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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.4, pp 2438-2445, July-Aug 2014

Selective Removal of Transition Metal ions from Waste water By ion Imprinting Technology

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Abstract: Transition Metal ion imprinted interpenetrating polymer networks were synthesized for selective removal of Fe(III), Co(II), Ni(II), Cu(II) ions from water. The polymers were prepared using template metal ions such as Fe(III), Co(II), Ni(II), Cu(II) ions a biopolymer alginic acid and N,N' Methylene-bis-acrylamide (NNMBA) crosslinked polyacrylamide using potassium persulphate as initiator. The non-imprinted polymer networks were also prepared without use of the metal ions. To determine the selectivity of ion imprinted polymers, competitive sorption studies were carried out and proved that ion imprinted polymers (IIP) showed good selectivity for the target metal ion and can be applied for water remediation.
Keywords: metal ion imprinting, template, selectivity, sorption, biosorbent.

1.Introduction

Metal ions are carcinogenic, hazardous and can cause environmental damage. So its removal from the environment is unavoidable and the remediation of metal-containing waste water needs much more attention [1]. Drinking water from a tap, such as a private well or public water system, is a source of potential exposure to environmental contaminants. The conventional techniques are commonly applied for the removal of metal ions from waste water including chemical or physical methods [2]. But they are often costly or ineffective. However, most of these methods are complicated and expensive. Recently, biosorption method has been suggested as an efficient, cost-effective and eco-friendly alternative to existing treatment techniques. Numerous investigations on IIPs and their use for selective separation of metal ions such as UO_2(II), Pd(II), Cu(II), Fe(III), Hg(II), Ni(II), Cr(II), Cd(II), and Zn(II) have been reported.[3-8]

Ion imprinted and non-imprinted polymers were synthesized using different transition metal ions as templates instead of using heavy metals. Transition metal ions like copper, zinc and manganese ions are essential for animals and plants. But they are toxic at high concentration and there are many reports based on their separation from waste water [9-13]. Similarly metal ions such as manganese, nickel and cobalt are hazardous to animals and plants at high concentration and can be separated from waste water by various methods[14]. Cobalt, one of the common toxic and low level radioactive metals affecting the environment, appears in waste waters of nuclear power plants and many other industries and it can produce variety of undesirable effects. The need of more selective system for separation of nickel has increased the development of the synthesis of new extractants and adsorbents. The World Health Organization has set a guideline value of

0.3 mgL^{-1} of iron in drinking water. The conventional method for the removal of iron from solution involves hydroxide precipitation, filter, electro coagulation, and ion exchange techniques.

In the present work we focus on synthesizing novel type of transition metal ion imprinted and non-imprinted interpenetrating polymer network using a natural biosorbent, alginic acid which is crosslinked by the hydrophilic crosslinker N N, Methylene bis acrylamide, and template metal ions. The newly prepared interpenetrating polymer networks are advantageous due to high sorption capacity and remarkable selectivity in transition metal ion separation from mixture of metal ions. The method of preparation of the IPN is simple, rapid, low cost and environment friendly due to the use of aqueous medium.

2. Materials and methods

2.1 Materials

Reagents of analytical and spectral grade were used for all experiments. Solutions of metal ions were prepared in millipore water. The monomers used in this study, namely acrylamide and crosslinking agent NNMBA were obtained from SRL, Mumbai. Alginic acid was obtained from Merk, India. Fourier transform infrared (FTIR) spectra of the metal ion imprinted, non-imprinted, and the metal ion bound polymers were recorded between 4000-400 cm^{-1}, using a Perkin Elmer 400 FTIR spectrophotometer. UV-vis. spectrophotometric measurements were carried out using Shimadzu 2400 UV-vis. spectrophotometer. SEM-EDAX was taken on JEOL-JSM-840A Scanning Electron Microscope in nitrogen atmosphere. Surface area measurements were carried out by BET method. The amount of metal ion adsorbed was determined before and after binding, using Perkin Elmer Atomic Absorption Analyzer 300.

2.2. Preparation of metal Ion Imprinted(IIP) and Non-imprinted Polymer (NIP) Networks

Alginic acid (7.5 g) was mixed with metal salts in aqueous medium. This mixture was added to acrylamide (10.66 g), NNMBA (7.71 g) and potassium persulphate (100mg) as initiator. The polymerization was carried out at 70^{o}C with constant stirring. The polymer obtained was washed with water to remove unreacted monomer and with 2N HCl to remove metal ions. The bulk polymer obtained was dried, sieved and weighed. Non-imprinted polymer networks were also prepared using the same procedure without metal ions.

