

An Investigation of Cadmium(II) and Nickel(II) Adsorption by Chitin Graft Copolymer

José A. R. Filho,¹ Erna E. Bach,¹ Reinaldo R. Vargas,² Demétrio A. W. Soares,³
Alvaro A. A. de Queiroz³

¹*IQ-Programa de Pós-Graduação em Biotecnologia, UNESP/Araraquara, Brazil*

²*Departamento de Química Fundamental, IQ- USP, Brazil*

³*Departamento de Física e Química/Instituto de Ciências, Universidade Federal de Itajubá-UNIFEI, 37-500-903 Itajuba, MG, Brazil*

Received 21 February 2003; accepted 10 October 2003

ABSTRACT: Chitin hydrogels of poly(vinylpyrrolidone) (VP) were prepared by means of the hydrogen peroxide graft copolymerization process. The effect of the VP grafted chain on water diffusion through the biopolymer was studied. Fourier transform infrared spectra of the VP-g-Ch showed an increase in the intensities of the hydroxyl and carbonyl stretching bands indicating a reduction in the hydrogen bonding of chitin. An investigation was undertaken regarding the adsorption of nickel(II) and cadmium(II) ions from aqueous solutions by the VP grafted chitin and the effects of the grafting degree on the Cd²⁺ and Ni²⁺ sorption

were studied. The Cd²⁺ and Ni²⁺ adsorption equilibrium data correlate well with the Freundlich equation. The results indicate that the Ch-g-VP graft copolymer under investigation is a potentially powerful chelating material that can be employed for Ni²⁺ and Cd²⁺ ion removal from wastewater effluents. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1310–1318, 2004

Key words: graft copolymers; hydrogels; chitin; metal–polymer complexes; cadmium(II) and nickel (II) sorption

INTRODUCTION

Many factors contribute to man's impact on the environment, and one of the most important of these is the explosive growth in industrial activities. Several industrial activities based on metal electrochemical deposition, paints, petrochemical synthesis, powder metallurgy, tanning, and others are completely dependent on water resources.

It is well known that anthropogenic sources such as industrial effluents,^{1,2} automobile emissions,^{3,4} mining activities,^{5,6} and agricultural practice^{7,8} are important sources of pollution of heavy metals ions.

There are several metal pollutants that are considered of potential threat to environmental systems. These include Cd, Cr, Cu, Hg, Ni, Zn, and Pb that, due to their distinct chemistry and characteristics, each represent a rather different hazard to the environment.^{9,10}

The advent of nickel–cadmium batteries, Ni–steel alloys, photocells, and other electroelectronic compounds based on the nickel and cadmium metals has received careful attention of the governmental organization due to their tendencies to accumulate in plants

and animals, causing severe environmental problems.^{11–18}

Various methods such as hydroxide precipitation,¹⁹ ion-exchange,²⁰ reverse osmosis,²¹ and electro dialysis techniques²² have been developed for the removal and recovery of harmful metals ions from sewage and industrial waste water. Despite their removal effectiveness, these techniques are often quite expensive.

The ability of some polymers to bind metal ions forming charge transfer complexes introduces a new and interesting technique to industrial wastewater treatment that introduces the chelating properties of a polymer with metal ions and the ultrafiltration through selective membranes as two combined separation processes.^{23–25}

The development of green technologies for water treatment processes has attracted the attention of several materials scientists due to limitations of the conventional processes based in the synthetic resins derived from the petrochemical route.

Due to their capability of binding metal ions by physical or chemical adsorption, wide availability, and environmental safety, the use of the biopolymer chitin and its derivatives for the removal and recovery of toxic metals ions has attracted enormous industrial interest.^{26–31}

The more common polymorphic crystalline structure of chitin obtained from the shells of crabs, lobsters, and shrimp is the α -structure.^{32–34} The tightly

Correspondence to: A. A. de Queiroz (alencar@efei.br).

compacted and high crystallinity cause the α -chitin to have poor swelling in water, limiting its uses in metal chelation processes.

The search for an effective and economic method for removing toxic metal ions from industrial effluents has stimulated several research groups to develop cellulosic materials type hydrogels due to their easy availability and wide application spectrum in both their natural and their chemically modified structures.^{35–43}

In view of the above, we have attempted to develop chitin hydrogels, a material that absorbs large amounts of water, in this manner exposing the biopolymer to a higher interaction with the polluted water.

Considering the ability of the poly(*N*-vinyl-2-pyrrolidone) (PVP) hydrogel to form charge transfer complexes with metallic ions, the aim of this study was to synthesize the chitin-*graft-N*-vinyl-2-pyrrolidone copolymer (Ch-g-VP). This hydrogel was used in the sorption of Ni²⁺ and Cd²⁺, some of the closely related common water pollutants.

EXPERIMENTAL

Materials

α -Chitin was isolated from exoskeleton of pink shrimp shell (*Solenocera melantho*) waste, after treatment with NaOH (2.5 N, 10 mL/g) at room temperature for 8 h followed by decalcification with HCl (1.7 N, 10 mL/g) at room temperature for 24 h.⁴⁴ After being washed with distilled water until neutral pH and dried at 90°C for 48 h, the obtained chitin was milled and screened to separate the 100 mesh fraction. *N*-Vinyl-2-pyrrolidone (VP) monomer (Aldrich) was vacuum distilled before use. Other reagents were of analytical grade and were used without further treatment.

Chitin grafting

VP grafting onto chitin was carried out after the creation of active epoxide groups on the biopolymer in the presence of hydrogen peroxide. The purified chitin powder (1.0 g) was dispersed in an aqueous solution of hydrogen peroxide (10% v/v, 3.0 mol) and deaerated with gaseous nitrogen (N₂). An aqueous solution of VP monomer containing 10⁻² M of Fe(II) sulfate was then added with constant stirring in a thermostatically controlled reaction flask at 60°C for 1 h. After copolymerization, the VP-g-Ch was purified in a Soxhlet extraction apparatus with ethanol–water mixture (1:1 v/v) to remove the ungrafted poly(*N*-vinyl-2-pyrrolidone) homopolymer and then exhaustively washed with water to remove the residual Fe(II) ions.

