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Synthesis and Characterization of New Chelating Resin: Adsorption Study of Copper(II) and Chromium (III) Ions

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Acrylamide based monomer, 5-methyl-2-thiozyl methacrylamide (MTMAAm) was synthesized by the reaction of 2-Amino-5-methyl thiazole with methacryloyl chloride in the presence of triethylamine(NR_3) at 0–5°C. The monomer MTMAAm was characterized by FT-IR and ^{1}H-and ^{13}C-NMR spectral studies. A new chelating resin, poly(5-methyl-2-thiozyl methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene) [MTMAAm/AMPS/DVB] was synthesized. This resin was characterized by FT-IR. In order to determine the adsorption behavior of chelating resin, the adsorption isotherm of Cr(III) and Cu(II) were studied. It was found that the adsorption isotherm of the ions fitted with Langmuir-type isotherms. From the Langmuir equation, the adsorption capacity of chelating resin for Cr(III) and Cu(II) was found to be 7.77 mg g^{-1} and 4.27 mg g^{-1}, respectively. Binding equilibrium constant was calculated to be 0.155 L mg^{-1} and 0.106 L mg^{-1} for Cu(II) and Cr(III), respectively.

Keywords: Poly(5-methyl-2-thiozyl) methacrylamide, adsorption isotherm, binding equilibrium constant

1 Introduction

Thiazole and its derivatives have biological significance, e.g., they are found in the vitamin B_1 molecule and in coenzyme cocarboxylase (1). The penicillin molecule also contains a thiazolidine ring. 2-Aminothiazoles are known mainly as biologically active compounds with a broad range of activity and as intermediates in the synthesis of antibiotics and dyes (2). Various thiazole derivatives have shown herbicidal, anti-inflamatory, anti-microbial, or anti-parasitic activity (3). However, the syntheses and physiochemical properties of (5-methyl-2-thiozyl) methacrylamide and their derivatives have not been reported so far. These compounds seem to be suitable candidates for further chemical modifications and may be pharmacologically active and useful ligands in coordination chemistry and polymer chemistry.

Several studies have been done in our laboratories on the synthesis of new methacrylamide monomers (4–6) and their radical copolymerization with commercially available monomers. These studies clearly show that the nature, as well as position of the substituent, had a large effect on monomer reactivity ratios, glass transition temperatures and anti-microbial properties. Copolymers with reactive or functional monomers are steadily gaining importance. Many polymers with reactive functional groups are now being synthesized, tested and used not only for their macromolecular properties, but also for the properties of functional groups (7–11). These functional groups provide an approach to a subsequent modification of the polymer for specific end applications (12). Copolymer networks with controlled porous structure are widely employed as starting materials for ion exchangers, as specific sorbents, packing for gel permeation chromatography and catalyst supports (3–17). The morphological control of the copolymer beads may result in many advantages concerning removal of metal ions and other pollutants from wastewater. These characteristics have a strong influence on the removal kinetics and flow properties (16). Crosslinked copolymers based on 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) have a great potential for many applications as ion-exchange resins, gas separation membranes, catalyst supports, in the water purification industry, in monitoring heavy metals, and as other useful materials (7–21). Chelating resins are superior in selectivity to solvent extraction and ion exchange due to their triple function of ion exchange, chelate formation and physical adsorption. Chelating and/or ion exchange type sorbents used in speciation pretreatment have shown a preferential affinity for a single oxidation state of chromium and copper. The chelating resin adsorbents, which have large specific surface areas and high adsorption