2.3. Metal Ion Binding

In order to investigate specific rebinding capacity, metal ion imprinted and non-imprinted polymers were equilibrated with different metal ion solution. The concentration of metal ions before and after binding was determined by atomic absorption spectrophotometry (AAS).

Optimization of the metal ion Rebinding Conditions

In order to optimize the conditions of Pb(II) ion rebinding by Pb(II) ion imprinted and non-imprinted polymer networks, factors affecting rebinding such as concentration, time and pH of the Pb(II) ion solution on binding were investigated.

2.4. Effect of Concentration

The batch wise metal ion binding experiments were carried out to evaluate the imprinting efficiency using 500 mg of polymer. Similar rebinding studies at various concentrations of metal ion (1-5mgL^{-1}) were carried out and from the difference in concentration of template metal ion solution before and after incubation, the amount of metal ion bound was determined by AAS.

2.5. ***Swelling Studies***

100mg of IIP, NIP and corresponding metal ion ion bound polymers were allowed to swell in 10 mL water for 24 h. After 24 h the polymers were filtered and surface water was carefully wiped off, and the final swollen weight was determined. From the swollen and the dry weights of the sample the EWC (%) was calculated, using the equation-

$$EWC\% = \frac{\text{weight of wet polymer - weight of dry polymer}}{\text{weight of dry polymer}} \text{ x } 100$$

2.6. Adsorption Studies

Adsorption studies were carried out by batch equilibration method, using different sets of polymer. Aqueous solution of metal ion (5 ppm, 10 mL) was added to IIP/NIP. The solutions were shaken in stoppered bottles. At regular time intervals the concentration of metal ion was found out by atomic absorption spectrophotometry.

3. Results and discussions

3.1. Preparation of transition metal ion-imprinted (IIP) and non-imprinted polymer networks (NIP)

The ion imprinted polymer networks were synthesized by the free radical polymerization using Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) ions as templates, alginic acid and acrylamide as functional monomers, NNMBA as crosslinking agent in presence of initiator potassium persulphate, at 70^{o}C in a water bath. The bulk polymer obtained is washed with water to remove unreacted monomers and then with dil HCl to remove metal ions. The polymers obtained are dried, crushed and sieved. Non-imprinted polymer networks were also prepared without using the template metal ions.

3. 2. Characterization

3.3. FT-IR spectra

FT-IR spectral values of ion desorbed and bound polymers are given in Table I. The characteristic peaks due to -COOH group of alginate is obtained around 1640 cm^{-1} in all the ion imprinted polymers. These values are shifted to higher wavelength region on metal ion binding. The absorption bands revealed that -COOH group of alginate is participated in sorption process. Imprinted polymer showed bands at 2919 cm^{-1} and non-imprinted polymers showed bands at 2922 cm^{-1} due to C-H stretching vibrations.

Table 1. FT-IR Characteristic peak values of metal ion desorbed and bound Polymers

Polymer used	IIP(cm^{-1})	Metal bound IIP(cm^{-1})
Fe(III) IIP	1634	1645
Co(II) IIP	1635	1644
Ni(II) IIP	1634	1644
Cu(II) IIP	1635	1643

3.4. UV-vis. Spectroscopy

UV-vis. Spectral values of imprinted and metal ion bound polymers are given in Table 2. The interaction of Cu(II) ion with the carboxyl group of alginate chain resulted a shift in the wavelength maxima. Imprinted polymer showed bands at 13245 cm^{-1}, which is shifted to 18115 cm^{-1} on sorption of Cu(II) ion. The band at 14388 cm^{-1} is shifted to 18115cm^{-1} in Cu(II) ion bound polymers. These shifts indicate E_g-T_{2g} transition in copper bound polymers, due to Jahn-Tellar distortion, distorted tetragonal geometry is suggested for Cu(II) ion bound polymer.The values describes the shift in wavelength maxima on metal ion binding which suggests that $Eg \rightarrow T_2g$ transition takes place in all ion bound polymers. The characteristic tetragonal geometry is indicated on metal ion binding.