After being dried under vacuum at 50°C to a constant weight, the grafting degree of α -chitin was de-

termined by the percentage increase in weight according to the equation

$$GD(\%) = \left[\frac{W_g - W_0}{W_0} \right] \times 100 \quad (1)$$

where W_0 and W_g denote the weights of chitin and grafted chitin, respectively.

FTIR examination of copolymer structure

Structure changes of chitin induced by VP grafting were analyzed by Fourier transform infrared (FTIR) spectroscopy. Infrared spectra were measured in KBr pellets with a Perkin–Elmer Model 1730 FTIR spectrometer at 4 cm⁻¹ resolution. The ratio of absorbance of the vibration bands at 1560 and 1070 cm⁻¹ corresponding to the amide II band and to the ether stretching band (C–O), respectively, were used to investigate the extension of the grafting degree reaction on the biopolymer.

Adsorption isotherms

The binding properties of the Ni²⁺ and Cd²⁺ to the VP-g-Ch hydrogel were investigated using the non-competitive adsorption by the batch method. The adsorption experiments were carried out by immersing a fixed amount of dry chitin and VP-g-Ch (1.0 g) in 0.10 dm³ of the metal ion solution at pH 4.6 (phosphate buffered solution, 0.1 M NaCl, 0.086 M KH₂PO₄, 0.041 M Na₂HPO₄) (PBS) for 24 h with constant stirring (130 rpm, shaker bath Firstek Model B 603).

The metal solutions were sampled and preserved before and after the deployment of the Ni²⁺ and Cd²⁺ adsorption experiments. After filtration, the concentrations of Ni²⁺ and Cd²⁺ were analyzed using an atomic absorption spectrophotometer (GBHC Model 932). Each measurement was undertaken in triplicate under identical conditions.

Swelling behavior

The water sorption and diffusion measurements were obtained after immersion of known weights of the dry α -chitin and Ch-g-VP membranes in PBS solution at pH 4.6 and 25°C until equilibrium was reached. After the sorption time the membranes were removed from PBS solution, blotted quickly with a filter paper to eliminate the free water on its surface, and weighed. The degree of swelling was calculated from the ratio of the weight of water involved in the swollen material to the weight of dry chitin according to the relation

$$\text{Swelling}(\%) = \left(\frac{W_t - W_0}{W_0} \right) \times 100 \quad (2)$$

where W_t is the weight of the swollen film at time t and W_0 is the initial mass of the film.

Electrical properties of VP-g-Ch metal complexes

The VP-g-Ch/Ni²⁺ and VP-g-Ch/Cd²⁺ complexes in the form of compact discs (10 mm in diameter and 1 mm in thickness) were produced by subjecting a specified amount of the copolymer powder (150 mg) to 10⁴ kg·cm⁻² pressure. Carbon paste was placed between the electrode and the sample, ensuring good electrical contact.

The circuit used for DC electrical conductivity measurements was interfaced with a computer device and a 610 C-Keithley digital electrometer. The measurements were made at room temperature (25°C) under vacuum (~10⁻³ mm Hg). A DC voltage of 100 V was supplied to the sample, and the bulk resistance was measured after 2 min.

Considering the sample's geometry, the value of specific resistance (ρ) was calculated by

$$\rho = \frac{rwh}{d} \quad (3)$$

where ρ is the specific resistance ($\Omega\cdot\text{cm}$), r is the electric resistance (Ω), w is the width of the electrode (in centimeters), h is the thickness of the disc (in centimeters) and d is the electrode distance.

RESULTS AND DISCUSSION

Mechanism of grafting

It is well known that peroxide groups may be easily introduced into cellulose and its derivatives by treatment of the biopolymer with hydrogen peroxide to form peroxides and α -hydroperoxide, respectively.⁴⁵ The resultant peroxide groups have the ability to initiate thermal grafting through the generation of $\cdot\text{OH}$ free radicals. Thus, the free radicals $\cdot\text{OH}$ might attack the chitin chain to give chitin macroradicals that are able to initiate VP grafting onto the biopolymer surface.

The chitin macromolecule contains two reactive groups at the C-2 and C-6 positions where the active sites are expected to appear. These chitin macroradicals will react with the VP monomer to initiate graft copolymerization.

Figure 1 shows the scheme of the suggested mechanism for the graft reaction of VP onto α -chitin (Ch). In the presence of VP, grafting occurs by the addition of further monomer molecules to give rise ultimately to the graft copolymer.

Effect of VP concentration

The thermally produced free radicals are also found in VP, which will initiate the homopolymerization of the

monomer. The grafting of VP onto chitin is controlled by the rate of VP diffusion to the vicinity of chitin macroradicals. Thus, the monomer concentration affects directly the rate of grafting and homopolymerization of the vinyl monomer onto chitin.

Figure 2 shows the effect of VP concentration on the grafting degree. The increasing VP concentration to 80% (m/m) was followed by a significant decrease in VP grafting onto chitin. The observed decrease in VP grafting degree might be due to the high concentration of free VP monomeric radicals in solution terminating the growing of the grafted VP chain; producing homopolymers and resulting in the grafting degree decrease. At the same time the grafted poly(*N*-vinyl-2-pyrrolidone) chains act as a diffusion barrier, thereby preventing the further copolymerization of VP with chitin, even if the former is used at concentrations as high as 80% (m/m).

FTIR examination of the copolymer structure

FTIR spectroscopy may be used for the investigation of the graft copolymerization between Ch and the VP monomer because it provides information on the graft copolymer composition.

Our discussion will mainly concentrate on the hydroxyl and carbonyl stretching vibration bands in the VP monomer and chitin, as they may be expected to be affected by the graft reaction.

