

Removal of Metal Ions Using Prepared Poly (Vinylpyrrolidone- Itaconic acid) Polymer

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Abstract: Template polymerization of itaconic acid (IA) in the presence of PVP as a template polymer using gamma rays as initiator were synthesized and characterized; and their use as sorbents in heavy metal removal was investigated. The capacity of the prepared polymer containing different amounts of PVP, N, N'-methylene-bis-acrylamide (NMBA) and IA concentration was investigated. It is obvious that the adsorption capacity increased with increasing itaconic acid content. P(VP-IA) was found to be a potential adsorbent for removal of metal ions from aqueous medium. The effects of pH of the adsorption medium, initial concentration of the metal ions and contact time and adsorbent dose were investigated as the effective parameters on the adsorption capacities. The selectivity of the resins for metal species was compared. Column experiments were applied using packed column with prepared polymer with specific eluting reagent that is efficient for separation of metal ions.

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1. Introduction

The term “template polymerization” usually refers to one phase systems in which the monomer and the template are soluble in the same solvent or are present in a form of a swollen gel. The nature of interaction between the monomer and the template polymer depends mainly on the nature of the forces acting between monomers and the template. These forces may be covalent bond, hydrogen bond, dipole-dipole bond or electrostatic forces. The presence of the template may influence the polymerization kinetics (e.g. Polymerization rate, activation energy, reaction order with respect to monomer and initiator), the characteristics of the produced polymer (average molecular weight, molecular weight distribution, microstructure, stereoregularity) and the reactivity ratios in the case of copolymerization.

Thermal gravimetric analysis of hydrogels showed that the thermal stability of hydrogel decreases slightly with incorporation of AMPS units into the structure.

In addition, the morphology of the dry hydrogel sample was examined by SEM. According to swelling experiments, hydrogels with higher AMPS content gave relatively higher swelling ratio compared to neat hydrogel. These hydrogels were used for the separation of Cd(II), Cu(II) and Fe(III) ions from their aqueous solutions (Kök Yetimoğlu, 2007).

Template polymerization leads to the formation of two types of products, interpolymer complexes and ladder-type polymers. The former are formed if the polymer or growing polymer chains interact with the template by intermolecular forces, while the latter are formed when the monomer units are connected by covalent bonds with the template, or when that type of

bond is formed in an interpolymer complex, for instance by thermal treating. The structure of polymer complexes formed in the course of template process is frequently different from the structure of complexes obtained by mixing component solutions. Such complexes can be used as highly efficient or selective adsorbents (Połowiński, 2002).

The competitive removal of Pb^{2+} , Cu^{2+} , and Cd^{2+} ions from aqueous solutions by the copolymer of 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and itaconic acid (IA), P(AMPS-co-IA), was investigated. Homopolymer of AMPS (PAMPS) was also used to remove these ions from their aqueous solution. In the preparation of AMPS-IA copolymer, the molar percentages of AMPS and IA were 80 and 20, respectively. In order to observe the changes in the structures of polymers due to metal adsorption (Selva, 2008).

The equilibrium swelling values of poly[2-(acrylamido)-2-methyl-1-propanesulfonic acid] and poly[2-(acrylamido)-2-methyl-1-propanesulfonic acid-co-itaconic acid] showed that the swelling of the copolymer is dominated by its completely ionizable constituent 2-(acrylamido)-2-methyl-1-propanesulfonic acid. Although the incorporation of itaconic acid into poly[2-(acrylamido)-2-methyl-1-propane sulfonic acid] did not affect the removal rates of poly[2-(acrylamido)-2-methyl-1-propanesulfonic acid-co-itaconic acid] for Pb^{2+} and Cd^{2+} ions (Selva, 2009). The polyethyleneglycolmethacrylate-co-vinylimidazole (PEGMA-VI) copolymers, that can be used in heavy metal removal applications, were synthesized and characterized; and their use as sorbents in heavy metal removal was investigated.

It was determined that the ligand vinylimidazole was successfully inserted into the polymer structure. Then, chromium (Cr(VI)) and nickel (Ni(II)) ions were used as model species to investigate the usability of the obtained microspheres in heavy metal removal (Erdal, 2010).

