Preparation of porous resin with Schiff base chelating groups for removal of heavy metal ions from aqueous solutions

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HIGHLIGHTS

- A new porous resin with Schiff base chelating groups was synthesized.
- Extraction of Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+} and Co^{2+} from aqueous solution was examined.
- The process of metal ions adsorption generally followed the Langmuir model.
- The adsorption kinetics follow the pseudo-second-order kinetic model.
- The resin was effective for removal of heavy metal ions from wastewater samples.

GRAPHICAL ABSTRACT
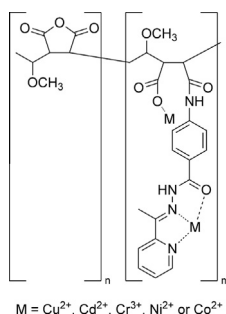
M = Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+} or Co^{2+}

ABSTRACT

A new chelating resin was synthesized in the reaction of poly(MVE-*alt*-MA) polymer with a Schiff base obtained in condensation of 2-acetylpyridine and 4-aminobenzoic hydrazide. Its composition, properties and morphology were characterized by Fourier transform infrared spectroscopy, elemental analysis, thermogravimetric analysis, derivative scanning calorimetry, scanning electron microscopy and N_2 sorptometry. The effects of several parameters that affect the adsorption of Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+} and Co^{2+} including concentration, contact time, temperature and pH were examined. The adsorption capacity of the resin for the ions studied was found in the range 29.95–157.25 mg g^{-1}. The adsorption process of ions studied generally followed the Langmuir adsorption isotherm model. The kinetics of this process was found to follow the pseudo-second-order kinetic model. The changes in thermodynamic parameters, particularly in standard enthalpy (ΔH°), standard entropy (ΔS°) and Gibbs free energy (ΔG°) were analyzed. The resin was found effective in removal of heavy metal ions from real wastewater samples that contained high concentrations of the above-mentioned ions.

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1. Introduction

Removal of heavy metal ions from wastewater and contaminated soil is a matter of great importance because of their toxic effects on the human health and on the natural environment in general. Techniques such as adsorption, ion exchange, dialysis, precipitation and extraction have been widely used to purify water containing excessive amounts of heavy metal ions. Adsorption technique has received much attention because it allows the use of many materials that are environmental friendly and have low production cost [1–6]. Moreover, the adsorbents are easy to remove from a purified solution which considerably reduces the total cost of overall process. Recently, the design and synthesis of hybrid materials for removal and sensing of metal ions has become a subject of increasing interest. Particularly interesting is the synthesis of materials with magnetic properties that would allow their easy recollection and repeated use with low loss [7–12]. Carbon

nanomaterials have been also used as an adsorbents, because of their high surface area for inorganic adsorption, excellent mechanical and thermal stability and exceptional water filtration capabilities. Interestingly, the weight loss of an adsorbent prepared from carbon nanotubes after many cycles of treatment is smaller when compared to that of the adsorbent made from activated carbon [13–15]. Zwitterionic hybrid polymers combine the advantages of organic and inorganic materials and also exhibit additional interesting properties, such as structural flexibility, thermal and mechanical stability. The pendant-side structure of ionic groups of the opposite signs on the polymer chains allows binding of heavy metal ions from solutions via electrostatic effect. This feature allows the use of materials of this type in the separation and recovery processes [16–18]. Chelating polymers possess functional groups that comprise one or more donor atoms acting as a ligands towards certain types of cations. These polymers usually show higher selectivity to metal cations than ionic polymers, therefore they have been used for transition metal ion separation [19–24].

Polymers that possess Schiff bases in their structure make an important group of chelating resins. Schiff bases that are built of nitrogen and oxygen donor atoms, are well known for their very good selectivity towards complexation of transition metals ions, and low affinity to alkali and alkaline earth metal ions. Moreover, many Schiff bases contain additional donor groups, which make them very good candidates for metal ion complexation. These Schiff bases can be obtained by simple self-condensation or even multiple self-condensation processes that take place in one synthetic step. Linking Schiff bases to polymers results in chelating resins that show well-defined molecular assemblies [25]. All these properties make Schiff base chelating resins very useful to removal of transition metal ions from solutions. Yan and Sun have prepared two novel chelating resins by anchoring diethylenetriamine bis- and mono-furaldehyde Schiff bases onto the macroporous GMA-DVB (glycidyl methacrylate-divinylbenzene) copolymer beads. These resins were used for the adsorption of Cu(II), Co(II), Ni(II) and Zn(II) ions [26]. Cross-linked magnetic chitosan-isatin Schiff's base resin was prepared and its usefulness in metal ion adsorption has been examined. The maximum adsorption capacities were 103.16, 53.51, and 40.15 mg/g for Cu^{2+}, Co^{2+} and Ni^{2+} ions, respectively. Cross-linked magnetic resin displayed higher adsorption capacity for Cu^{2+} in all pH ranges studied [27]. Duolite XAD 761 has been modified with 2-(2,4-dichlorobenzylideneamino) benzenethiol to produce a Schiff base containing a chelating resin. The material obtained was used for the sorption of Cr^{3+}, Co^{2+}, Cu^{2+}, Fe^{3+}, Ni^{2+}, and Zn^{2+} ions. A solid-phase extraction method based on the use of this new chelating resin has been applied to determine the contents of metals in real food samples [28]. Two chelating resins were synthesized by condensing Schiff bases derived from 2-aminophenol, 2-hydroxy-5-chloroaniline and terephthaldehyde with formaldehyde in an alkaline medium. The metal ion uptake of the resins was investigated by the batch method. The resins showed a preferential selectivity towards Cu(II) than Pb(II) metal ions [29]. Commercially available poly(vinyl chloride) has been synthetically modified to a polymer containing pendant primary amino groups. The amino polymer was reacted with salicylaldehyde to yield a Schiff-base chelating polymer. The polymer has been used to prepare polymer-supported copper complex which was a catalyst in the one-pot three-component Mannich reaction between aldehydes, ketones and anilines under mild and environmentally friendly conditions [30].