Figure 3 shows the FTIR spectra for Ch and the graft copolymer VP-g-Ch. Stretching vibrations of the hydroxyl groups in chitin appear around 3450 cm⁻¹. The stretching vibration spectra of acetamide group of chitin appear at 1663 and 1564 cm⁻¹ while the sharp band at the 1041 cm⁻¹ peak in the pure chitin becomes separate bands in the graft copolymer. Moreover, the peak intensity of the graft copolymer is stronger than that of pure chitin relative to amide and carbonyl bands. The observed dependence on the grafting degree and the amide and hydroxyl stretching intensities may be indicative of the reduction on the VP grafting since the grafted PVP chains could have a strong influence on the hydrogen bonding interactions present in chitin.⁴⁶

The distribution of the grafted PVP chains in the region near the surface was investigated by ATR/FTIR spectroscopy. As shown in Figure 4, the values of the ratios of the NH/C = O peak were calculated and plotted against the grafting degree. The ratios of the NH/C = O absorption bands decreased with the degree of grafting, indicating an inhomogeneous distribution of the VP grafted chain in the bulk of the biopolymer.

Swelling behavior of the VP-g-Ch graft copolymer

The grafted vinylpyrrolidone chain is hydrophilic and its presence onto chitin will increase the water diffu-

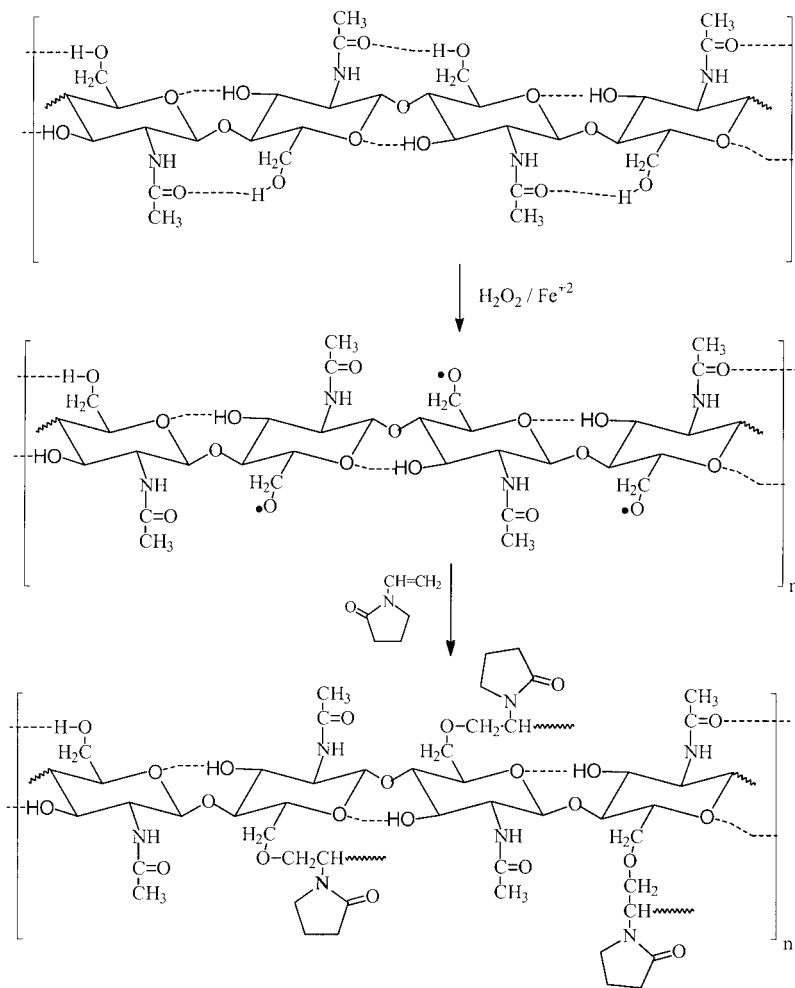


Figure 1 Proposed mechanism for the grafting reaction of *N*-vinyl-2-pyrrolidone onto chitin catalyzed by the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ system.

sion through the biopolymer. Since the water swelling of the VP-g-Ch is directly proportional to both the pore size of the gel network and the volume of the hydrogel, the water sorption by the grafted chitin was studied.

For characterization of the swelling behavior, VP-g-Ch membrane samples were allowed to swell to equilibrium in aqueous swelling medium at pH 4.6 (PBS) to avoid the precipitation of the Ni^{2+} and Cd^{2+} ions and constant ionic strength (equivalent to 0.010 M NaCl).

The water transport through hydrophylic polymers may be described by the well-known Fick's second law:⁴⁷

$$\frac{\partial C(x,t)}{\partial t} = D_x \frac{\partial^2 C(x,t)}{\partial x^2} \quad (4)$$

where C is the water concentration, D_x is the diffusivity normal to the surface, i.e., in the x -direction, and t is the diffusion time.

In the case of isotropic thin VP-g-Ch membranes, the one-dimensional analytical solution of Eq. (4) at equilibrium of water diffusion gives

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D(2n+1)^2\pi^2}{h^2t}\right] \quad (5)$$

where n is a integer, M_t is the mass of water sorbed at time t , M_∞ is the mass of water sorbed at equilibrium time, and h is the initial thickness of the polymer membrane.

