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Separation of heavy metal ions by complexation on poly (N-vinyl imidazole) hydrogels

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Summary

Poly (N-vinyl imidazole) (PVIm) hydrogels were prepared by γ-irradiating binary mixtures of N-vinyl imidazole-water in a ^{60}Co-γ source having 4.5 kGy/h dose rate. These hydrogels were characterized with gravimetric and spectrophotometric studies. Hydrogels with equilibrium swelling ratio of 600% in distilled water were used in the metal ion adsorption studies. The effects of pH, equilibration time, and initial metal ion concentration were considered in batch equilibrium study on the chelation of Cu^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+} ions. Maximum metal ion adsorption were observed at pH=6.0. It has also been observed that the amount of adsorbed metal ions decreased at lower pHs because of protonation of PVIm ring.

Introduction

With increasing industrialization, one of the most important problems threatening our world has become environmental pollution. In nature, sea-, river or lake waters, biological and inorganic-organic samples, it is possible to meet with toxic metal ions and compounds. It is assumed that the life of these metal ions and their compounds is infinity due to their toxicity. The removal of toxic and polluting metal ions from industrial effluents, water supplies, as well as mine waters is an important challenge to avoid one of the major causes of water and soil pollution. Various methods have been proposed to remove heavy metal ions from seawater and wastewaters using ion-exchange resins, biosorption, chelating resins etc. [1,2].

Chelating resins have many practical applications in water treatment, environmental protection, chemical analysis, etc. Recently, many scientists have prepared and studied many kinds of chelating resins containing various ligands and have used these resins for the removal and recovery of heavy metal ions from industrial wastewater, the recovery of uranium and vanadium from sea water [3-5]. We are particularly interested in the application of hydrogels for the removal of heavy metal ions from aqueous systems for water purification purposes [6,7]. Major attractions of hydrogels are their potential for regeneration after uptake of the contaminants and easy applicability.

The general aim of the present study has been to investigate the interaction of Cu^{2+}, Co^{2+}, Cd^{2+} and Pb^{2+} ions with PVIm hydrogels. Adsorption isotherms have been constructed to investigate these interactions as a function of initial metal ion concentrations and pH of metal ion solutions.

Experimental

Materials and Methods

N-vinyl imidazole (VIm) was obtained from Merck (Darmstadt, Germany). All metal chlorides, $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $CdCl_2.1/2H_2O$, and $PbCl_2$ were obtained from BDH (Poole, UK).

Aqueous solutions of N-vinyl imidazole were prepared in different compositions. These solutions were irradiated in PVC straws in ^{60}Co-γ source, Gammacell 220 in air at room temperature at a dose rate of 4.5 kGy/h. Hydrogels obtained in long cylindrical shapes were cut into small pieces and dried in air and in vacuum and ground into powder form. Preparation and characterization of PVIm hydrogels have already been reported elsewhere [8].

Using metal chlorides, Me^{2+} solutions were prepared (150 – 1500 mg/L). PVIm hydrogels (with an average particle size of 800 μm) with a weight of 0.01 g were added to 10 mL of Me^{2+} solutions. The solutions were stirred for the time necessary to attain the adsorption equilibrium at 25 ± 1°C. Hydrogels were separated from the liquid phase with a centrifuge. Me^{2+} concentrations of the supernatant were measured using a Philips PU 8715 UV-vis spectrophotometer. The amount of Me^{2+} adsorbed on PVIm hydrogels was determined from the difference between the Me^{2+} concentrations from these readings. The influence of pH on metal adsorption by PVIm hydrogels was investigated. Throughout this study, the pH of the solutions was adjusted by a 0.1 N CH_3COOH-COONa buffer.

Spectroscopic and thermogravimetric analysis

FT-IR spectra of PVIm hydrogels with and without Me^{2+} were taken with a Nicolet 520 FT-IR spectrophotometer. The thermal behavior of the Me^{2+} ion adsorbed PVIm hydrogel was investigated using a Du Pont 951 thermogravimetric analyzer.

