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Preparation of A Chelating Polymer and Its Use in Removal of Copper and Cobalt Ions from Polluted Water

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Abstract

Methylene bis acrylamide (MBA) was modified by grafting with itaconic acid to synthesize a chelating copolymer. The structure of this compound was investigated using FTIR. The grafting ratio of MBA to itaconic acid was 1:1 g/g, ratio of copolymer to initiator 1:0.017 g/g, grafting time three hours and the grating temperature was 60ºC. The obtained graft copolymer was used as adsorbent for removal of Cu^{2+} and Co^{2+} ions from aqueous solutions. The effects of pH value, contact time, initial metal concentration and polymer dosage on metal ion uptake were reported. Adsorption data for adsorbate concentration are most commonly described by adsorption isotherms, such as Langmuir, Freundlich and Temkin isotherms. Experimental results showed that the metal ions removal percentages increased at pH = 4, using initial concentration of metal ions of 60 mg/L after 60 min of stirring.

Keywords: copolymer, metal removal, copper, cobalt, isotherm.
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1. Introduction

Excessive release of heavy metals into the environment due to industrialization and urbanization activities has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products [1] and, more seriously, can cause various diseases, e.g., headaches, nausea, vomiting, abdominal pain, insomnia, neurological disorders and liver damage [2–4]. The presence of heavy metal ions is of major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, radiator manufacturing, smelting, alloy industries and storage batteries industries [5].

The removal of heavy metal ions from wastewaters has been a subject of extensive industrial research. At the same time, some of them (e.g., Pt and Au) are precious and can be recycled and reused for extensive applications [6,7]. Various techniques have been utilized to remove and recycle heavy metals from aqueous solutions such as chemical precipitation, ion exchange, membrane separation, electrochemical treatment, adsorption, etc. [8–11]. Among them, adsorption is one of the most simple and common methods. The adsorption of metal ions can be achieved by using polymer materials containing specific functional groups, for example, amino, carboxyl, phosphoric, tetrazine and amidoxime, etc. [12] to form strong complexes with metal ions via the coordination reaction. The adsorption of metals onto these materials mainly depends on the functional groups on the adsorbent surfaces. Amidoxime group, in particular, has exhibited superior adsorption ability because it contains both amino and carboxyl groups.

2. Experimental

Itaconic acid, Methylene bis acrylamide, Benzoyl peroxide, DMF and salts of Copper, Cobalt and Chromium ($CuSO_4.5H_2O$, $CoCl_2.4H_2O$ and $Cr(NO_3).H_2O$) were obtained from Sigma Co. Graft copolymerization of itaconic acid onto methylene bis acrylamide was carried out with benzoyl peroxide as an initiator under vacuum. Itaconic acid and methylene bis acrylamide were dissolved in least amount of DMF, then benzoyl peroxide was added to the solution and heated on a thermostat at a water bath for experimental time at 60 ºC. The reaction product was washed with petroleum ether (40/60) then dried.

Sorption experiments were carried out by stirring 0.05 g of polymer in 25 ml solution containing different concentrations of (Cu^{2+} and Co^{2+}) ions at 60 min. After centrifugation, the remaining metal ions were determined using Atomic Absorption (AA) spectrophotometer.

The adsorption capacity was calculated from the following Eq. (1).

$$q_e = (C_0 - C_e)\frac{V}{m} \qquad (1)$$

Where, q_e is the adsorption capacity of adsorbent (mg/g), C_o and C_e (mg/L) are the initial and final concentration of each heavy metal in the solution, and V (L) and m (g) are the volume of the adsorption solution and the dose of each adsorbent, respectively.

3. Results and discussion

To characterize the functional groups of the synthesized polymer, an FTIR spectrum was carried out. The resulting spectrum of the free polymer was compared with the spectra of the two metal-loaded polymers to identify the nature of the removal process. Fig (1). The FTIR spectrum of the polymer is illustrated in Fig (1) and compared with those of Cu^{2+} and Co^{2+} loaded polymers. It is clear from the figure that there is no difference in the resulting spectra between the free and the loaded polymer, so the removal process could be through adsorption rather than chelation.