The adsorption of Cu(II) ions from aqueous solutions onto poly(acrylic acid-co-acrylamide) hydrogels was investigated. The hydrogels were prepared via free-radical solution polymerization using Irgacure 754 as a photoinitiator and ethylene glycol dimethacrylate as a cross-linking agent. Loading of acrylamide/acrylic acid moieties on the surfaces of hydrogels and the amount of cross-linking agent were varied to determine the maximum metal uptake (Eulogio, 2010). Copolymer network hydrogels were prepared by gamma irradiation of aqueous solutions of poly(vinyl pyrrolidone) (PVP) and acrylic acid monomer (AAc). The composition of the final hydrogels compared to the composition of the initial preparation solutions of hydrogels was determined (Safaaa, 2007).

The present work reports the study of interpolymer complexes formed by template polymerization of itaconic acid on poly(vinyl pyrrolidone) as a preformed template using NMBA as a crosslinker and gamma rays as initiator. The effects on the adsorption capacity, such as initial monomer concentration, template concentration and amount of crosslinker were investigated. The adsorption properties of the polymer in the aqueous solution of metal ions were also investigated in details.

2. Materials and Methods

2.1. Materials

Itaconic acid (IA) and poly(vinyl pyrrolidone) (PVP) were obtained from Fluka and used without further purification. N, N'-methylene-bis-acrylamide (NMBA) was purchased from Merck and used as received. Analytical grade reagents (Merck) of metal ions salts were used without purification. All solvents were distilled before use.

2.2. Instruments

The functional groups of the prepared polymers were examined by Fourier transform infrared spectroscopy (FTIR), on Bomem, Hartman & Borunz spectrometer, MB 157 Model using a KBr pellet. The capacity of the prepared polymers was determined by Shimadzu UV/V-double beam spectrophotometer model UV/V-210A, Tokyo. A cobalt-60 gamma cell of type MC-20 (Russia) was used as irradiation source for polymerization. It has two chambers with 5 liters for irradiated samples. The dose-rate of irradiation source was found to be 2.5 kGy h⁻¹.

2.3. Preparation of polymer complex

Samples were prepared by template polymerization of IA on PVP in water using gamma rays. The acid concentration (IA), PVP and amount of crosslinker were investigated. The complexes were precipitated and separated from the solution, washed twice with water and dried under vacuum at room temperature to constant weight.

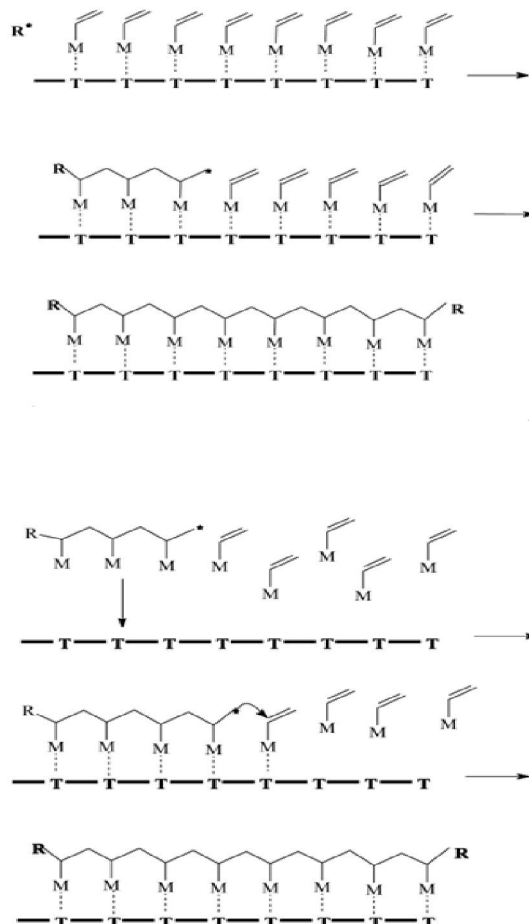


Fig. 1. Schematic representation of chain template polymerization typeI (zip mechanism) and typeII (pick-up mechanism)

2.4. Morphological characterization (SEM)

The surface morphology of P(AN-co-MMA) was observed after coating with gold with the help of a scanning electron microscopy (Joel Jsm 6360LA, Japan) at an accelerated voltage of 20 kV.