Results and Discussion

Hydrogels can swell to a considerable extent in many organic solvents as well as in water or in a variety of organic or inorganic aqueous solutions. This is particularly important for biomedical and environmental applications. Swelling studies were conducted on nonprotonated and protonated (at pH 5.0) PVIm hydrogels. Detailed information about swelling experiments was given in our previous work [8]. Figure 1 shows the percent swelling as a function of time for both plain and protonated PVIm hydrogels. It can be seen that percent swelling of PVIm hydrogel rise to very high values after protonation due to the Coulombic repulsion between protonated $^{+}$N-H groups. To optimize the time required for complexation, PVIm and weakly protonated PVIm hydrogels were mixed with 1500 ppm Cu^{2+} solutions at 25°C. During the adsorption, aliquots were taken from the adsorption medium occasionally and their absorbencies at

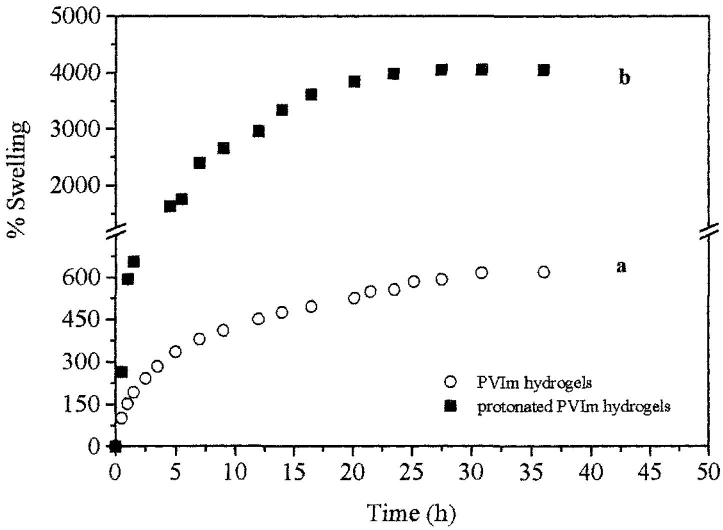


Figure 1. Percent swelling values of PVIm (a) and weakly protonated (at pH 5.0) PVIm (b) hydrogels

maximum wavelength were measured using UV-vis spectrophotometer. The amount of adsorbed Cu^{2+} on PVIm hydrogels versus time plots was constructed to determine the optimum equilibration time. Figure 2a shows that the amount of metal ions adsorbed per gram of dry hydrogel increases during the first 50 h and then reach almost a constant value. For weakly protonated (at pH 5.0) PVIm hydrogels (Figure 2b), adsorption equilibrium was attained within 25 h. Intake volume increasing upon excessive swelling due to Coulombic repulsion. Therefore, the active sites of weakly protonated PVIm hydrogel interact with metal ions easily. Tan et al. [9] studied the effect of protonation on the conformation of soluble poly(N-vinyl imidazole) using potentiometric titration. The polymer coil contracts during the initial stages of protonation but then expands upon further protonation. The conformational changes are explained in terms of competition between internal hydrogen bonding between protonated and nonprotonated rings and charge repulsion.

Chelation of a metal ion by a polymeric ligand is highly dependent on the pH of the medium [10]. Since most of the metal ions are prone to precipitation at higher pH, investigations were limited to those pH values where precipitation was just prevented. pH of medium has two kinds of influence on metal uptake: an effect on the solubility and speciation of metal ion in aqueous solution, and an overall charge of the ligand of the adsorbents. The amount of adsorbed metal ions on PVIm hydrogels as described in experimental section, as a function of the pH were determined and listed in Table 1. As seen from the table, the amount of adsorbed Me^{2+} ions increased with increasing pH value due to reduction in the amount of protonated N atom at 3 position of imidazole ring. In other words, there is little adsorption occurring at pH=2.5 (protonation 98%). At pH=5.0 (protonation 40-50%), the number of protonated nitrogen atoms on imidazole ring is decreased when compared to pH=2.5 causing the adsorption value to increase. When pH is increased further, i.e., pH=6.0, there will be less protonated nitrogen atoms on imidazole ring giving rise to higher metal ion adsorption. The electron pair on the N atom of imidazole ring lead to an enhanced electrostatic interaction between metal ions and corresponding interaction sites. At even higher pHs, Me^{2+} ions start precipitation as hydroxides.

