

Removal of toxic metal ions from simulated wastewater using hydrophilic interpenetrating polymer networks

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ABSTRACT

The synthesis and characterization of interpenetrating polymer networks (IPN) comprised of chitosan and polyacrylamide, which could be used as a biosorbent was successfully achieved. The uptake of metal ions such as Cr(VI), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) was investigated and the conditions were optimized. Various spectroanalytical tools such as FT-IR, EPR, SEM, SEM EDAX and PXRD were used for the characterization of the synthesized IPN and the derived metal complexes. Parameters such as pH of the solution, concentration of the metal ion solution, and temperature were found to control adsorption process and the order of adsorption capacities for the studied metal ions was Cr(VI) > Fe(II) > Cu(II) > Zn(II) > Ni(II) > Co(II). Of the various adsorption isotherms Freundlich isotherm explains the experimental data satisfactorily. Thermodynamic study revealed the exothermic nature as well as the spontaneity of Cr(VI) adsorption by IPN. The possibility of IPN to be used as an effective adsorbent was evident from the selectivity towards Cu(II) from simulated waste water. This study showed that IPN could be used as an efficient adsorbent material for the removal of metal ions from aqueous solutions.

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KEYWORDS

Adsorption;
Interpenetrating network;
Polyacrylamide;
Metal uptake;
Schiff's base.

INTRODUCTION

The accumulation of metal ions in the environment is a threat to human health and remediation becomes important^[1,2]. Of the various methods that have been used for pre concentration and separation of trace metals, sorption is regarded as the most effective and economical method^[3]. Biosorption is effective in removing contaminants from the effluents^[4]. Chitosan obtained from chitin^[5] is one of the commonly used adsorbents^[6,7]. Modification of raw chitosan becomes necessary for the improvement of its properties including adsorption

capacity^[8,9]. Chemical modifications include cross-linking using a suitable crosslinking agent and formation of networks by incorporation of another polymer matrix. By incorporating chitosan in an inert hydrophilic media like polyacrylamide porosity, surface area and particle characteristics can be improved^[10]. Bifunctional glutaraldehyde is the crosslinking agent used for chitosan leading to the formation of Schiff's base^[11]. An interpenetrating network could be made from chitosan and acrylamide. In this study such an interpenetrating network was prepared and investigated for its metal uptake characteristics.

EXPERIMENTAL

Materials

Chitosan (deacetylation percentage 90%), was purchased from Marine Chemicals, Kochi, Kerala, India and used as received. Cr(VI), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) salts were obtained from Merck, India. Glutaraldehyde (25%) was purchased from Lobo, India. All other chemicals and solvents were of analytical grade and used as received.

Instrumentation

Fourier transform infrared spectra (FT-IR) were recorded on a Perkin - Elmer Spectrum 400 FTIR spectrophotometer. Metal ion concentrations were determined using Shimadzu UV-vis spectrophotometer model 2450. ESR spectrum was recorded at liquid nitrogen temperature, on a varian spectrophotometer (USA). SEM and SEM EDAX pictures were taken using Jeol JSM - 6390 A scanning electron microscope. For selectivity studies, the metal ion concentrations were determined using Perkin - Elmer Analyst 300 atomic absorption spectrophotometer.

Preparation of IPN

The chitosan dissolved in 2% acetic acid was mixed with glutaraldehyde solution and stirred mechanically for 1 hour. Solutions of acrylamide, N, N'-methylenebisacrylamide (NNMBA) and TEMED (N,N,N',N'-tetramethylethylenediamine) (3wt% of the acrylamide monomer) were added into the chitosan solution and stirred for further 1 h. The gel formed was washed several times with water, dewatered in methanol, dried at 50°C and kept in a sealed container.

Adsorption experiments

Batch equilibration experiments were carried out in 120 mL flasks for 3 hours, with 10 mL of standard solutions of Cr(VI), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) and 50 mg IPN. The concentration of Cr(VI), Fe(II), Co(II), Ni(II), and Cu(II) ions in the residual solution was followed spectrophotometrically and that of Zn(II) ions titrimetrically. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium Q_e was obtained as follows.

$$Q_e = \frac{(C_0 - C_e)V}{WM} \quad (1)$$

where Q_e is the equilibrium adsorption capacity in meq g^{-1} of the IPN, C_0 and C_e are the initial and equilibrium concentration of the solute ($mg L^{-1}$). V is the volume of the solution (L), W is the weight of the IPN(g) and M is the atomic weight of the corresponding metal ion.

The optimum pH for maximum complexation was determined by studying the metal uptake of the IPN as a function of pH. The IPN was added to the metal salt solution of definite pH and kept for complexation for 3 h. The concentration of metal ion in the solution was determined by suitable methods.

RESULTS AND DISCUSSION

Synthesis of interpenetrating polymer network

Crosslinking of chitosan leads to higher stability. As this reaction involves amino groups a decrease in the adsorption capacity may result. But actually the creation of a three dimensional network produced an enhancement in adsorption capacity.