2.5. Particle size analysis

Particle size of P(AN-co-MMA) was analyzed by using Submicron Particle Size Analyzer (Beckman Coulter – USA). The sample dispersed in water, at a temperature 20 °C, of viscosity 1.002 and refractive index 1.33.

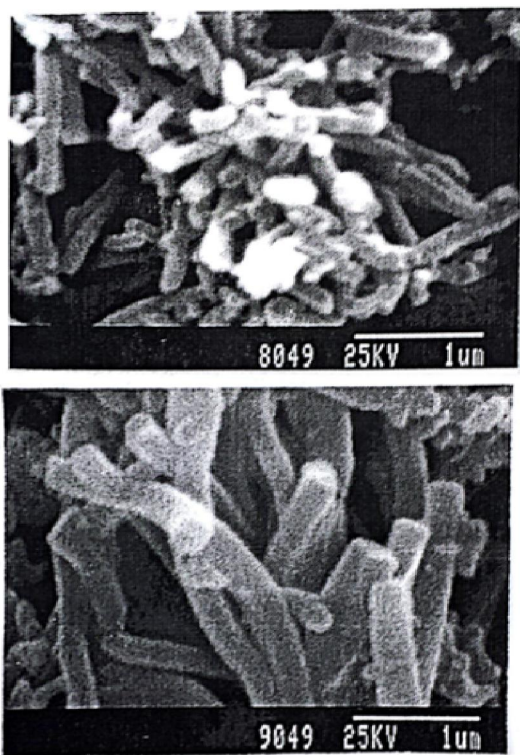


Fig. 2. Typical SEM images of Poly(Vinylpyrrolidone-Itaconic acid) polymer synthesized by template-free method



Fig. 3. Typical TEM images of Poly(Vinylpyrrolidone-Itaconic acid) polymer synthesized by template-free method

2. 4. Adsorption of metal ions

The chemicals used for the study were analytical grade of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), FeSO_4 and

NiSO_4 . Copper ion adsorption isotherms were developed from copper sulfate solutions that ranged in concentration from 1500 to 2500 mg L^{-1} of copper ions. 50 mg of P(VP-IA) was shaken in a flask containing 20 ml of copper sulfate at a constant temperature of 25°C , using a flask shaker for predetermined equilibrium time of 120 min. The mixture was filtrated with filter paper and the residual Cu^{2+} concentration in the filtrate was measured using a spectrophotometric method. The adsorption capacity of the metal ions at different acidic pH was also studied. For this, the initial pH of metal ions was adjusted by adding hydrochloric acid. Adsorptive quantity of metal ions was calculated according to:

$$q_e = \frac{V(C_o - C_e)}{m} \quad (1)$$

where q_e is the mass adsorption equilibrium copper uptake quantity (mg g^{-1}), V is the sample volume (ml), C_o is the initial metal ion concentration (mg L^{-1}), C_e is the metal ion equilibrium concentration (mg L^{-1}) and m is mass the dry weight of the adsorbent (mg).

3. Results and Discussions

3. 1. Characterization of polymer by FTIR

According to the chemical structure of the polymers, hydrogen bonding must be between the carboxylic group and the amide group. Fourier transform infrared spectroscopy was used for the identification of hydrogen bonds in the complexes as shown in Fig. 4.

It is well known that acids tend to self-associate with the formation of dimers, so pure poly(itaconic acid) shows a broad band at 3430 cm^{-1} , while the carbonyl stretching band for PIA lies at 1715 cm^{-1} (Cesteros, 1994). The carbonyl group of PVP exhibits a peak between 1650 and 1680 cm^{-1} . When the carbonyl group forms intermolecular bonding there is a negative shift exhibited in the IR spectrum.

