Preparation of a Cu(II)-Immobilized Co-polymer(CIC) for Effective Removal of Urea

S. K. Bajpai[a]; Abhishek Pathak[a]

[a] Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College (Autonomous), Jabalpur, M. P., India

PLEASE SCROLL DOWN FOR ARTICLE

Preparation of a Cu(II)-Immobilized Co-polymer(CIC) for Effective Removal of Urea

S. K. BAJPAI and ABHISHEK PATHAK

Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College (Autonomous), Jabalpur, (M. P.), India

The study describes the preparation of Cu(II)-immobilized copolymer(CIC) under optimum conditions for the effective removal of urea. The copolymeric hydrogels, synthesized by free-radical aqueous copolymerization of monomers acrylamide and sodium acrylate, have been analyzed for their Cu(II) uptake behavior. The sorption of Cu(II) into polymer follows a Langmuir–type pattern and amount sorbed depends upon the composition of copolymeric gels, presence of other co-ions in the solution, pH of the solution, initial concentration of sorbate, degree of crosslinking of the copolymeric hydrogel, temperature of the solution etc. In the preliminary study, the Cu(II) immobilized co-polymer(CIC) sorbent demonstrated a fair tendency to remove urea from aqueous solutions.

Keywords: sorption; Langmuir; hydrogel; urea; hemodialysis

1 Introduction

Hemodialysis is the most widely used therapy for the treatment of patients suffering from kidney failure. The materials used for hemodialysis are natural polymers like cellulose or modified cellulose and synthetic polymers like polyacrylonitrile, polymethylmethacrylate, polysulfone, etc. (1). Membranes, composed of these materials remove urea (and other uremic toxins also) via filtration through micropores. However, in order to enhance urea removal rate, material scientists have been making continuous attempts, to develop some more novel polymeric materials that could effectively remove urea through sorption. These materials include activated carbon (2), polyethylenepolyamine/Cu(II) complex (3), tolyene di-isocynate crosslinked β-cyclodextrin (4), and others. However, due to low urea sorption capacity of these materials, they still can't be used practically.

In our previous work (5), we observed that poly(acrylamide–co-sodium acrylate) hydrogel demonstrated sharp volume–phase transition when the swollen gel was put in the solutions of transition metal ions. Now, keeping in mind this excellent metal–ions uptake behavior of hydrogels, we hereby propose a unique study in which Cu(II)-immobilized copolymer will be synthesized and shall be evaluated for its ability to remove urea from aqueous solutions by sorption.

In the present study, a detailed investigation of sorption of Cu(II) into the proposed copolymer will be carried out and the resulting Cu(II)-immobilized copolymer(CIC) sorbent, so prepared, will also be exploited for urea sorption from aqueous solution.

The reasons for selecting poly(acrylamide-co-sodium acrylate) for the present work include greater Cu(II) uptake tendency of this material, its hydrophilic nature which will minimize its interactions with blood proteins and finally, its non-degradability.

2 Experimental

2.1 Materials

The monomer acrylamide (AAm), the crosslinker N,N′– Methylene bisacrylamide (MB) and initiator potassium persulphate (KPS) were obtained from Hi-Media Mumbai, India. The monomer sodium-acrylate (SA) was synthesized by neutralization of corresponding acid (i.e., acrylic acid, Merck, India) with a methanolic solution of sodium hydroxide at 20°C as described elsewhere (6). AAm was recrystallized in methanol to remove the inhibitor. Other chemicals such as cupric chloride, potassium-ferrocyanide and urea were received from Research Lab, Pune, India. The double distilled water was used throughout the investigations.

2.2 Synthesis of Co-polymeric Sorbent

The proposed co-polymer was synthesized by carrying out free-radical aqueous polymerization of AAm and SA using

Address correspondence to: Dr. S. K. Bajpai, Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College (Autonomous), Jabalpur, (M. P.) 482001, India. E-mail: mnlbpi@rediffmail.com

MB as crosslinker and KPS as initiator. In brief, 7.04 mM of monomer AAm and 7.97 mM of monomer SA were dissolved in water and to this, 19.45×10^{-2} mM of crosslinker was added to give a total volume of 5.0 ml. Finally, 5.54×10^{-2} mM of initiator KPS was added and the solution was poured into PVC straws and kept in an electric oven (Tempstar, India) at 60°C for a period of 2 h. After the polymerization was over, the resultant transparent cylindrical gels were cut into small pieces and equilibrated in water for 72 h to remove unreacted chemical species and then dried in a dust-free chamber till they attained constant weight. The length, diameter and mass of the dry samples were found to be 1.50 ± 0.01 cm, 0.35 ± 0.01 cm, 0.24 ± 0.01 g, respectively. It is also to be noted that for studies of sorption of Cu(II) into polymeric hydrogels, gels were grinded into fine powder and passed through standard sieve of mesh size 25 and collected on the sieve with mesh size 85 to finally yield 710 μm sized particles.