In a Fickian diffusion, the water diffusivity through VP-g-Ch is related to the rate of initial water absorption according to the equation

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2}{h^2} \quad (6)$$

According to 6 the plot of $\ln[1 - M_t/M_\infty]$ versus time should be linear at long diffusion times, and slopes of

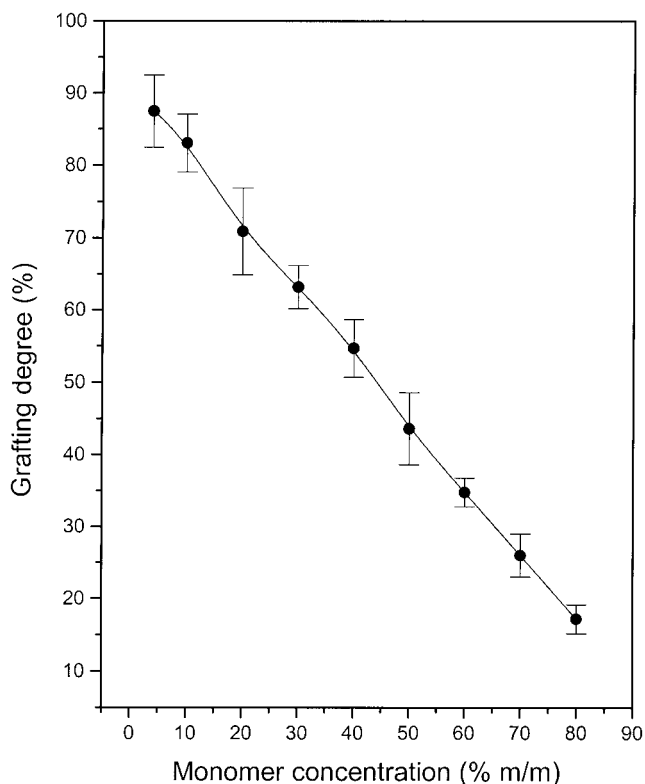


Figure 2 Grafting degree as a function of *N*-vinyl-2-pyrrolidone content in the monomer mixture. Solvent, water; $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ concentration, $3.0\text{ M}/10^{-2}\text{ M}$; temperature, 60°C ; reaction time, 1 h.

these lines are proportional to the diffusion coefficients.

Figure 5 shows the dependence of the water diffusion coefficients of the lactam composition on Ch-g-VP copolymers. The water diffusion coefficients increased with the VP content on the biopolymer, indicating that the motional freedom of the water molecules is higher in the Ch-g-VP than in the ungrafted biopolymer.

It is known that α -chitin is a polymer with a low water sorption capacity. The grafting of the biopolymer with the VP monomer should increase the water uptake of the grafted α -chitin. However, the water uptake measurements may be used as an indication of the concentration of the PVP hydrophilic parts present in the hydrophobic chitin matrix.

Figure 6 shows a plot of the VP grafting degree against water uptake for the VP-g-Ch copolymers at 25°C . It is clear from Figure 6 that the grafted biopolymer swells more than does the ungrafted chitin. These swelling characteristics suggest that the grafted chitin performs as a polymeric hydrogel, which is potentially useful for metal ion sorption.

Most industrial applications expose the materials to a wide range of temperatures. As a result, the temperature effect on water diffusion represents the major

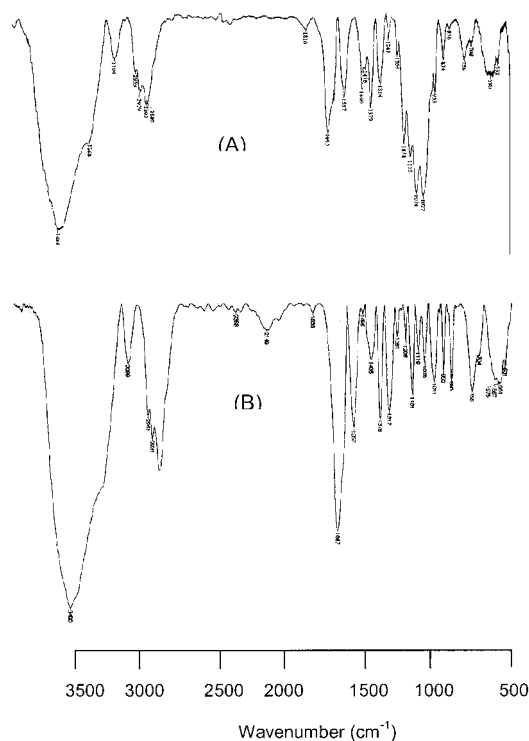


Figure 3 FTIR spectra of chitin (A) and VP-g-Ch (B). VP grafting degree (g), 80% m/m.

practical repercussion. Since the diffusion is a thermally activated process, the water diffusivity is very sensitive to temperature.

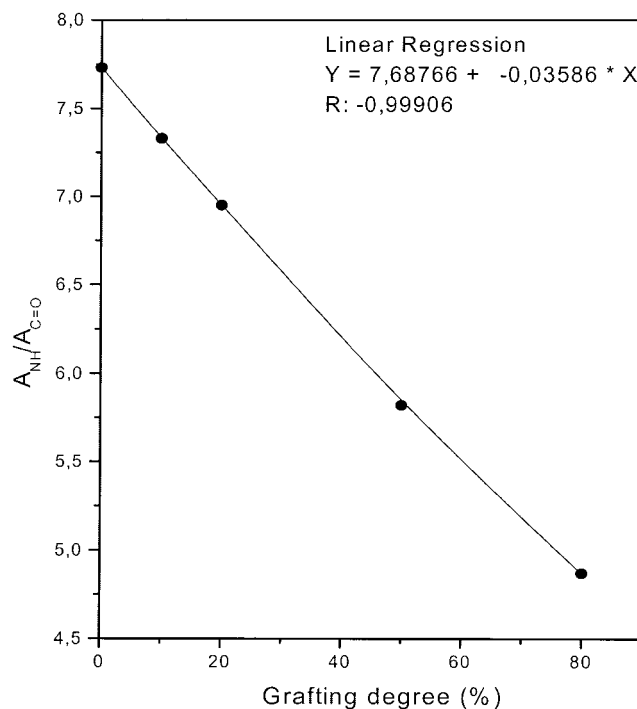


Figure 4 Ratios of the NH/C=O peaks of different grafting degree for VP-g-Ch systems obtained from ATR/FTIR spectroscopy.