As shown in Fig. 5, the absorption peak around 3500 cm^{-1} can be ascribed to the C-N group. The absorption peak at 1670 cm^{-1} is associated with the C=O group, the absorption peaks at 3433 cm^{-1} ascribed to the COOH group and 1729 cm^{-1} for C=O of P(VP-IA).

The spectra of the interpolymer complexes show spectral features similar to those for the homopolymers, but the bands appear at shifted positions. Hydrogen bonds are formed between the proton-donor and proton-acceptor molecules. The intensity of the hydrogen bond band depends on the acidity of the hydrogen in the proton-donor, the alkalinity of the proton-acceptor and possibility of their close contacts (Abdel-Aziz, 2011).

As a consequence of hydrogen bonding, the covalent bonds in the donor and acceptor are weaker,

while the energy barrier for angle deformation becomes higher.

Hence, in the groups which are involved in the hydrogen bonding formation, the frequency of the valence vibrations decrease with the simultaneous increase in the frequency of the deformation vibrations. Hydrogen bonding has the strongest influence on the donor (in our case the O–H of the polyacid) and the absorption maxima of the stretching vibration shifts

toward lower wave numbers compared to that for the pure polyacid.

Formation of hydrogen bonds increases the frequency of the valence vibrations in the acceptor, as well ($\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$). In the spectrum of pure PVP, the $\nu(\text{C}=\text{O})$ band lies at 1670 cm^{-1} whereas in the spectra of the complexes this band appears at the lower frequency of 1654 cm^{-1} .

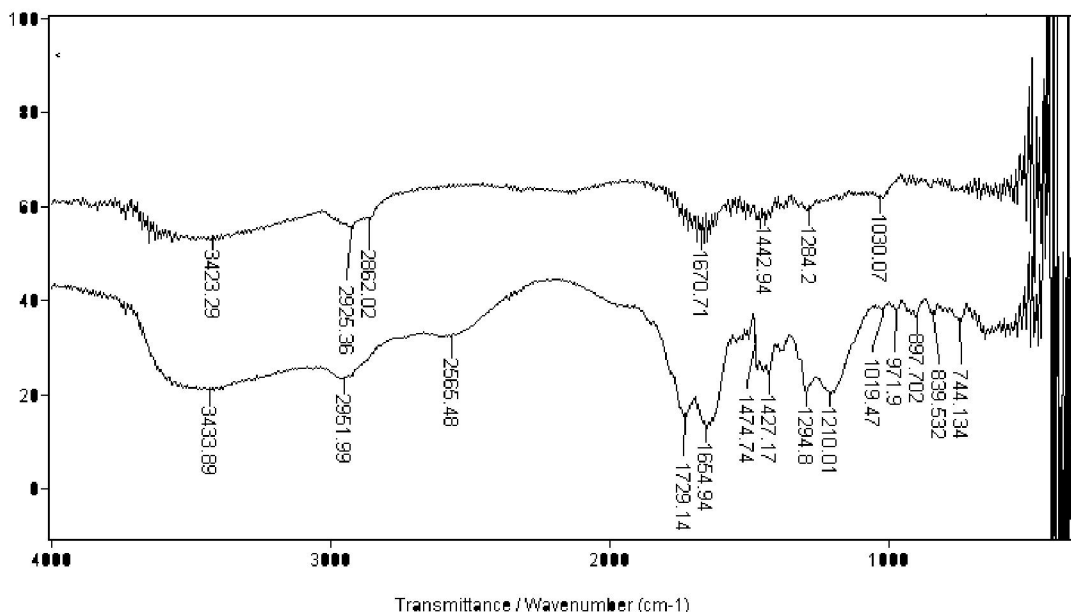


Fig. 4. FTIR spectrum of P(VP-IA).

3. 2. Effect of itaconic acid concentration

In general the concentration of the comonomer in the reaction solution affects the properties of the resulting polymer or copolymer, the kinetics of the reaction, and the economics of the process (Weng, 2007).