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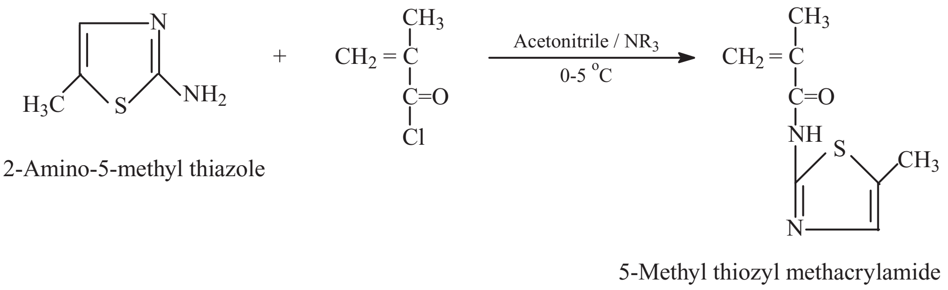

Fig. 1. Reaction scheme of 5-methyl-2-thiozyl methacrylamide (MTMAAm) Monomer.

rates are increasingly used in removal of toxic metal ions and preconcentration of trace elements from aqueous solution (22–31). The adsorption of heavy metal ions from aqueous solution to adsorbents is usually affected by the surface functional groups of the adsorbents (32–34).

In the present paper, a newly synthesized chelating resin, poly(5-methyl-2-thiozyl methacrylamide-co-2-acrylamido-2-methyl-1-propanesulfonic acid-co-divinylbenzene) [MTMAAm/AMPS/DVB] was characterized and used for the adsorption of Cu(II) and Cr(III) ions.

2 Experimental

2.1 Materials

2-Amino-5-methylthiazole (E. Merck, Darmstadti Germany) and methacryloyl chloride (Alfa Easer, MA) were used as received. (5-Methyl-2-thiozyl) methacrylamide has been synthesized according to the literature (19). 2,2′-Azobisisobutyronitrile (AIBN) was purified by successive crystallizations from chloroform- methanol mixture. All solvents were of analytical grade and, where appropriate, were purified by standard procedures. Cr(III) stock solutions (1000 mgL^{-1}) was prepared from $Cr(NO_3)_3 \cdot 9H_2O$ (Merck, Darmstadt, Germany). Analytical grade reagent (Merck) of copper(II) nitrate $Cu(NO_3)_2 \cdot 3H_2O$ was used without purification. The working solutions of the metals were obtained by appropriate dilution of the stock solutions. The stock solutions of interfering ions prepared from their high purity compounds (Merck). The required pH adjustments were made by the use of buffer solutions. pH values were adjusted with HCl (pH 1–3) and buffer solutions of CH_3COOH/CH_3COONa (pH 4–6) and NH_3/NH_4Cl (pH 8–10).

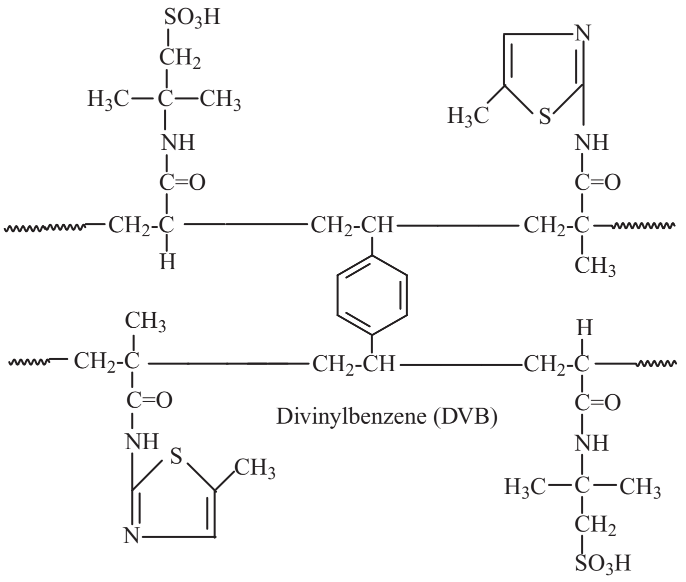

Fig. 2. The structure of the chelating resin.