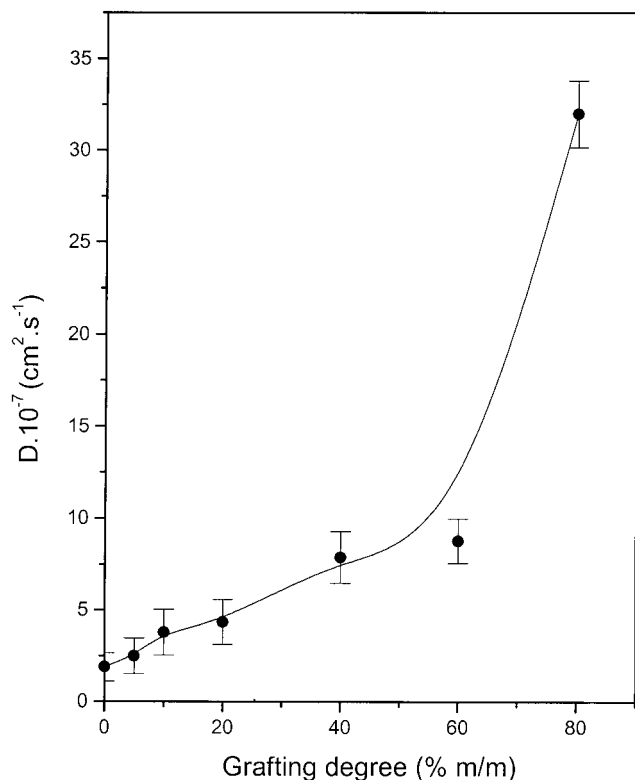


Figure 5 Dependence between the water diffusion coefficients and the lactam composition on the Ch-g-VP copolymers. Temperature = 298 K; pH 4.6 (PBS).

The water diffusion coefficient through Ch-g-VP copolymers obeys the activated transition state theory and its temperature dependence can be expressed by the Arrhenius equation:⁴⁸

$$D = D_0 e^{-E_D/RT} \quad (7)$$

where D_0 is the preexponential factor, R is the molar gas constant, T is the absolute temperature, and E_D is the activation energy required to produce an opening between polymer chain segments large enough to allow the water diffuse. The exponential correlation of diffusivity with $1/T$ results in a very strong temperature dependence.

Figure 7 shows the required activation energy, E_D , to the water diffusion through the VP grafted chitin. It may be noted that the energy for water diffusion through the grafted biopolymer decreases linearly with the VP grafting yield, which suggests a facility associated with the movement of the aggregates of water molecules through the grafted chitin.

Metal-ion complexation studies

In the graft copolymer VP-g-Ch, the lactam unit of the grafted VP chains is an active binding site to form charge transfer complexes with the heavy metal ions

in solution. For this particular purpose, the Ni^{2+} and Cd^{2+} ions sorption kinetic is an important physico-chemical parameter for evaluating the selectivity as well as the chelating capacity of the VP-g-Ch graft copolymers.

Figure 8 gives the effect of the grafting degree on the adsorption of Cd^{2+} and Ni^{2+} ions onto Ch-g-VP copolymers. As shown, the Ch-g-VP chelating properties decrease with the grafting yield, suggesting that the ligand, although present in excess, occupies only some of the coordination sites of the metals and the remainder of the sites are occupied by water.

In contrast, the low adsorption of Cd^{2+} relative to the Ni^{2+} ions may be a consequence of their lack of affinity to the lactam rings present in the Ch-g-VP copolymer. Apart from the contribution of the charge density and hydration energy of the VP-g-Ch hydrogels in ion uptake, the hydration sphere of these ions also contributes significantly to the selectivity in the observed results. In this work, the sorption order is $\text{Ni}^{2+} > \text{Cd}^{2+}$.

A common mathematical approach for the description of metal sorption by the macromolecules is the definition of sorption isotherms. The Freundlich model is perhaps the most popular adsorption model and has found a wide acceptance because of its accuracy and broad applicability.

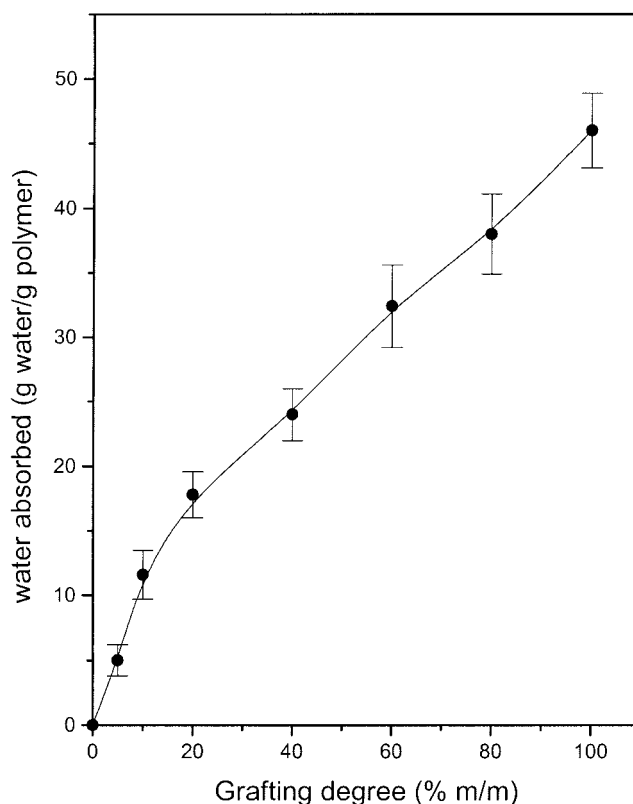


Figure 6 Water uptake per dry polymer weight (g/g) for Ch-g-VP copolymers with different grafting degree. Temperature, 298 K; pH 4.6 (PBS); swelling time, 2 h.