Fig. 5 shows the effect of adsorption amount of ions of P(VP-IA) as a function of itaconic acid concentrations. It is obvious that the adsorption amount of ions increased with increasing itaconic acid content. This increase in adsorption of P(VP-IA) can be attributed to the ionization of carboxylic groups ($-\text{COOH}$) in the polymer matrix.

3. 3. Cross linking effect

The influence of N, N'-methylene-bis-acrylamide as a crosslinkers on adsorption amount of ions of P(VP-IA) is depicted in Fig. 6. It is clearly observed from the Fig. 6 that at lower concentration of NMBA the adsorption capacity is high and with increases crosslinker concentration the capacity of the polymer

space between the polymer chains thereby suppressing the capacity of the polymer.

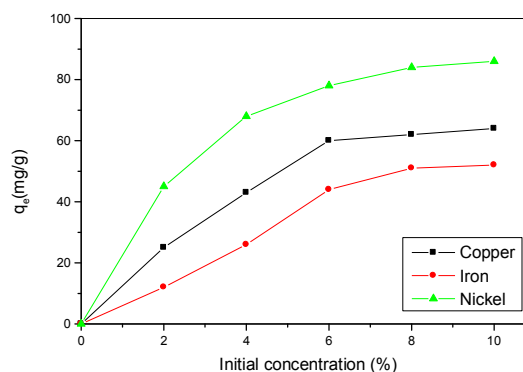


Fig. 5. Effect of IA concentration on the sorption of metal ions by P(VP-IA).

This behavior can be explained on the basis of formation of networks in the copolymer chains. At lower crosslinker concentrations the formed copolymer has lower crosslink density, whereas at higher crosslinker concentrations the formed polymer has higher crosslink density causing decrease in the

3. 4. Effect of PVP content

The capacity of the prepared polymer containing different amounts of PVP was investigated as shown in Fig. 7. It is clear that the presence of PVP as a template polymer reduces the capacity of P(VP-IA). This can be attributed to the interpolymer complex

formed between the PVP and PIA which is responsible for the reduction in the capacity of the prepared polymer.

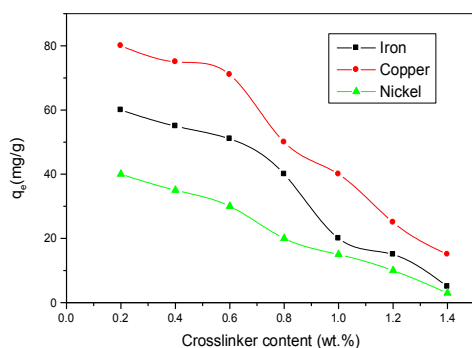


Fig. 6. Effect of NMBA concentration on the sorption of metal ions by P(VP-IA).

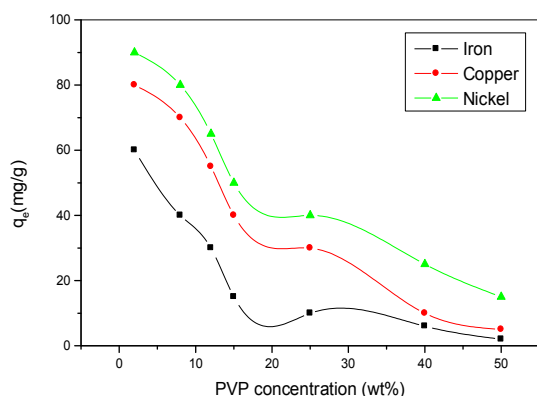


Fig. 7. Effect of PVP on the sorption of metal ions by P(VP-IA).

3. 5. Effect of pH on adsorption of metal ions

Fig. 8. depicts the effect of metal ions removal at various pH levels (2.0–5.0) for an initial metal ion concentration of 2500 mg L^{-1} . It is evident from Fig. 5 that Cu adsorption increases with increase in pH of the solution and reaches maximum at pH 4.7. For iron adsorption reaches maximum at pH 4, while adsorption of nickel reaches to maximum value at pH 3. Further increase in pH (beyond pH 4.7) may be attributed to the precipitation of metal ions as X(OH)_2 (Devine, 2005).