Table 2. UV-vis. Spectral values of metal ion desorbed and bound polymers

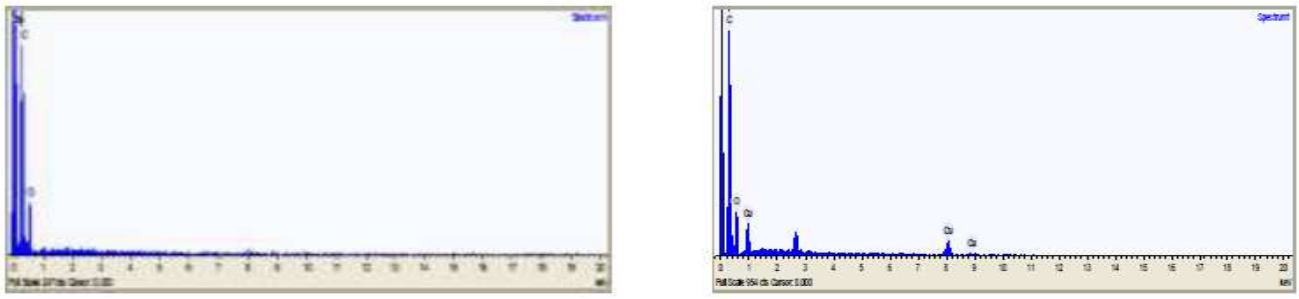
Polymer used	IIP (cm^{-1})	Metal bound IIP(cm^{-1})
Fe(III) IIP	15873	18726
Co(II) IIP	14388	18115
Ni(II) IIP	12626	18392
Cu(II) IIP	13245	18118

3.5. X-ray diffraction patterns

The XRD curve of metal bound polymer networks showed the characteristic peaks corresponding to each metal ion which is not seen in the XRD curve of IIP. This result indicates the binding of metal ion in metal bound polymer. The XRD curve of Cu(II) bound polymers showed the characteristic peaks corresponding to copper at 2θ values, 28.39, 47.25 and 56.07 degree respectively, which is not seen in the XRD curve of imprinted polymer, indicates the presence of Cu(II) ion in bound polymers and are placed in (200) plane of face centered cubic lattice**.** Co(II) ion bound polymer showed characteristic peak at 63 degree 2 theta value corresponding to (102) plane of hexagonal plane. In the case of Ni(II) ion bound polymer the characteristic peak is obtained at 44 degree 2 theta value corresponding to (111) plane of cubic plane. Fe(III) ion bound polymer showed a sharp peak at 47 degree 2 theta value. No such sharp peaks are seen in desorbed polymer.

3.6 SEM-EDAX

The SEM-EDAX of the Cu(II) ion desorbed and metal bound polymers are given in (Fig.1)**.** SEM-EDAX of IIPs of each metal ions indicate the absence of metal ions while the metal bound polymer networks showed the characteristic peaks corresponding to each metal ions.



(a) (b)

Fig. 1. SEM-EDAX of Cu(II) ion (a) desorbed and, (b) bound polymers

4. Swelling studies

The metal ion binding studies of the ion imprinted interpenetrating polymer networks in aqueous medium were influenced by the extent of swelling. The swelling behavior of metal ion imprinted, non-imprinted and the corresponding metal ion bound polymer networks were investigated (Table.3). In all the metal ion imprinted polymers maximum EWC (%) was obtained for ion imprinted polymers and it decreases on metal ion binding.

Table 3. EWC (%) values of ion-imprinted, non-imprinted and metal ion bound polymers

Polymer used	**EWC (%) values**			
	IIP	**NIP**	**Metal bound IIP**	**Metal bound NIP**
Fe(III) ion bound polymer	68	66	62	64
Co(II) ion bound polymer	89	82	84	86
Ni(II) ion bound polymer	94	92	88	91
Cu(II) ion bound polymer	94	92	89.5	91.5

5. Binding studies with metal ions

Metal ion binding studies of each of the interpenetrating polymer networks towards different metal ions of varying concentrations are given in (Fig.2). AS the concentration increases, binding of metal ion increases. The sorption capacity value of the IIP towards each metal ion was also higher than that of NIP. This result could be explained on the basis of a high driving force for mass transfer, where the increase in concentration of metal ion increases the competition to occupy all the available coordination sites in the adsorbent.