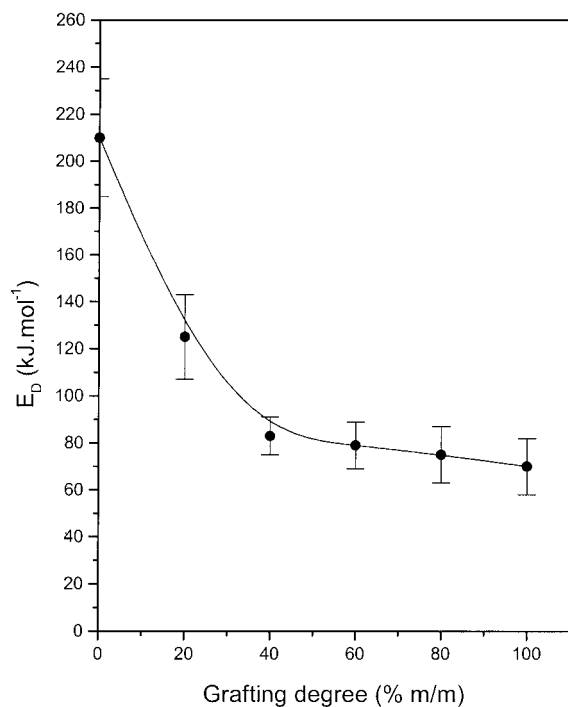


Figure 7 Activation energy dependence of the VP grafting degree for water diffusion on Ch-g-VP copolymers in PBS solution at pH 4.6.

The distribution of the heavy metal between the graft copolymer VP-g-Ch in aqueous phase at equilibrium may be described by the Freundlich isotherm as⁴⁹

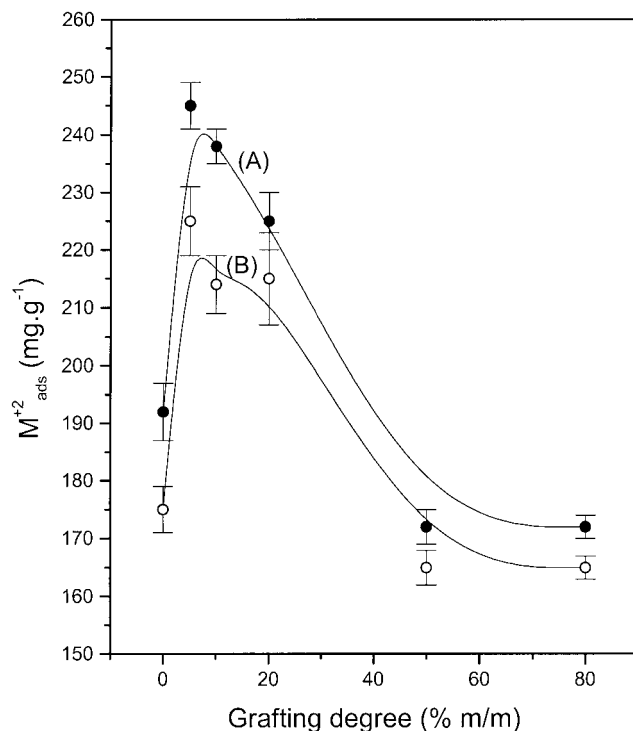


Figure 8 Effect of the grafting degree on the Ni²⁺ (A) and Cd²⁺ (B) adsorption ions by Ch-g-VP copolymers. Contact time, 120 min; pH 4.6 (PBS); temperature = 298 K.

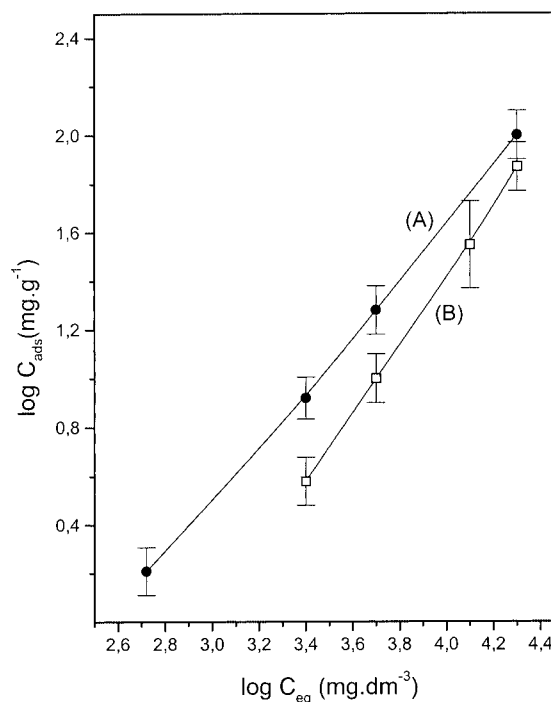


Figure 9 Freundlich isotherm for the Ni²⁺ (A) and Cd²⁺ (B) adsorption by Ch-g-VP copolymers. [Cd²⁺] = [Ni²⁺] = 0.5 mol·L⁻¹; pH 4.6 (PBS); temperature = 298 K and Ch-g-VP = 1.0 g.

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C_{\text{eq}} \quad (8)$$

where x/m is the amount of Ni²⁺ and Cd²⁺ sorbed per unit weight of Ch-g-VP (mg·g⁻¹), C_{eq} is the metal concentration in equilibrium solution (mg·g⁻¹), and K and $1/n$ represent the sorption capacity and the metal sorption intensity, respectively.

Applying the Freundlich equation to the analytical data for single solutions, the parameters K and n for the Ni²⁺ and Cd²⁺ monocomponent adsorption were obtained. The parameter K is related to the distribution coefficients and consequently to the Ch-g-VP affinity to Ni²⁺ and Cd²⁺ ions.

Figure 9 shows the Freundlich isotherm for the Ni²⁺ and Cd²⁺ sorption ions by VP-g-Ch copolymers. It was assumed at a 95% level of significance that the Freundlich model adequately represented the data.

Of particular interest in Figure 9 are the values for the constants $1/n$ and K . Similar values for the constants mean similar adsorptive properties for the VP-g-Ch graft copolymers.