This can be explained in terms of amide and carboxylic groups which provide additional binding sites for the metal ions. At higher acidic conditions, low pH of about 2-3, little copper ions adsorption was occurred. These results may be related to H^+ ions are abundant at its surface, where COO^- groups and H^+ ions produce COOH groups, which form hydrogen bonds causing the surface layer to shrink. This surface layer acts as a barrier slowing down the adsorption amount of ions. With increase in the pH of the solution, the amount of adsorbed copper ions

increased and maximum adsorption was obtained at pH of 4.7. In the region of pH 4.0 to about 5, the adsorption amount increases with increasing of pH. This occurs because the poly(itaconic acid) carboxylic groups become progressively more ionized so the complexes break and the electrostatic repulsion between the carboxylate groups pushes the network chains apart giving rise to excessive adsorption.

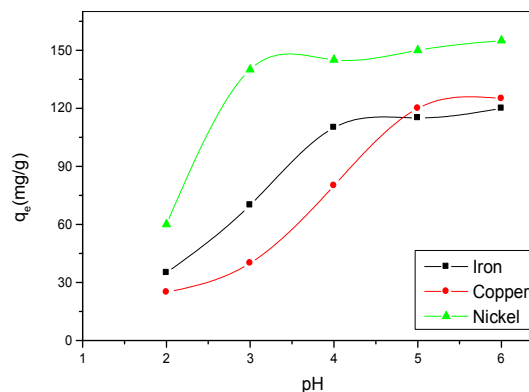


Fig. 8. Adsorption of metal ions as a function of pH.

3. 6. Effect of contact time

The results of adsorption of metal ions at different shaking time are shown in Fig. 9., at the beginning of adsorption, the uptake of Cu^{2+} increased quickly, after 60 min, the process of adsorption nearly reached equilibrium. After this equilibrium period, the amount of adsorbed Cu^{2+} did not significantly change with time. The results suggested, at the beginning of the process, the adsorption occur at polymer surface, so, a fast adsorption rate was found. After that, the adsorption took place at the inner surface of the polymers, so, the adsorption rate was slow due to the pore diffusion of metal ions into the polymer matrix. On the other hand, the system did not show any desorption of Cu^{2+} after long time of stirring. That demonstrated the resultant materials formed strong bonds with copper ions, not just physical adsorption. According to the adsorption equation (Kaşgöz, 2003):

$$-\ln(1 - F) = Kt + c \quad (2)$$

where t is the adsorption time, k the adsorption rate constant and c is a constant, F is given as

$$F = \frac{q_t}{q_e} \quad (3)$$

Here q_t and q_e are the amount of adsorption at time t and equilibrium, respectively.

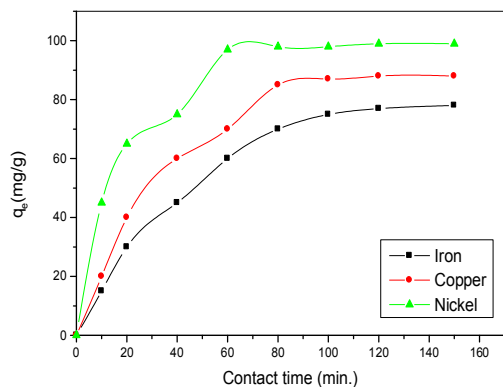


Fig. 9. The effect of contacting time for the adsorption of metal ions on P(VP-IA)

3. 7. Effect of mass of adsorption

The adsorption amount (mg g^{-1}) and percentage adsorption of Cu^{2+} at different doses of P(VP-IA) are shown in Fig. 10. It was observed that the adsorption quantity per gram of P(VP-IA) decreased from 240 to 80 mg g^{-1} with the dose of P(VP-IA) increasing. This is because adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increases by increasing the adsorbent dose. Thus, with increasing adsorbent dose, the amount of metal ions adsorbed per unit mass of adsorbents reduced, thus causing a decrease in q_e value (Wang, 2011).