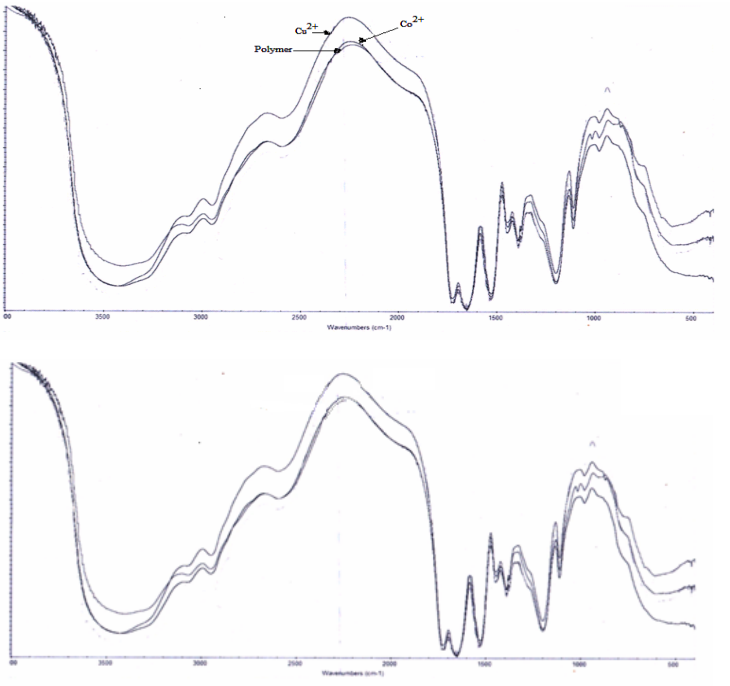

Fig (1): FTIR spectra of free polymer and Cu- and Co-loaded polymers.

Wavenumber (cm^{-1})	Assignment
983	=C-H bend
1020	=C-O-C sym.
1112	C-O-C stretch
1198	C-O stretch, O=C-O-C
1393	CH_3 C-H bend
1453	C-H bend,
1529	N-H bend
1651	C=O stretch, N-H bend
1729	C=O stretch
2596	O-H stretch
2950	C-H stretch, O-H stretch
3400	O-H stretch, N-H symmetric& asym. stretch

The structure of the synthesized polymer is shown in Fig (2).

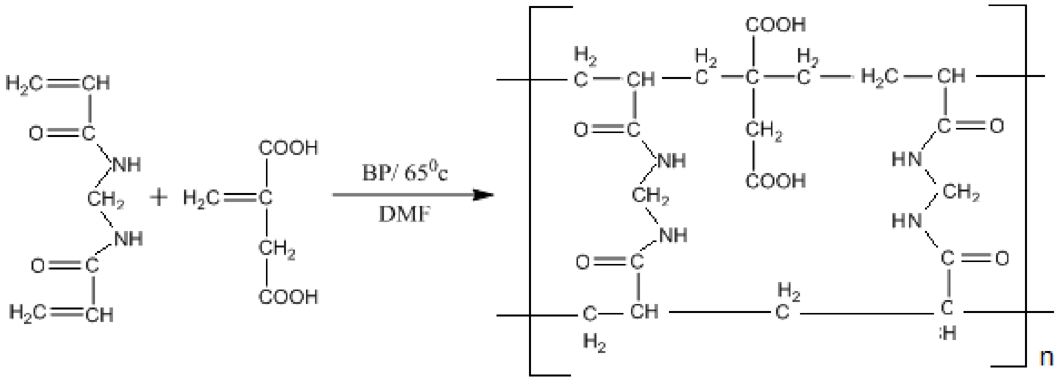

Fig (2): Chemical structure of the polymer.

The ability of the resulting polymer to remove of Cu^{2+} and Co^{2+} ions from aqueous media was examined and optimized by considering the different parameters. The initial concentration of metal ions is an important factor for effective adsorption process. The removal percents of metal ions Cu^{2+} and Co^{2+} at different metal ion concentrations were performed by keeping all other parameters constant. As shown in Fig (3), the removal percent decreased for the two metal ions by increasing the initial metal concentration. In the same time, increase in metal ion concentration was observed to cause higher q_e values which can be explained by the concentration gradient which provide driving force for the mass transfer rate. At lower heavy metal concentration, the active sites were enough to interact with metal ions, but the sites became less available and reached saturation with increased metal ions concentration.

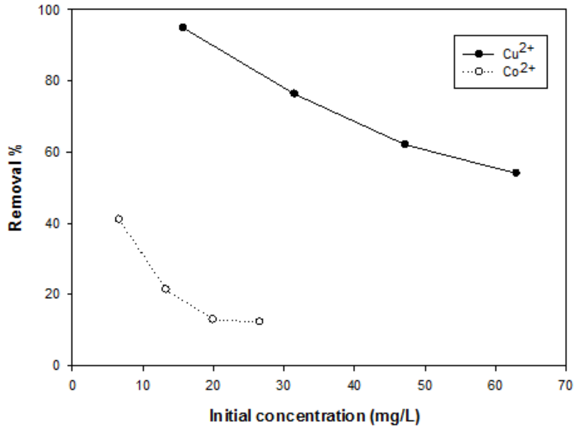

Fig (3): Effect of initial metal ion concentration on removal percent

The effect of adsorbent dosage on Cu^{2+} and Co^{2+} adsorption was investigated by changing the adsorbent dosage from 1 to 4 g/L, keeping all other parameters constant. The results illustrated in Fig (4) show that the removal percent of metal ions Cu^{2+} and Co^{2+} increased for the two metal ions by increasing the polymer dosage concentration. When increased adsorbent surface and availability of more adsorption sites with a fixed amount of metal ions.