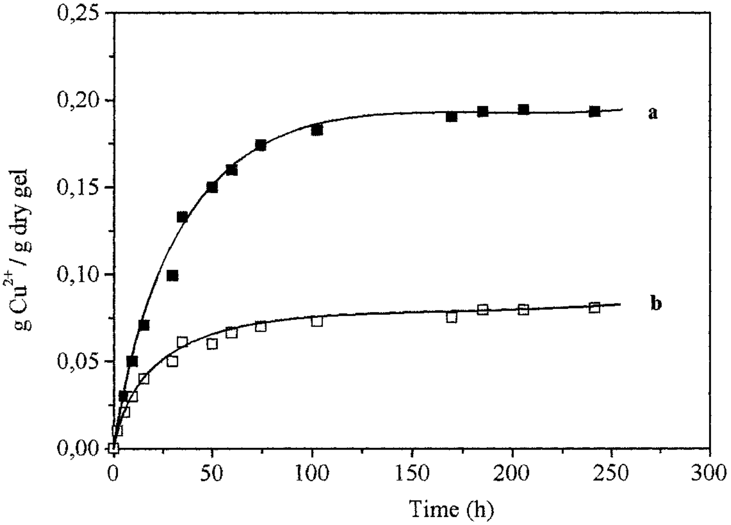


Figure 2. Adsorption kinetics of PVIm (a) and weakly protonated (at pH 5.0) PVIm (b) hydrogels

Adsorption isotherms were constructed by plotting the amount of adsorbed Me^{2+} at equilibrium versus concentrations of Me^{2+} ions remaining in the solution at equilibrium at pH=6.0. Figure 3 shows the adsorption isotherms of PVIm hydrogels for Cu^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+} ions. When the initial Me^{2+} concentration increases, the amount of adsorbed Me^{2+} by PVIm hydrogels increases and then levels off. Adsorption isotherms obtained for protonated PVIm hydrogels are also shown in Figure 4. As shown in Figure 4, the maximum amount of Me^{2+} adsorbed is lower than with nonprotonated PVIm hydrogels. During chelation, a metal forms a coordinate bond with the electron pair of nitrogen atom at 3 position of imidazole ring. After protonation, the amount of adsorbed Me^{2+} decreases due to the formation of $^{+}$N-H group at 3 position of imidazole ring. As can be seen from Figures 3 and 4, the adsorption curves appear to be of the Langmuir type [11]. In addition, Cu^{2+} ions show strong interaction with PVIm hydrogels while Co^{2+}, Cd^{2+}, and Pb^{2+} are interacting weakly with PVIm hydrogels. There are two components to any complexation reaction, the metal ion and the complexing agent, both contribute to the formation of the complex and both have their own characteristics. Only if these characteristics match a strong bond can form between the two [12]. Therefore, Cu^{2+} ion is strongly attached to PVIm chains because of its small size, charge capacity, and tendency to participate in bond formation. Detailed information was reported in our previous study about complexation of soluble poly (N-vinyl imidazole) and divalent metal ions [13].

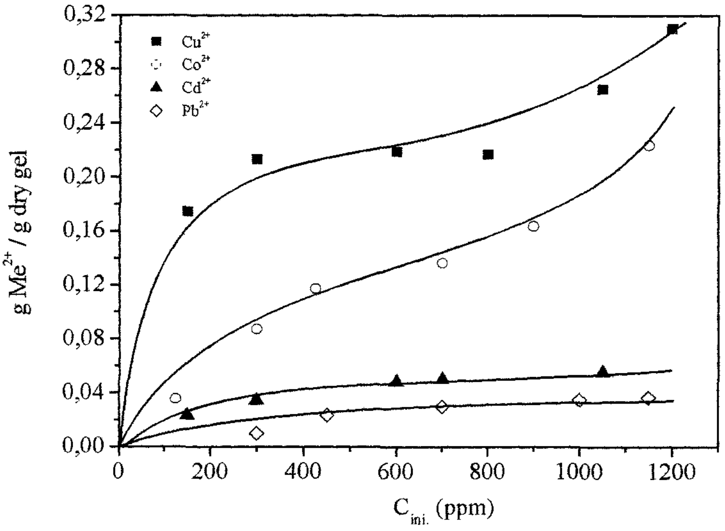


Figure 3. Adsorption isotherms for PVIm hydrogels with various Me^{2+} ions at pH 6.0