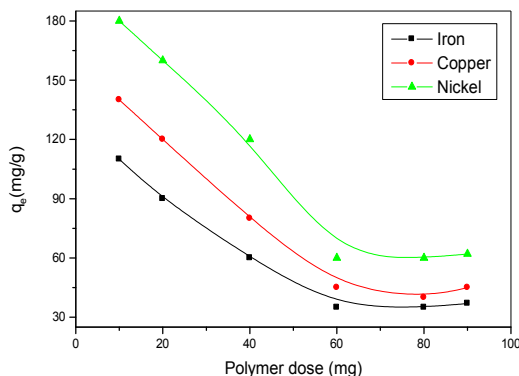


Fig. 10. The effect of P(VP-IA) dose on the adsorption of metal ions

3. 8. Column experiments

3. 8. 1. Breakthrough curves of metal ions

The loading capacity of P(VP-IA) polymer for sorption the $\text{Cu}(\text{II})$, $\text{Fe}(\text{III})$ and $\text{Ni}(\text{II})$ could be determined by breakthrough technique. A glass columns (7mm diameter \times 12 cm length) contain 0.7 g of P(VP-IA) polymer was prepared. Fig. (11) illustrates the breakthrough behavior of metal ions onto the P(VP-IA) column fed with 50 ml of 0.017 M $\text{Cu}(\text{II})$, $\text{Fe}(\text{III})$ and $\text{Ni}(\text{II})$ (2mg/mL) solution in 0.2M HCl acid passed through the column with a flow rate 1 ml/min.

It is clear that the exchanger has a high retention affinity towards $\text{Cu}(\text{II})$ and $\text{Ni}(\text{II})$ in the first 50 ml of the feed solution, while $\text{Fe}(\text{III})$ appear with 60% breakthrough.

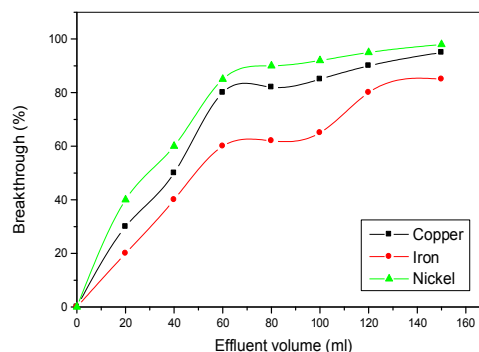


Fig. (11) Breakthrough curves of metal ions onto polymer in solution 0.2 M HCl

3. 8. 2. Elution studies of metal ions

Elution of indium was experimented using 0.01M of acetate buffer at pH4 from glass columns containing P(VP-IA) polymer, the obtained results were represented in Figs. (12). the first 30 ml of eluate iron was eluted, nickel and copper are eluted at 50 and 80 ml respectively.

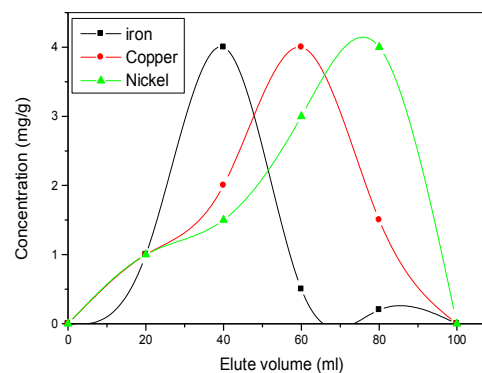


Fig. (12) Elution of metal ions from P(VP-IA) polymer using 1 M acetate buffer

4. Conclusion

In this study P(VP-IA) was prepared by the template polymerization of itaconic acid (IA) in the presence of PVP as a template polymer using gamma rays as initiator. The capacity of the prepared polymer containing different amounts of PVP, NMBA and IA concentration was investigated. It is obvious that the adsorption capacity increased with increasing itaconic acid content. While it decreased with increasing the concentration of PVP and NMBA. The present study revealed that P(VP-IA) resin could be employed as a potential adsorbent for the removal of heavy metals, The adsorption of metal ions was found to be dependent on pH, contact time, and adsorbent dosage.

Column studies was showed that elution of metal ions separately occurred using 1 M acetate buffer at pH 4.

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