2.2 Characterization Techniques

Infra-red spectra were measured on a Jasco 460 Plus FT-IR spectrometer. ^{1}H-and ^{13}C-NMR spectra of the polymers were recorded in $CDCl_3$ with tetramethylsilane as the internal standard using a Bruker 400 MHz NMR spectrometer. A Perkin-Elmer Analyst 800 model flame atomic absorption spectrometer (FAAS, Norwalk, CT) was used for the determination of Cu(II) and Cr(III). The operating conditions were as follows: wavelength: 324.8 and 357.9 nm for Cu(II) and Cr(III), respectively, lamp currents: 25 mA, bandpasses: 0.7 nm and acetylene/air flow rates: 3.0/18 L.min^{-1} for both elements. A Consort C533 model digital pH meter (Turnhout, Belgium) was used for all the pH measurements.

2.3 Synthesis of 5-Methyl-2-thiozyl Methacrylamide (MTMAAm) Monomer

To a well-stirred solution of 30 mmole 2-Amino-5-methylthiazole and 90 mmole of triethylamine (NR_3) in 30 ml dichloromethane, 30 mmole of methacryloylchloride was added dropwise under cooling in ice bath (0–5°C), (Fig. 1). After the complete addition of methacryloyl chloride, the reaction mixture was stirred for 12 h at room temperature, then filtered and evaporated with a rotavapor. A yellow product was obtained and recrystallized from ethanol as a yellow powder (yield: 75%). The reaction scheme of the monomer is shown in Figure 1.

2.4 Synthesis of Chelating Resin

The preparation of MTMAAm/AMPS/DVB resin was carried out with a radical initiator in dimethylformamide solution. To a polymerization flask, the two appropriate monomers MTMAAm (0.55 g, 3.0 mmol) and AMPS (0.62 g, 3.0 mmol), the crosslinking reagent DVB (0.52 g, 4.0 mmol), and the initiator AIBN (0.018 g, 0.1 mmol) were added. The system was kept under N_2 for 3 h at 70 ± 1°C. Subsequently, the resin was filtered and washed with abundant diethylether and dried under vacuum at 50°C until a constant weight was obtained. The conversion of monomer to polymer resin was determined gravimetrically (yield: 80%). The structure of the chelating resin is shown in Figure 2.

3 Results and Discussion

3.1 Characterization of Monomer(MTMAAm) and Chelating Resin

The ^{1}H- and ^{13}C-NMR spectra of MTMAAm and its attributions are shown in Figure 3(A) and (B), respectively. The structure of MTMAAm is confirmed by ^{1}H- and ^{13}C-NMR spectral data. The NMR spectra of the monomer have the characteristic peaks of the monomeric units. The FTIR spectra of the monomer MTMAAm is shown in Figure 4(A). IR (neat), cm^{-1}: 3430 (NH), 3000–3100 (=C-H in aromatic ring), 2960, 2922, 2865 (aliphatic C-H), 1630 (CH_2 =C-), 1605, 1526, 1450 (aromatic, C=C), 1690 (amide carbonyl), 1150 (C-O-C), 848, 790, 710 (aromatic C-H def. out-of-plane).

The FTIR spectrum of synthesized chelating resin is illustrated in Figure 4(B). The FTIR spectrum of the resin shows a strong band at 3430 cm^{-1} which is attributed to υ_{NH}. The peak at 3050 cm^{-1} corresponds to the C-H stretching of the thiazole ring. The symmetrical and asymmetrical stretching due to the methyl and methylene groups are observed at 2980, 2940 and 2860 cm^{-1}. The absorption at 1680 cm^{-1} could be assigned for a complex stretching vibrations of N—C=O and C—N. The broad band at

