrid sorbent for the Hg^{2+} selective separation using Hg^{2+} and surfactant micelles cetyltrimethylammonium bromide (CTAB) as templates, *N*-[3-(trimethoxy-silyl)propyl]ethylenediamine (TPED) as functional monomer, and tetraethoxysilane (TEOS) as cross-linking reagent. The adsorption capacity and selectivity coefficients were much higher than those obtained for the adsorbent prepared without the CTAB template. Similar to this procedure, a double-imprinted polymer based on (3-aminopropyltrimethoxysilane) and cetyltrimethylammonium bromide (CTAB) was synthesized for retaining Cu^{2+} ; it exhibited good selectivity and high adsorption capacity when compared to the imprinted polymer without CTAB [25].

Our research group has recently published a pioneer study dedicated to the preparation of hierarchically imprinted organic polymer [19]. In this study, a cross-linked poly(methacrylic acid-co-ethylene glycol dimethacrylate) was synthesized in the presence of Ni^{2+} and CTAB as templates. Therefore, inspired in this study and bearing in mind the incipient data in the literature on this subject, we synthesized a novel hierarchically imprinted cross-linked poly(acrylamide-co-ethylene glycol dimethacrylate) for selective extraction of copper from aqueous medium. Acrylamide has been chosen as chelating monomer once acrylamide-based materials has been employed as efficient adsorbent for removal of toxic metal ions and organic pollutants [26,27].

The adsorbent material was characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, thermogravimetry (TG), elemental and nitrogen adsorption-desorption measurements and compared to the single-imprinted (IIP-no CTAB) and non-imprinted (NIP-no CTAB and NIP-CTAB) polymers. Adsorption properties were assessed by isotherm and kinetic studies, whereas selective features were discussed on the basis of distribution (K_d), selectivity (k) and relative selectivity (k') coefficients.

2. Experimental

2.1. Instrumentation

Measurements of the Cu^{2+} concentration were performed on a Shimadzu AA-7000 flame atomic absorption spectrometer (Kyoto, Japan) equipped with a copper hollow cathode lamp as radiation source, deuterium lamp for background correction, and acetylene–air burner for flame ignition. The hollow cathode lamp was operated at 6.0 mA and 324.8 nm. Acetylene and air were supplied to the burner at 1.8 and 15.0 L min^{-1} , respectively. pH values of solutions were measured with a Metrohm 826 pH mobile digital pH meter (Herisau, Switzerland).

For the polymers characterization, infrared spectra were recorded on a Shimadzu FTIR-8300 Fourier transform spectrometer in transmission mode (4000–400 cm^{-1}) to elucidate functional groups present in the materials, whereas the surface morphology was analyzed using a Philips FEI Quanta 200 scanning electron microscope (Amsterdam, The Netherlands).

Average pore sizes and volumes of the polymers were estimated by the Barrett–Joyner–Halenda (BJH) method based on nitrogen adsorption experiments using a Quantachrome Nova 1200e automatic instrument coupled to an automatic gas analyzer (all – Quantachrome, Boynton Beach, FL, USA). Specific surface areas were determined from adsorption isotherms according to the Brunauer–Emmett–Teller (BET) method.

Carbon, nitrogen and hydrogen contents in the synthesized materials were determined using a Perkin Elmer 2400 elemental analyzer (Waltham, MA, USA).

The thermal stability of the materials was analyzed on a Perkin Elmer TGA 4000 thermogravimetric instrument in the temperature range of 30–800 °C (scanning rate 10 °C min^{-1} , and nitrogen flow rate 20 mL min^{-1}).

2.2. Solutions and reagents

All solutions were prepared from analytical-grade chemicals using water from a Millipore Milli-Q purification system (Billerica, MA, USA). To prevent any risk of metal contamination, all glassware was kept in a 10% (v/v) HNO_3 solution for 24 h and then washed with deionized water. Cu^{2+} working solutions for adsorption studies were prepared from a 1000 mg L^{-1} Cu^{2+} standard stock solution (Merck, Darmstadt, Germany) by making appropriate dilutions immediately prior to use.

For the polymer synthesis, the following reagents – $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (as ion template), acrylamide (as functional monomer), ethylene glycol dimethacrylate – EGDMA as cross-linking reagent, and 2,2'-azo-bis-isobutyronitrile – AIBN (as initiator) – were acquired from Sigma–Aldrich (Steinheim, Germany) and used without purification. Ethanol (FMAia, Olinda, Brazil) chosen as solvent, and cetyltrimethylammonium bromide (CTAB) as surfactant were purchased from Acros Organics (Morris Plains, NJ, USA).

Phosphate and acetate buffer solutions were prepared from their respective salts (Merck) without further purification. The desired pH of solutions was adjusted with NaOH and/or HNO_3 solutions (all – from Merck).

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