Various kinds of chelating resins, ion-exchange membranes etc. have been studied extensively for the recovery and enrichment of valuable ions, and the removal of undesirable ions from waste water, especially to extract toxic metal ions worldwide. As compared with other works in literature, we obtained fairly high adsorption values for PVIm hydrogels; for example, PVIm hydrogels adsorb more Cu^{2+}, Pb^{2+} [14] ions, while PVIm gels adsorb less Co^{2+} [15], Cd^{2+} [16] ions. In addition to these studies, Peters [17] investigated different functional group containing structures for chelant extraction of heavy metals from contaminated soils and showed that the lower adsorption efficiency values than our PVIm-metal ion systems. Cárdenas et. al. studied the synthesis of chitosan mercaptanes as heavy metal retention agent and obtained low adsorption values [18]. Cobianco et. al. investigated that Cu(II)-complexes of chelating resins containing nitrogen and sulfur atoms in the chelating groups and showed low adsorption capacity of these resins [19]. Due to higher adsorption capacity of PVIm gels for Cu^{2+} ions, we have investigated the interaction between these two by spectroscopy and thermal analysis. In order to explain the bindings between the Cu^{2+} ions and imidazole group, the FT-IR spectra were taken of Cu^{2+} adsorbed (Figure 5b) and plain PVIm (Figure 5a) hydrogels. As a result of the interaction between Cu^{2+} ion and imidazole group, some band strengthening and a certain shift took place in the FT-IR spectra. We observed a $15cm^{-1}$ shift in the spectrum of Cu^{2+} ion adsorbed PVIm (Figure 5b) due to the interactions with Cu^{2+} ions in the C=N and C=C stretching of imidazole ring at $1500cm^{-1}$ in the plain PVIm hydrogels (Figure 5a). Bands observed at $915cm^{-1}$ (Figure 5a) belonging to ring stretching and $1085cm^{-1}$ belonging to C-H in-plane bending are shifted to $945cm^{-1}$ and $1096cm^{-1}$ (Figure 5b), respectively, upon the complexation with Cu^{2+} ions. In addition, the existence of band at $915cm^{-1}$ (Figure 5b) showed the free imidazole groups, which are no affected by Cu^{2+} ions. All these findings showed that the binding was caused by the nitrogen atoms at 3 position of imidazole ring with Cu^{2+} ion.

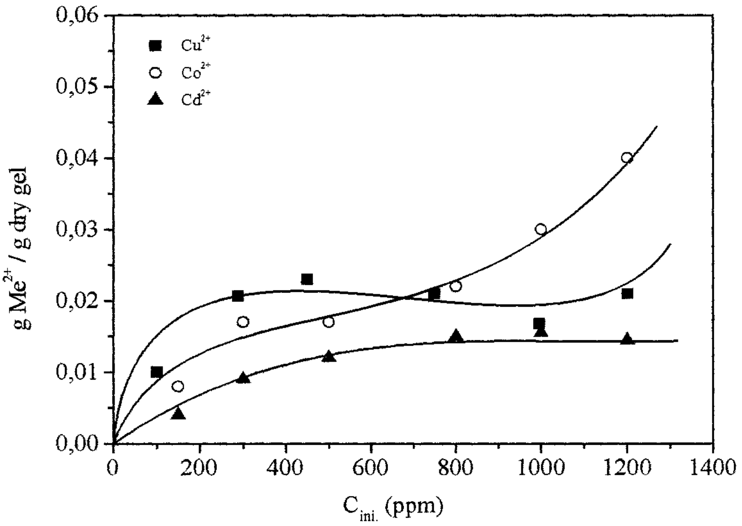


Figure 4. Adsorption isotherms for weakly protonated (at pH 5.0) PVIm hydrogels with various Me^{2+} ions

To investigate the thermal stability of polymer-metal complex, TGA thermograms and their derivative curves were taken for both PVIm and Cu^{2+} adsorbed PVIm hydrogels, Figure 6. The thermal decomposition behavior of a polymer-metal complex depends on the macromolecular characteristics of the polymeric base and the type of coordination geometry [20]. The TGA thermogram of PVIm hydrogel (Figure 6a) showed single step decomposition with the temperature intervals 370°C – 520°C showing a maximum decomposition temperature of 453°C. The TGA thermogram of Cu^{2+} adsorbed PVIm hydrogel (Figure 6b) showed however two-step decomposition.