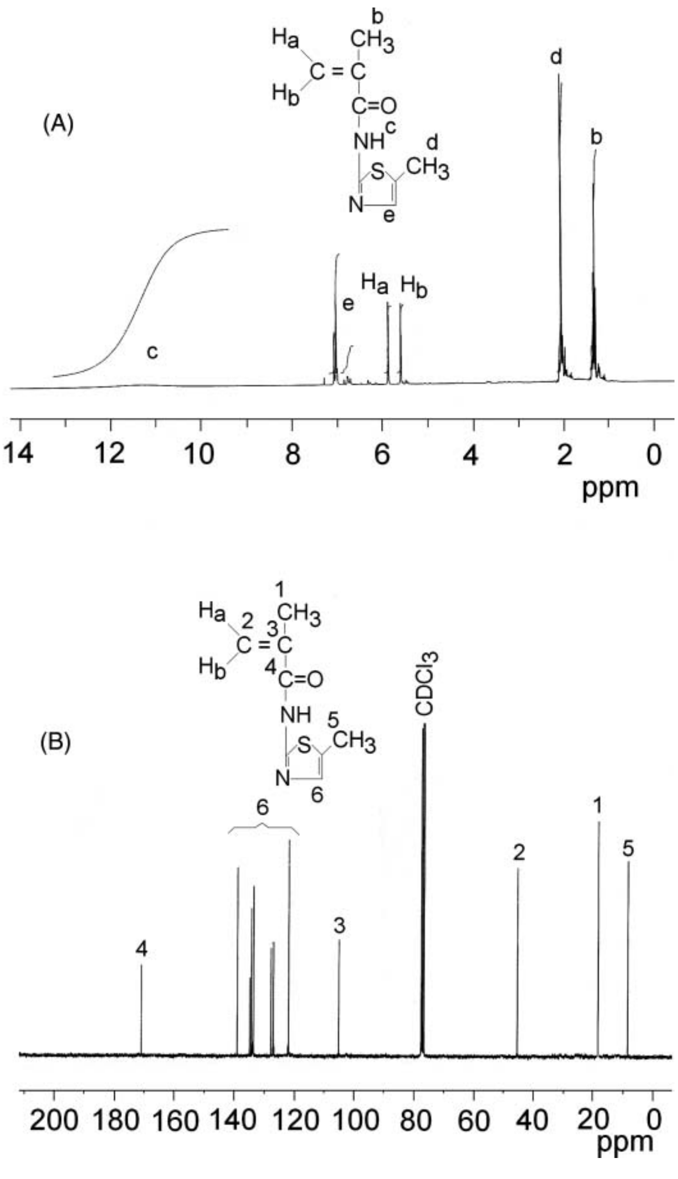

Fig. 3. ^{1}H-NMR spectra of MTMAAm (A) and ^{13}C-NMR spectra of MTMAAm (B)

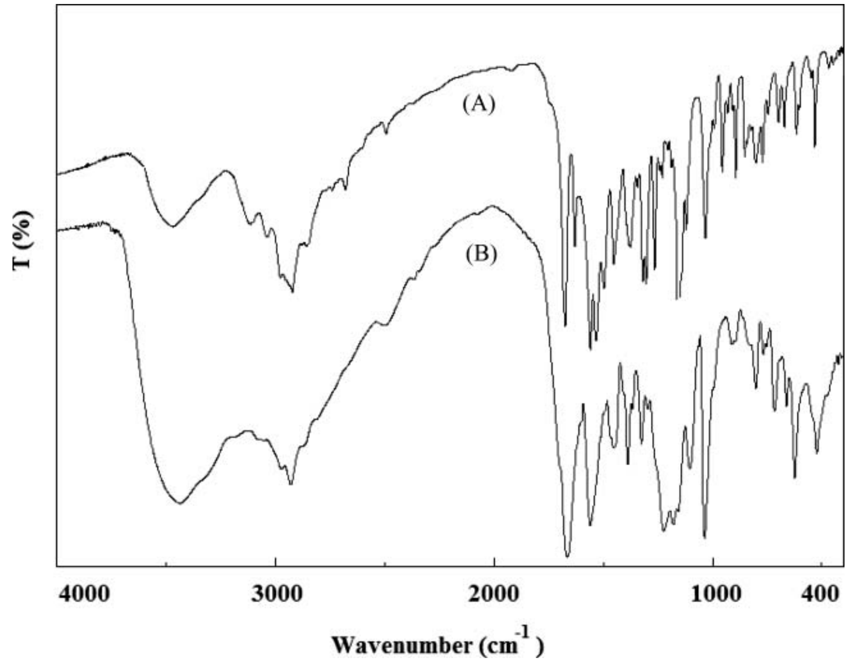

Fig. 4. FTIR spectra of MTMAAm (A) and chelating resin (B).