From Figure 9, the values for the slope and intercept of the linear regression line can be determined. The values for K and $1/n$ for Ni²⁺ adsorption are $1.13 \pm 0.098 \text{ mg}\cdot\text{g}^{-1}$ and $0.34 \pm 0.10 \text{ g}\cdot\text{dm}^{-3}$, respectively. The estimated K and $1/n$ values for the Cd²⁺ adsorption are $1.52 \pm 0.22 \text{ mg}\cdot\text{g}^{-1}$ and $0.23 \pm 0.14 \text{ g}\cdot\text{dm}^{-3}$,

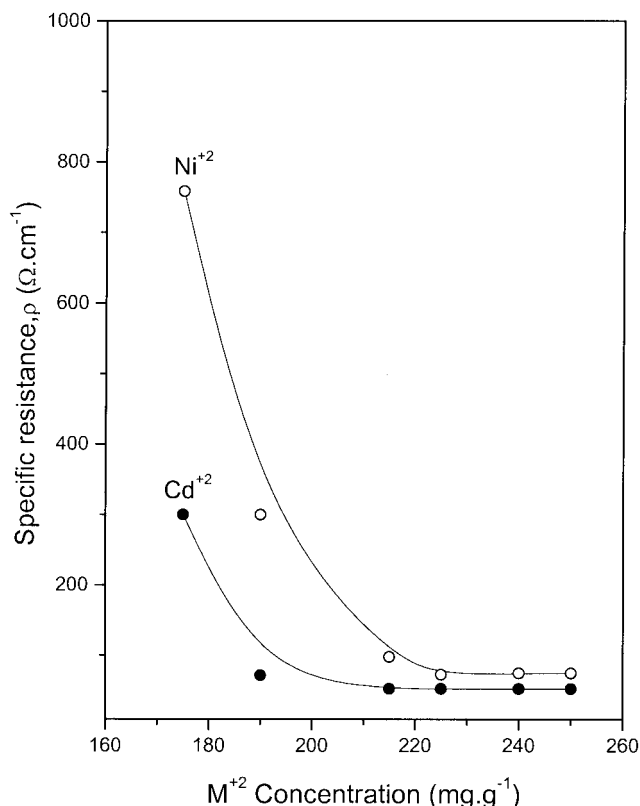


Figure 10 Effect of the Cd^{2+} and Ni^{2+} content on specific resistance of VP-g-Ch copolymers at 298 K and relative humidity of 50%.

respectively. The $1/n$ values suggest that the adsorption forces of Ni^{2+} actuating on the Ch-g-VP surface are stronger compared to those of the Cd^{2+} , confirming that the mechanism of sorption is mainly ionic with a part of physical sorption.

Electrical measurements

To avoid hyperaccumulation of the VP-g-Ch primarily used to the Ni^{2+} and Cd^{2+} remotion, alternative uses of the VP-g-Ch hydrogel metal complexes were developed in our laboratories. In this sense, the use of Ni^{2+} and Cd^{2+} grafted chitin complexes as antistatic agents in the rubber industry was considered in this work. Taking the utilization of the VP-g-Ch metal complexed as antistatic material, the specific resistance of VP-g-Ch/ Ni^{2+} and VP-g-Ch/ Cd^{2+} complexes should be measured.

Figure 10 shows the relation between the metallic ion content and the specific resistance of VP-g-Ch/ Ni^{2+} and VP-g-Ch/ Cd^{2+} complexes. A stronger dependence between the conductivity and the metal content on the graft copolymer can be observed from Figure 10. The nickel VP-g-Ch complexes are found to exhibit a higher conductivity when compared to the cadmium VP-g-Ch complexes, indicating that the mo-

bility of Cd^{2+} ions (ionic radius = 109 pm) is lower than the mobility of Ni^{2+} (ionic radius = 83 pm).

CONCLUSION

A graft copolymer of *N*-vinyl-2-pyrrolidone onto chitin was synthesized using the peroxidation technique. The Ni^{2+} and Cd^{2+} adsorption equilibrium data correlate well with the Freundlich isotherm equation. The Ni^{2+} and Cd^{2+} binding ability corresponding to the poly(vinylpyrrolidone)-chitin graft copolymer suggests that the grafted biomass possesses a higher potential for Ni^{2+} and Cd^{2+} adsorption. Apart from the contribution of microstructural aspects of the VP hydrogels in ion uptake, charge density, hydration energy, and size of hydration sphere of these ions also contribute significantly to the selectivity in the observed results. In this work the sorption order is $\text{Ni}^{2+} > \text{Cd}^{2+}$. The VP-g-Ch hydrogel has proved to be a promising material for removing Cd^{2+} and Ni^{2+} ions for the cleanup of contaminated wastewater release by industry.