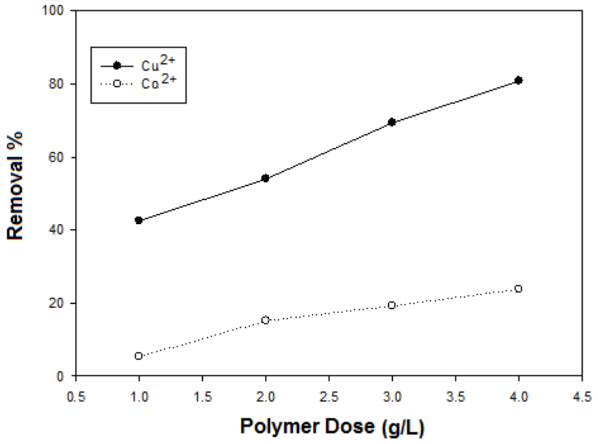

Fig (4): Effect of polymer dose on metal ion removal percent.

The effect of contact time was depicted in Fig (5). As could be seen from the figure, the adsorption increased with increasing contact time. The rapid adsorption at the initial stage is probably due to the abundant availability of active sites on the surface of grafted polymer. The adsorption capacity of metal ions becomes less, and equilibrium was achieved within 90 min.

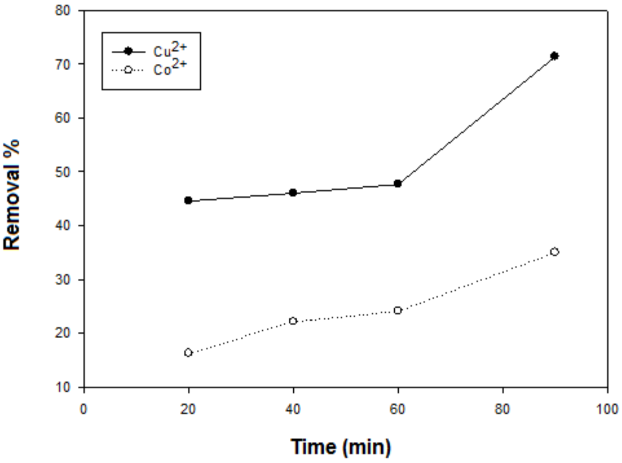

Fig (5): Effect of contact time on metal removal percent.

The pH of the aqueous solution of metal ion is an important operational parameter in the adsorption process as it affects the solubility of the metal ion, concentration of the counter ions on the functional groups of the adsorbent as well as the degree of ionization of the adsorbate during reaction. As shown in Fig (6), an increase in solution pH causes a corresponding increase in percent of metal removal. This behavior is expected [13] and may be due to the electrostatic attraction between metal ions and the functional groups on the adsorbent surface which increases with decrease of H^+ ions as the solution acidity decreased. The low removal values found at acidic solutions may be attributed to the competition between H^+ and metal ions for the same adsorbing sites [14].

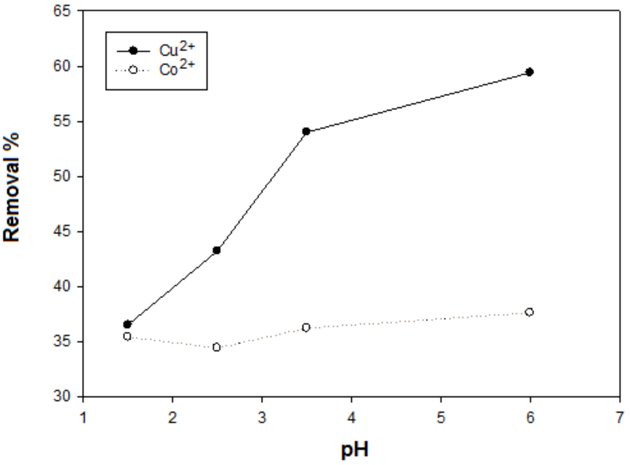

Fig (6): Effect of pH on metal removal percent.

3.3. Adsorption isotherms

Three isotherms were tested for their ability to describe the experimental results, namely Langmuir isotherm, Freundlich isotherm and Temkin isotherm.

3.3.1. Langmuir isotherm

This isotherm is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent and there is no significant interaction among adsorbed species and that the adsorbent is saturated after one layer of adsorbate molecules formed on the adsorbent surface. The linearized Langmuir isotherm equation can be written as follows [15]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \qquad (2)$$

where q_e (mol/g) is the amount of solute adsorbed per unit mass of adsorbent, C_e (mol/L) is the equilibrium concentration of solute, Q_0 (mol/g) is the maximum amount of adsorbate to form a complete monolayer on the surface, *b* (L/mol) is a constant related to the heat of adsorption. When C_e/q_e is plotted against C_e (Fig. 36) and the data are regressed linearly, Q_0 and b constants can be calculated from the slope and the intercept, respectively (Table 1).