1430 cm^{-1} could be due to the C-N scissoring vibration of the $-N-C=O$ group. The ring breathing vibrations of the aromatic nuclei are observed at 1600, 1510 and 1480 cm^{-1}. The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1380 and 1358 cm^{-1}. A strong band at 1040 cm^{-1} is attributed to υ_{SO}. The C$-$H and C$=$C out of plane bending vibrations of the thiazole ring nuclei are observed at 800 and 570 cm^{-1}, respectively.

3.2 Effects of pH on Adsorption

It is well known that the pH of the medium has a great effect on the adsorption behavior of chelating resin and the surface structure of sorbents, as well as the formation of metal ions (25, 35). At different pH values, the protonation and deprotonation behaviors of acidic and basic groups would be influenced. The surface structure of the resin and the metal ions would exist in different forms. The effect of pH on the retention of Cu(II) and Cr(III) ions on the column was studied by passing Cu(II) and Cr(III) solutions containing one of the species. The pH of the solution was adjusted in a range of 1–10 by using appropriate buffer solutions. The optimum pH was found to be 2.5. The retained ions were eluted with 10 mL of 1 molL^{-1} nitric acid. Cu(II) and Cr(III) ions in the eluate were determined by FAAS.

3.3 Adsorption Capacity

The adsorption isotherm of the resin for Cr(III) and Cu(II) was studied by using the column method by using FAAS. The adsorption capacity of chelating resin was obtained by using the Langmuir equation (36) given in the following:

$$\frac{C}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right) \times C \qquad (1)$$

Where C (mg L^{-1}) is the concentration of the analyte ions in solution at equilibrium and n (mg g^{-1}) is the adsorption amount. A breakthrough curves were gained by plotting the concentration (mg L^{-1}) vs. the milligrams of Cu(II) and Cr(III) adsorbed per gram resin. The adsorption capacity (n_m) and the binding equilibrium constant (K) were obtained from the slope and the intercept of the regression plot obtained by the least squares method, respectively. Aliquots of 25 mL of the model solutions containing Cr(III) and Cu(II) at increasing concentrations (20–600 mg L^{-1}) and (20–800 mg L^{-1}) were adjusted to the appropriate pH and the proposed method was applied. Figures 5 and 7 shows the relationship between concentration (C) of Cu(II) and Cr(III) ions and the adsorption amount (n). It is clear from Figures 5 and 7, the adsorption amount of Cu(II) and Cr(III) ions increased with increasing ion concentration. The plots of C/n vs. C in Figures 6 and 8 were drawn from the experimental data given in Figure 5 and 7. The relationship between C/n and C is linear, and this indicates the adsorption behavior of resin fit to the Langmuir isotherm.

The adsorption capacity of the chelating resin for Cr(III) and Cu(II) was found to be 7.77 mg g^{-1} and 4.27 mg g^{-1}, respectively. And binding equilibrium constant was calculated to be 0.155 L mg^{-1} and 0.106 L mg^{-1}for Cu(II) and Cr(III), respectively. The results showed that the sorbent had a quite high adsorption capacity for Cr(III).