(Refer supplementary information for scheme)

Characterisation

Fourier transform infrared (FT-IR) spectroscopy

The reaction between chitosan and glutaraldehyde leads to the formation of azomethine group (C=N). It appears as a strong peak at $1656 cm^{-1}$. The -NH deformation vibration of amino group appears at $1450 cm^{-1}$. The peak at $1374 cm^{-1}$ is due to -C-N stretching vibration and that at $1656 cm^{-1}$ is due to the carbonyl group of secondary amide of the incorporated crosslinked polyacrylamide. The strong band in the range $3050-3200 cm^{-1}$ corresponds to N-H stretching frequency. IPN metal complexes show shifts in the band corresponding to azomethine group and secondary alcoholic group ($10-16 cm^{-1}$) thus giving evidence for the involvement of these groups in chelation.

X-ray powder diffraction analysis

The suitability of IPN for the metal uptake is evident from the XRPD pattern (supplementary information).

Metal ion complexation

The results of the batch adsorption experiments are summarized in Figure 1. The metal uptake follows the order Cr(VI) > Fe(II) > Cu(II) > Zn(II) > Ni(II) >

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Co(II). The hydrophilic nature and flexibility of the crosslinker also plays a significant role in allowing the metal ions to diffuse into the polymer matrix^[12].

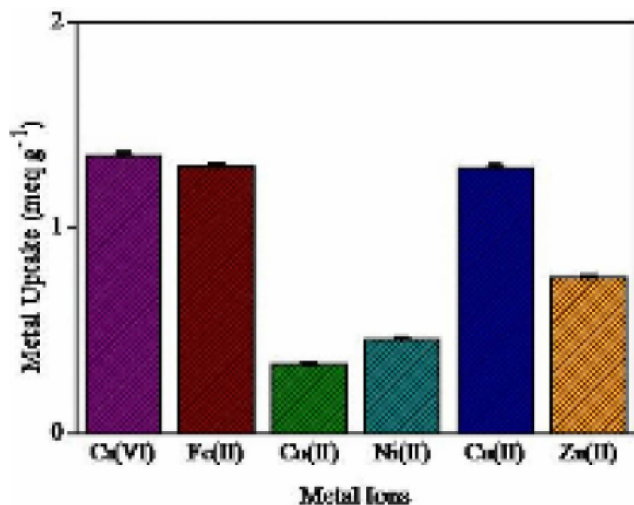


Figure 1: Metal ion complexation of IPN

Influence of pH

Metal ion sorption is dependent on the pH of the experimental solution and also on the nature of the metal ion. H⁺ occupies most of the adsorption sites at low pH^[13] and hence the metal sorption is low. The reverse is the case with Cr(VI) ions. In aqueous solution Cr(VI) ions can exist in various forms depending on the concentration and pH of the solution. HCrO₄⁻ is the predominant species in the acidic solutions (pH 2-5). Due to protonation the IPN remains positively charged at low pH. The prevalent electrostatic attraction between the positively charged IPN and the monovalent HCrO₄⁻ ion leads to an increased uptake at lower pH^[14]. At higher pH deprotonation of IPN occurs and Cr(VI) ion uptake shows a decrease. The metal uptake shows an increase from pH 1.5 to 3.6 and then shows a drastic decrease, with increasing pH.

Graph is included in the supplementary information.

Adsorption isotherms

Equilibrium adsorption data for the adsorption of Cr(VI) ion on IPN were subjected to Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms.

1. Langmuir isotherm

Discussion is included in supplementary informa-

tion.

2. Freundlich isotherm

Freundlich isotherm equation is

$$Q_e = kC_e^{1/n} \quad (3)$$

where Q_e is the amount of metal ions adsorbed (mg g⁻¹), C_e is the equilibrium concentration of metal ions (mg L⁻¹). The linearised form of the equation is

$$\log Q_e = 1/n \log C_e + \log k \quad (4)$$

where k and n are Freundlich constants indicating adsorption capacity and intensity respectively. A smaller $1/n$ value indicates a heterogeneous system, a value approaching unity indicates a homogeneous system^[15]. The plot of $\log Q_e$ versus $\log C_e$ results in a straight line. This isotherm expresses adsorption to be taking place on heterogeneous surfaces^[16]. Figure 2 illustrates a linear Freundlich plot for the adsorption of Cr(VI) on IPN. The constants are tabulated in the Table SI 3.

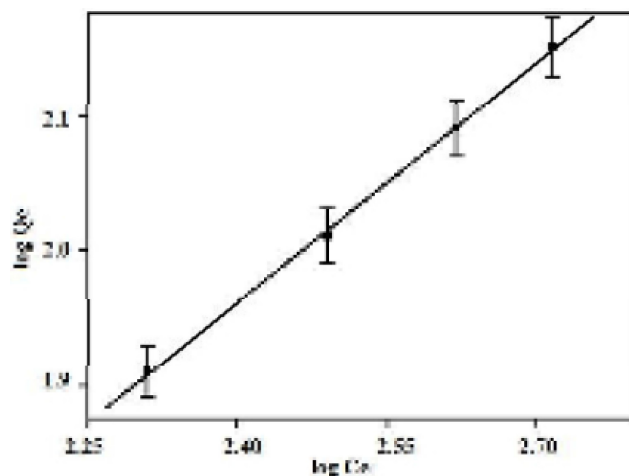


Figure 2: Freundlich isotherm for the adsorption of Cr(VI) ions on IPN

The R value is 0.9991 which indicates best fit of the experimental data with Freundlich isotherm equation. The validity of Freundlich isotherm supports the heterogeneous nature of the sorption.