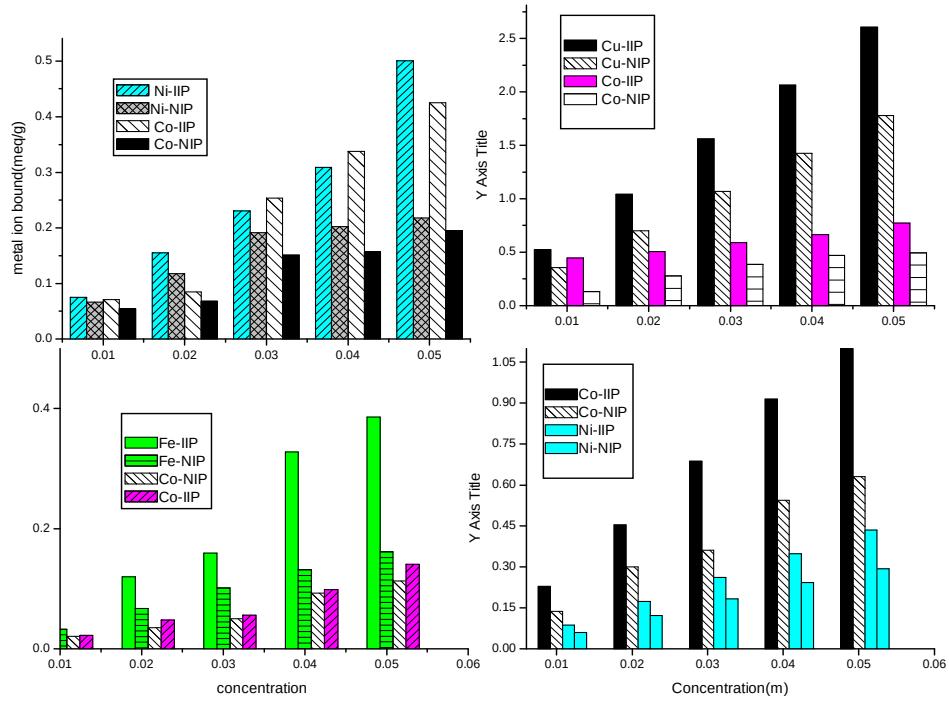


Fig .2. Metal ion binding by Ni(II),Cu(II) , Fe(III), Co(II), ion imprinted and non-imprinted polymers

The investigation was carried out by comparing the specific binding of imprinted polymer with a non-imprinted polymer. To find out the specific binding of each metal ion, definite amount of imprinted and non-imprinted polymers were equilibrated with metal ion solution and the amount of metal ion bound was determined by atomic absorption spectrophotometry. From the difference in binding between imprinted and non-imprinted polymers, it is evident that metal ion imprinted polymers showed specificity towards the imprint metal ion than non-imprinted polymer due to memory effect.

6. Sorption studies

The effect of concentration of metal ion solution on sorption rate and capacity were studied. Definite amount of imprinted and non-imprinted polymers were added to 10 ml of metal ion solution. The solutions were shaken in closed flasks. At regular intervals of time metal ion bound was determined by AAS. The sorption characteristics were assessed by plotting both Langmuir and Freundlich isotherms. The results obtained are given in Fig.3. which describes that Langmuir type sorption took place in each transition metal ions. Increasing the initial metal ion concentration causes an increase in the sorption capacity of the sorbent which stems from the fact that the probability of collusion between metal ions and biosorbent increases in this condition which enhances the biosorption ability.

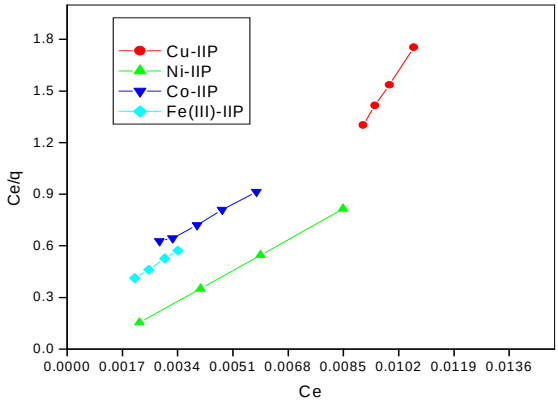


Fig. 3. Langmuir isotherms for ion adsorption on imprinted polymers

7. Selectivity studies

To investigate the metal ion selectivity of each of the imprinted polymers, competitive sorptions of Fe(III), Co(II), Ni(II), Cu(II) ions were conducted by column experiment, in which 1 g of the IIP was treated with 10 ml of a solution of these metal ions (5 ppm). When sorption equilibrium was reached, the concentration of metal ions in the eluted solution was measured by AAS. The results are given in (Fig.4). in each case IIP selectively bind the imprinted metal ion from its mixture with coexisting metal ions which indicate that the functional host molecules on the surface of IIP are immobilized with the strict configuration suitable for the imprinted metal ions, and that the ionic recognition is influenced by the nature, radius, charge and size of the metal ions.