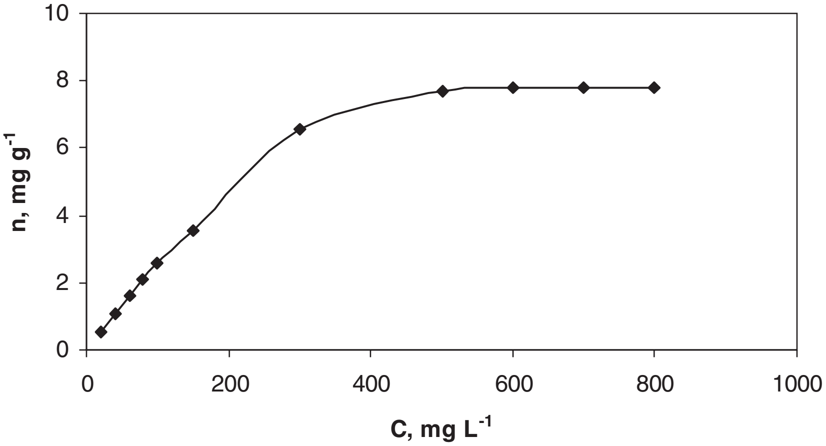

Fig. 5. Adsorption isotherm for Cu(II) ion.

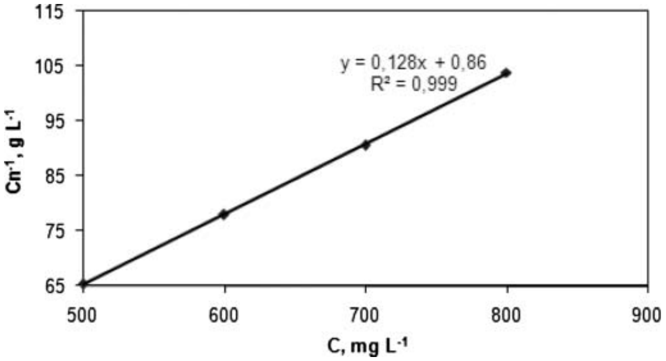

Fig. 6. Plot of C/n vs C for Cu(II) ion.

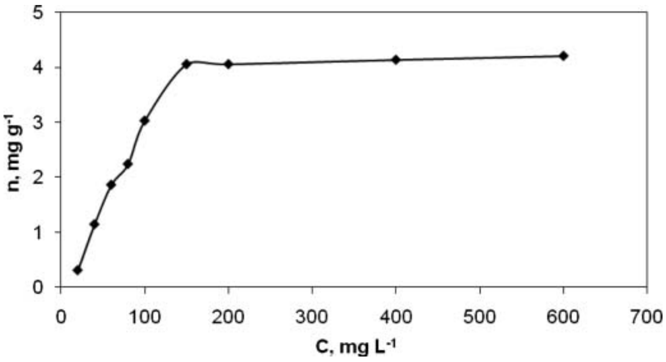

Fig. 7. Adsorption isotherm for Cr(III) ion.

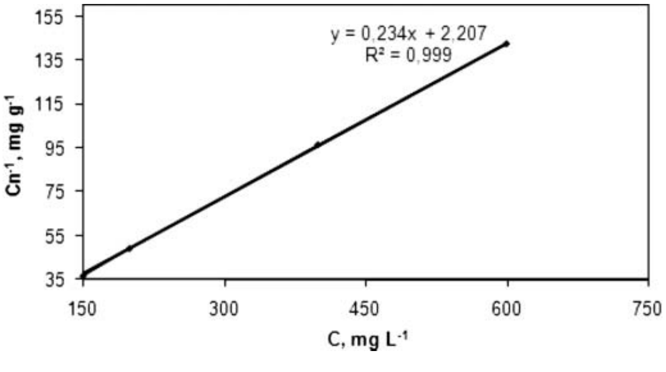

Fig. 8. Plot of C/n vs C for Cr(III) ion.

4 Conclusions

A new chelating resin was synthesized, characterized and applied for the separation and preconcentration of copper(II) and chromium(III) ions in aqueous solutions. A 0.70 g of the synthesized resin was used throughout all the work without any loss in recovery values of copper(II) and chromium(III). High adsorption capacity for Cr(III) is the main advantage of the proposed method. It is an accurate, simple and economical method.

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