References

- Gibson, M. J.; Farmer, J. G. In Proceedings of the 4th International Conference on Heavy Metals in the Environment; CEP: Edinburgh, 1983; Vol. 2, pp 1141.
- Culbald, E. B.; Thornton, I.; Watt, J.; Moorcroft, S.; Brooks, K. Sources and distribution of lead and cadmium in United Kingdom dusts and soils. In Proceedings of the 4th International Conference on Heavy Metals in the Environment; CEP: Edinburgh, 1983; pp 426–429.
- Fergusson, J. E.; Hayes, R. W.; Tan, S. Y.; Sim, H. T. N Z J Sci 1980, 23, 293.
- Miragaya, G. J. Soil Sci 1984, 138, 147.
- Davies, B. E.; Ginnever, R. C. J Agric Sci Camb 1979, 93, 753.
- Culbald, E. B.; Johnson, L. R. In Environmental contamination; CEP, Edinburgh, 1984; pp 276–281.
- Colbourn, P.; Thornton, I. J Soil Sci 1978, 29, 513.
- Ma, L. Q.; Gade N.; Rao, J. Environ Qual 1997, 26, 259.
- Shaw, A. J. Heavy Metal Tolerance in Plants: Evolutionary Aspects. CRC Press: Boca Raton, FL, 1990.
- Lauchli, A.; Bielecki, R. L. Encyclopedia of plant physiology. Springer-Verlag: Berlin, 1982; Vol. 15A.
- Sajwan, K. S.; Ornes, W. H.; Youngblood, T. V.; Alva, A. K. Water Air Soil Pollut 1996, 91, 209.
- Quaife, C. In McGraw-Hill Encyclopedia of Science and Technology; McGraw-Hill: New York, 1981; Vol. 3, p 122.
- L'Huillier, L.; d'Auzac, J.; Durand, M.; Michaud-Ferriere, N. Can J Botany 1996, 74, 1547.
- McIlveen, W. D.; Negusanti, J. J. Sci Total Environ 1994, 148, 109.
- Rascio, N.; Dallavecchia, F.; Ferretti, M.; Merlo, L.; Ghisi, R. Arch Environ Contam Toxic 1993, 25, 244.
- Salim, R.; Isa, M.; Al-Subu M. M.; Sayrafi, S. A.; Sayrafi, O. J Environ Sci Health A Environ Sci Eng Toxic Hazardous Subst Control 1995, 30, 831.
- Malan, H. L.; Farrant, J. M. Seed Sci Res 1998, 8, 445.
- Ma, L. Q.; Rao, G. N. J Environ Qual 1997, 26, 259.
- Pawłowski, L. Physicochemical Methods for Water and Wastewater Treatment; Pergamon: London, 1980.
- Mulder, M. Basic Principles of Membrane Technology; Kluwer Academic: Dordrecht, The Netherlands, 1991.

21. Li, N. N. *Recent Developments in Separation Science*. CRC Press: Cleveland, 1977; Vol. 3.
22. Meares, P. *Membrane Separation Processes*. Elsevier: Amsterdam, 1976.
23. Leinonen, H.; Lehto, J.; Mäkelä, A. *React Polym* 1994, 23, 221.
24. Sahni, S. K.; Reedijk, J. *Coord Chem Rev* 1984, 59, 1.
25. Udaybhaskar, P.; Iyengar, I.; Prabhakara, R. A. V. S. *JAppl Polym Sci* 1990, 39, 739.
26. Schmuhl, R.; Krieg, H. M.; Keizer, K. *Water SA (Pretoria)* 2001, 27(1), 1–7.
27. Kamiński, W.; Modrzejewska, Z. *Sep Sci Technol* 1997, 32, 2659.
28. Weltrowski M.; Martel, B.; Morcellet, M. *JAppl Polym Sci* 1996, 59, 647.
29. Chui, V.W.D.; Mok, K. W.; Cy, N. G.; Luong, B. P.; Ma, K. K. Removal and recovery of copper (II), chromium (III) and nickel (II) from solutions using crude shrimp chitin packed in small columns. *Environ Int* 1996, 22, 463.
30. Deans, J. R.; Dixon, B. G. Uptake of Pb^{+2} and Cu^{+2} by novel biopolymers. *Water Res* 1992, 26, 469.
31. Singh, D. K.; Ray, A. R. Biomedical applications of chitin, chitosan and their derivatives. *JM S Rev Macromol Chem Phys* 2000, C40(1), 69–83.
32. Dweltz, N. E. *Biochem Biophys Acta* 1960, 44, 416.
33. Dweltz, N. E. *Biochem. Biophys. Acta* 1961, 51, 283–294; Clark, G. L.; Smith, A. F. *J Phys Chem* 1936, 40, 863.
34. Gow, N.A.R.; Gooday, G. W.; *Carbohydr Res* 1987, 165, 105.
35. Izume, M. *Fragrance J* 1996, 12, 112.
36. Rinaudo, M.; Dung, P. L.; Milas, M. In *Advance in Chitin and Chitosan*; Brine, C. J.; Sandford, P. A.; Zikakis, J. P., Eds.; Elsevier: New York, 1992; pp 516–525.
37. Muzzarelli, R.A.A. *Carbohydr Polym* 1992, 19, 231.
38. Kurita, K.; Yoshino, H.; Nishimura, S. I.; Ishii, S. Preparation and biodegradability of chitin derivatives having mercapto groups. *Carbohydr Polym* 1993, 20, 239.
39. Zheng, M.; Hirano, S. Novel N-unsaturated fatty acid and n-trimethyl acetyl derivatives of chitosan. *Carbohydr Polym* 1995, 26: 205–209.
40. Hirano, S.; Konda, Y.; Fuji, K. *Carbohydr Res* 1985, 144, 338.
41. Sashiwa, H.; Saimoto, H.; Shigemasa, Y.; Tokura, S. *Carbohydr Res* 1994, 242, 167.
42. Varum, K. M.; Ottoy, M. H.; Smidsrod, O. *Carbohydr Polym* 1994, 25, 65.
43. Muzzarelli R. A. A.; Jeuniaux, C.; Gooday, G. W. *Chitin in Nature and Technology*; Plenum: New York, 1986.
44. Rocha Filho, J. A.; Bach, E. E.; Vargas, R. R.; deq Ueiroz, A. A. *Mater Res* 2001, 4, 53.
45. Abdel-Mohdy, F. A.; Waly, A.; Ibrahim, M. S.; Hebeish, A. *Polym Polym Composites* 1998, 6, 147.
46. Razzak, M. T. Radiation Grafting Studies on the Modification of Fluoropolymers and Natural Rubber for Biomaterials, Ph.D. Thesis; Tokyo University: Tokyo, 1988.
47. Crank, J; Park, G. S. *Diffusion in Polymers*. Academic Press: New York, 1968.
48. Barrer, R. M. *Trans Faraday Soc* 1943, 39, 237.
49. Atkins, P. W. *Physical Chemistry*. Oxford University Press: Oxford, 1998; p. 776.