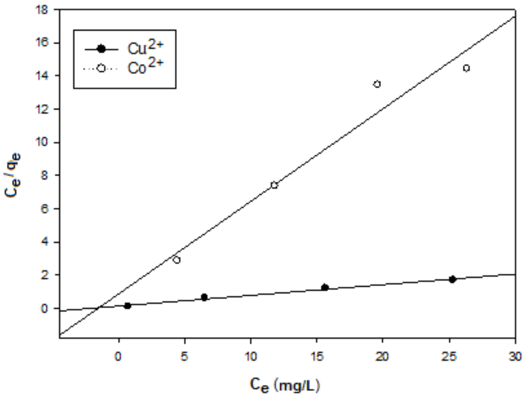

Fig (7): Langmuir isotherm for Cu^{2+} and Co^{2+} adsorption onto polymer

3.3.2. Freundlich isotherm

Freundlich isotherm takes the multilayer and heterogeneous adsorption into account. Its linearized form can be given as follows [16]:

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \qquad (3)$$

where q_e and C_e have the same definitions as in Langmuir equation above. Freundlich constant, K_F ($mol^{1-(1/n)}L^{1/n}g^{-1}$) is related to the adsorption capacity of different adsorbents and 1/n is another constant related to the surface heterogeneity. When ln q_e is plotted against ln C_e and the data are treated by linear regression analysis, 1/n and K_F constants are determined from the slope and intercept. The value of 1/n is known as the heterogeneity factor and ranges between 0 and 1; the more heterogeneous the surface, the closer 1/n value is to 0.

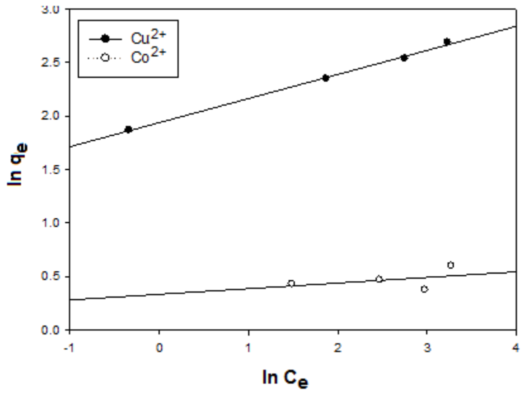

Fig (8): Freundlich isotherm for Cu^{2+} and Co^{2+} adsorption onto polymer

3.3.3. Temkin isotherm

A plot of q_e versus ln C_e enables the determination of the isotherm constants B and A from the slope and the intercept, respectively [17]. b_T is the equilibrium binding constant (L/g) corresponding to the maximum binding energy. As shown from Table 1.

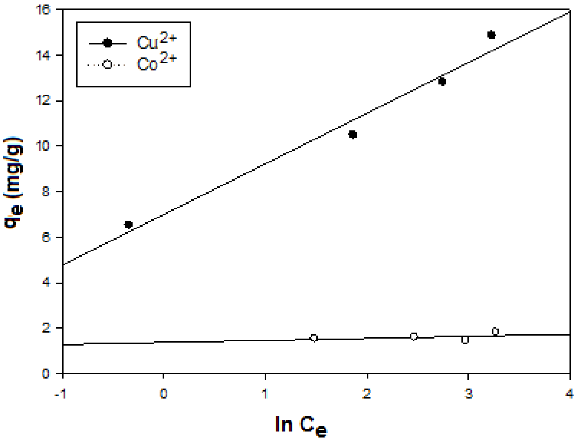

Fig (9): Temkin isotherm for Cu^{2+} and Co^{2+} adsorption onto polymer

Table (1): Langmuir, Freundlich and Temkin isotherm constants for adsorption of Cu^{2+} and Co^{2+}.

Metal ion	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	Q_O (mg/g)	b (L/mg)	R^2	K_F ($L^n mg^{1-n}/g$)	n	R^2	K_T (L/g)	B_T (KJ/mol)	R^2
Cu^{2+}	15.57	0.457	0.866	6.958	4.442	0.997	23.05	2.226	0.972
Co^{2+}	1.79	0.639	0.951	1.422	20.53	0.146	1.875	0.084	0.168

4. Conclusion

The experiments applied to the synthesized polymer proved its ability to act as an adsorbent for the two metal ions; Cu^{2+} and Co^{2+} from aqueous solutions. The parameters examined for studying the adsorption process of cobalt proved that it follows only Langmuir isotherm model, while that of copper follows mainly Freundlich model.

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