Distinction between physical and chemical adsorption can be done with the help of Dubinin-Radushkevich isotherm^[9].

$$\ln Q_e = K\varepsilon^2 + \ln Q_{DR} \quad (5)$$

Polanyi potential (ε) is given by

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (6)$$

The plot of $\ln Q_e$ versus ε^2 gives a straight line plot.

The mean energy of adsorption was calculated using the equation 7.

$$E = (-2K)^{-1/2} \quad (7)$$

The mean adsorption energy (E) involved the transfer of one mole of the solute from infinity to the surface of the adsorbent. The mean adsorption energy in the range 1-8 kJ/mol predicts physical adsorption. The mean adsorption energy (E) based on Dubinin-Radushkevich isotherm is found to be 8.32 kJ/mol. Thus the physical adsorption is involved in the adsorption process. The constants are tabulated in Table SI 3.

Adsorption thermodynamics

Discussion included in supplementary information

Competitive adsorption

The complexation behaviour of a given chelating polymer towards various metal ions can be better understood by the parameter distribution Coefficient (K_d)^[17].

$$K_d = \frac{C_{ad} \times V}{C_{eq} \times W} \quad (8)$$

where C_{ad} is the amount of complexed metal ion (mg), V is the volume of the solution (mL), C_{eq} is the amount of uncomplexed metal ion (mg) and W is the weight of the polymer (g).

Cr(VI) has the highest value for the distribution coefficient and hence could be selectively separated from a mixture of other metal ions. (For the distribution coefficient values of metal ions under study refer supplementary information)

From the results of the competitive adsorption by IPN shown in the Figure 3, it can be seen that Cu(II) ions undergo selective binding from binary mixtures {Fe(II), Cu(II)}, {Ni(II), Cu(II)} and {Cu(II), Zn(II)} as expected, and from zinc contaminated solution almost complete removal was effected. Cu(II) ions undergo selective binding from the mixture of three metal ions viz. {Cr(VI), Cu(II), Zn(II)}; {Cr(VI), Cu(II), Cd(II)}; and {Cr(VI), Ni(II), Cd(II)} (For figure refer supplementary information). The enhanced selectivity for Cu(II) from the mixture of three different metal ions may be because of the proximity of the experimental pH to the optimum pH for Cu(II) ion adsorption. The separation of metal ions from simulated waste water can be carried out by the proper management of ex-

perimental pH.

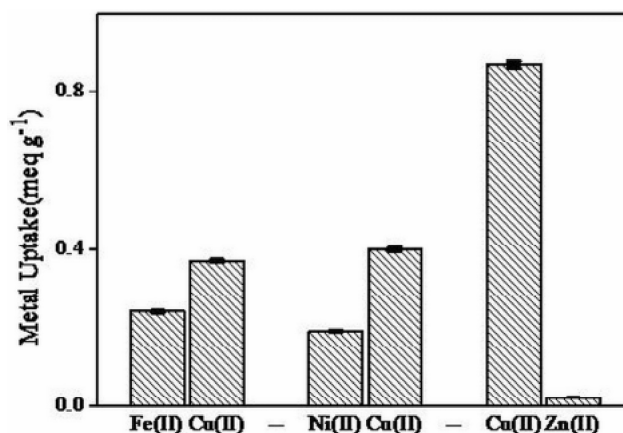


Figure 3 : The selective adsorption from a mixture of two metal ions

Stability and shelf life of the adsorbent

IPN can be stored for a long time without appreciable loss in metal uptake capacity. The polymer was kept in sealed container in a desiccator for a period of one year. The metal uptake property was found to be comparable with that of the initial values (supplementary information).

CONCLUSIONS

IPN could be conveniently prepared from chitosan and acrylamide. Crosslinking and also the entanglement lead to chemical as well as physical stability. The adsorption processes were found to depend on pH of the metal ion solution and temperature. IPN exhibited high selectivity for copper ions. The studies show that IPN could be used as an effective chelating agent for the removal of metal ions from waste water.

ACKNOWLEDGEMENTS

Shiby Susan Kuriakose is thankful to UGC for the award of teacher fellowship. The services rendered by Dr. C. Arunan, School of Chemical sciences, Mahatma Gandhi University, Kerala, CEPCI, Kollam, Kerala and STIC, CUSAT, Kochi, Kerala, as well as SAIF, IIT Mumbai are greatly acknowledged.

SUPPLEMENTARY INFORMATION

A supplementary Information file which contains ad-

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ditional figures and tables is available

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