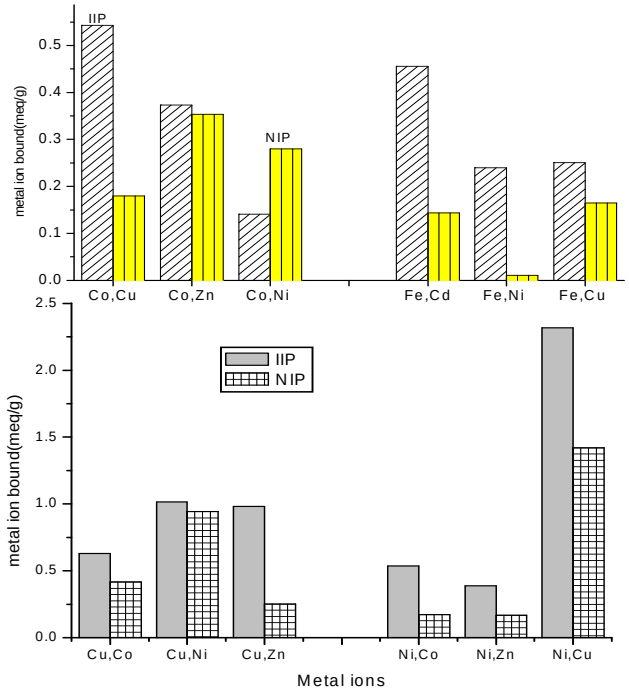


Fig.4. Selectivity studies of -Co(II), Fe(III), Cu(II), Ni(II), ion imprinted polymers

8. Reusability studies of ion imprinted polymers

Table .4. Reusability studies of ion imprinted polymers

	Metal ion sorption capacity in extraction cycles (meq/g)						
	1	2	3	4	5	6	Recovery(%)
Fe(III) IIP	0.51	0.51	0.50	0.489	0.488	0.488	97.4
Co(II)IIP	0.98	0.98	0.98	0.96	0.955	0.955	96.7
Ni(II)IIP	0.45	0.45	0.45	0.44	0.435	0.42	94.9
Cu(II)IIP	2.1	2.1	2.1	2.1	1.975	1.96	97.5

In order to investigate the reusability of imprinted polymers of each metal ions, it was subjected to several loading (50mg/10mL) of metal ion solution and elution operations. The elution operations were carried out with 4 mL of HCl (3N) found as the optimum elution condition. The calculated percentage recovery of the imprinted polymers showed no considerable decrease after 6 cycles of repeated experiments (Table 4). The percentage recovery of the recycled IIP could still be maintained at 97 to 98% at the 6th cycle.

9. Application of the method

Table .5. Analysis of environmental water samples

Metal ions	Canal water (mg/L)		Lake water (mg/L)		Recovery (%)
	Found	Recovered	Found	Recovered	
Fe(III)	0.42	0.415	0.399	0.388	97
Co(II)	0.04	0.031	0.024	0.021	95
Ni(II)	0.02	0.009	0.02	0.01	94
Cu(II)	0.06	0.056	0.04	0.033	98.5

The ion imprinted polymers of each transition metal ions are applied for the selective separation of corresponding metal ions from water samples collected from canal and lake and analysed. The obtained values describe the suitability of the developed transition metal ion imprinted polymers for the removal of corresponding metal ions from water samples. The results are listed in Table.5.

10. Conclusions

In conclusion the developed ion imprinted polymer networks reveals its great potential as an advantageous as sorbent for transition metal ions. Metal ion imprinted polymer networks were prepared using alginic acid and NNMBA-crosslinked polyacrylamide with different template metal ions such as Fe(III), Co(II), Ni(II), Cu(II) ions and characterized by different analytical methods. Metal ion binding studies described that IIP showed high sorption capacity than NIP and good reusability. Compared to sorption capacities, copper ion imprinted polymer showed high sorption capacity among other ion imprinted polymers. Selectivity studies of each ion imprinted polymers revealed that IIP selectively bind the imprint metal ion faster than non-imprinted polymers. The prepared IIPs are successfully applied for the removal of corresponding metal ions from water samples collected from environment.

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