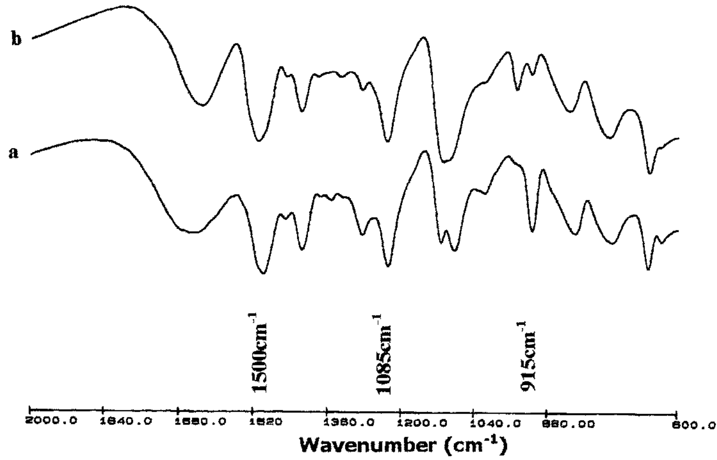


Figure 5. FT-IR spectra of PVIm (a) and Cu^{2+} ion adsorbed PVIm (b) hydrogels

The first-step decomposition with maximum at 337°C corresponds to decomposition of complex structure formed between Cu^{2+} ion and imidazole group and second-step decomposition with another maximum at 418°C corresponds to free (unbounded) imidazole group. While the weight loss for PVIm hydrogel was found to be 90% in the heating process of up to 700°C, the weight loss for Cu^{2+} adsorbed PVIm hydrogel was 65% at the same temperature.

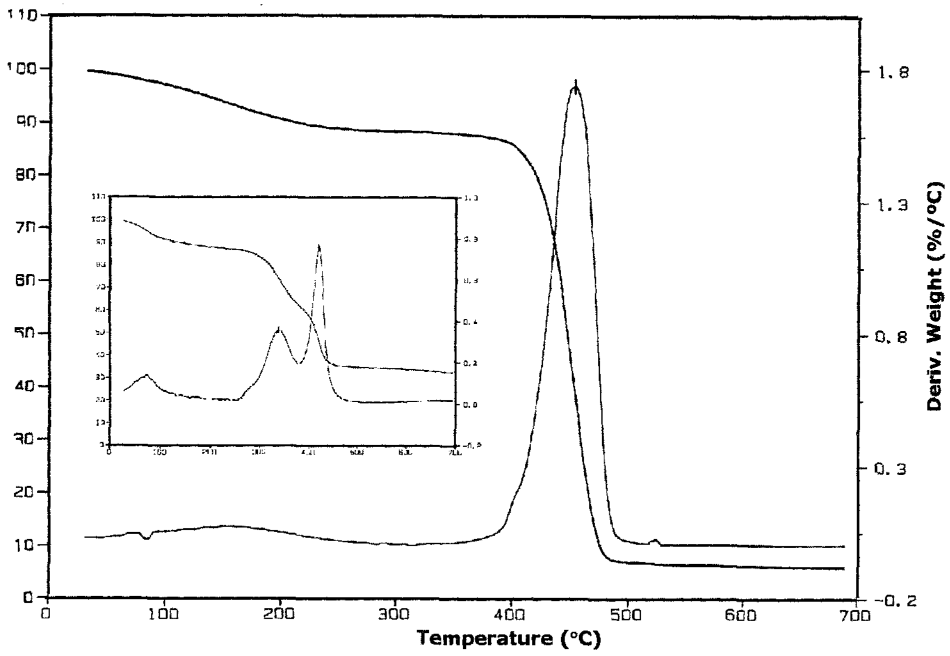
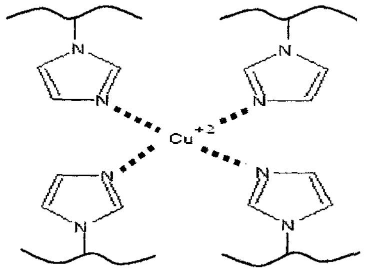


Figure 6. TGA thermograms of PVIm (a) and Cu^{2+} ion adsorbed PVIm (b) hydrogels

All these indications and previous complexation studies (4 : 1 stoichiometry between imidazole ring vs. copper) allow us to propose the structure of the complexes given below:



Scheme. The binding mechanism between Cu^{2+} ion and imidazole group.

We performed a study of interaction of vinylimidazole (monomer base unit) and divalent metal ions for the determination of stoichiometric ratios and published elsewhere [13]. In this current study we observed that the same stoichiometric ratio (1 metal ion : 4 imidazole unit) using molar ratio method. We also searched literature related to the binding mechanism of vinylimidazole-metal complexes to support our suggestion and we found that the stoichiometric ratio between metal (II) and imidazole unit is 1 : 4 for most of studies and especially Cu (II) centers have a square planar coordination with four nitrogen as ligands [19,21,22].

Conclusion

PVIm hydrogel is prepared by irradiating of binary mixtures of VIm-water using ^{60}Co-γ source. These gels were used in heavy metal ion adsorption studies. The complexation of imidazole ring with Me^{2+} ions showed that the complexation decreased in the following order : $Cu^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$. The ability of PVIm hydrogel to adsorb metal ions increase with initial metal ion concentration and tends to saturate at higher concentrations. Adsorption was observed to decrease with decreasing pH value due to the protonation of VIm ring.

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