The aim of this study was to synthesize resin with Schiff base chelating groups and examine its effectiveness in heavy metal ion removal from aqueous solutions. To the best of our knowledge, this is the first study describing functionalization of poly(methyl vinyl ether-*alt*-maleic anhydride) with Schiff base and its use in adsorption of heavy metal ions. Moreover, the polymer obtained showed very interesting, porous structure, which can have additional impact on its adsorption properties. The influence of factors affecting the adsorption of Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+} and Co^{2+} such as concentration, contact time, temperature and pH were investigated. The resin obtained was used to adsorb heavy metal ions from real wastewater samples.

2. Experimental

2.1. Materials and chemicals

All reagents used were commercial products. 2-Acetylpyridine, 4-aminobenzoic hydrazide, poly(methyl vinyl ether-*alt*-maleic anhydride) (poly(MVE-*alt*-MA)) of average M_w = 216,000 and metal perchlorates: $Cu(ClO_4)_2 \times 6H_2O$, $Cd(ClO_4)_2 \times 6H_2O$, $Cr(ClO_4)_3 \times 6H_2O$, $Ni(ClO_4)_2 \times 6H_2O$ and $Co(ClO_4)_2 \times 6H_2O$ obtained from Sigma–Aldrich (St. Louis, MO, USA). Anhydrous ethyl alcohol and all other solvents of the purity grade p.a., were purchased from POCH (Gliwice, Poland) and were used without further purification. Wastewater samples were obtained from PRESSEKO (Bolechowo near/Poznan, Poland) company.

2.2. Instruments

A Shimadzu AA-7000 atomic absorption spectrophotometer (Shimadzu, Japan) was used for determination of Cu^{2+}, Cd^{2+}, Cr^{3+}, Ni^{2+} and Co^{2+} concentrations. The measurement was performed in 3 replications, and the % RSD did not exceed 5%. The FTIR spectrum of the resin was recorded on a Bruker IFS 66s spectrometer (Billerica, MA, USA) using KBr pellets (about 1.5 mg of sample in 200 mg of KBr). NMR spectra were recorded on Agilent DD2 800 MHz (Santa Clara, California, USA). Elemental analyses were carried out on a Vario EL III Element Analyzer (Hanau, Germany). Thermal data were obtained by using a Setaram Setsys 1200 (Caluire, France). The thermal stability of the resin was investigated by thermogravimetric analysis and derivative scanning calorimetry in air stream at a heating rate of 5 °C min^{-1}. The pore structure of the resin obtained was characterized on the basis of low-temperature nitrogen adsorption–desorption isotherms measured on a sorptometer Quantachrome Autosorb iQ (Boynton Beach, Florida, USA). Surface area and pore size distribution were calculated by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Electron impact spectra were recorded using Bruker 320-MS spectrometer. The pH measurements were performed using Elmetron CP-505 apparatus (Zabrze, Poland) equipped with a combined pH electrode. Scanning electron microscopy images were obtained on a Hitachi Scanning Electron Microscope SU3500 (Tokyo, Japan).

2.3. Synthesis of acylhydrazone ligand (**1**)

Acylhydrazone ligand (**1**) was synthesized according to a literature method that was used to synthesize similar acylhydrazone ligands [31]. 2-Acetylpyridine (1.603 g, 13.23 mmol) was added to a solution of 4-aminobenzoic hydrazide (2.00 g, 13.23 mmol) in anhydrous ethanol (120 mL) and a few drops of concentrated hydrochloric acid were added. The solution was heated under reflux for 12 h. Upon overnight cooling, a bright yellow precipitate was recovered. The solid was filtered off, washed with cold ethanol and dried.

^{1}H NMR (DMSO-d6) δ: 2.42 (s, 3H); 5.86 (s, 2H); 6.66 (d, 2H); 7.59 (m, 1H); 7.62 (d, 2H); 7.81 (d, 1H); 8.11 (t, 1H); 8.91 (d, 1H). ^{13}C NMR (DMSO-d6) δ: 25.0; 116.3; 122.6; 123.3; 127.6; 131.9; 141,7; 144.5; 150.9; 155.8; 158.5; 165.8. EI-MS *m/z* (%):