The hydrogel samples shall be designated as HG(X) where the number X in parenthesis denotes the percent mole fraction of sodium-acrylate in the feed mixture. For example, the sample, described above will be designated as HG 53 where 53 is the percent mole fraction of sodium-acrylate.

2.3 FTIR Analysis

The FTIR spectra of plain and Cu(II)-immobilized hydrogel samples were recorded on a FTIR spectrophotometer (Shimadzu, 8400 S) using KBr pellets.

2.4 Swelling Studies

Completely dried and pre-weighed hydrogel samples were placed in 250 ml of distilled water at 30°C. The swollen gels were taken out at regular time-intervals, wiped superficially with tissue paper to remove loosely bound surface water, weighed and then put in the same bath. The mass measurements were continued till the gels attained constant weight. The percent mass swelling was determined using the following expression (7):

$$\%S_M = \frac{M_t - M_c}{M_o} \times 100$$

Where, M_t and M_o are the mass at different time intervals and the initial mass, respectively. All the swelling experiments were done in triplicate and average values are reported in the data.

2.5 Sorption Studies

Bath mode sorption studies were carried out by agitating 50 ml of Cu^{2+} solution of a desired concentration with 0.10 g of ground hydrogel powder (particle size 710 μm) in a temperature-controlled shaking water bath. Continuous mixing was provided during the experimental period with a constant agitation speed of 60 rpm. After equilibrium,

sorbent was then separated by filtration and the supernatant was analyzed spectrophotometrically (Systronics, India) for the remaining concentration of Cu^{2+} using a standard method described elsewhere (8).

2.6 Desorption of Cu(II)

As mentioned in the introduction section, the major objectives of the present work are to develop a Cu(II)-immobilized copolymer(CIC) and to investigate its urea sorption capacity so that, in the near future, it may be considered as an alternative membrane material for hemodialysis. Since free Cu^{2+} ions in the blood induce the reactive oxygen species and cause serious injury for the cells and tissues, it is extremely important that CIC must not desorb Cu^{2+} ions back. Therefore, a Cu(II)-immobilized sorbent was investigated for desorption of Cu(II). 60 mEq of Na^+ ions, 4.0 mEq of K^+ ions, 40 mEq of HCO_3^- ions were added into distilled water and the final pH was adjusted to 7.4. The concentrations of electrolytes in this solution were roughly the same as found in normal human blood. To 25 ml of this solution, varying amounts of Cu(II)-immobilized sorbent were added and stirred at constant rate for 4 h. After filtration, the filtrate was assayed for Cu(II).

2.7 Preparation of Porous Film

In order to prepare porous copolymeric film, a definite amount of sucrose was added to the reaction mixture and it was spread over a Petri dish (diameter 6.0″) and kept in an electric oven at 60°C for 2 h. After polymerization, the film formed was taken out carefully and equilibriated in distilled water for 72 h. The water was changed at regular time intervals of 6 h. In this way, all sucrose was leached out, resulting in the formation of porous film, which was air-dried till it attained constant weight.

## 3 Results and Discussion

3.1 FTIR Analysis of Polymer Sample

The IR spectra, as depicted in the Figure 1 (A), confirmed the formation of a copolymer of acrylamide and sodium acrylate as is evident from bands which appeared at 3444 cm^{-1} (N-H stretching band), 1680 cm^{-1} (C=O) stretching band), 1600 cm^{-1} (asymmetric stretching of COO$^-$) and 1422 cm^{-1} (due to symmetric stretching of COO$^-$).

3.2 Network and Swelling Parameters of Hydrogels

The equilibrium water uptake of a polymer sample reflects its swelling capacity and is a function of the network structure, crosslinking ratio, and degree of ionization of its functional groups etc. (9). The various significant structural network parameters such as average molar mass between
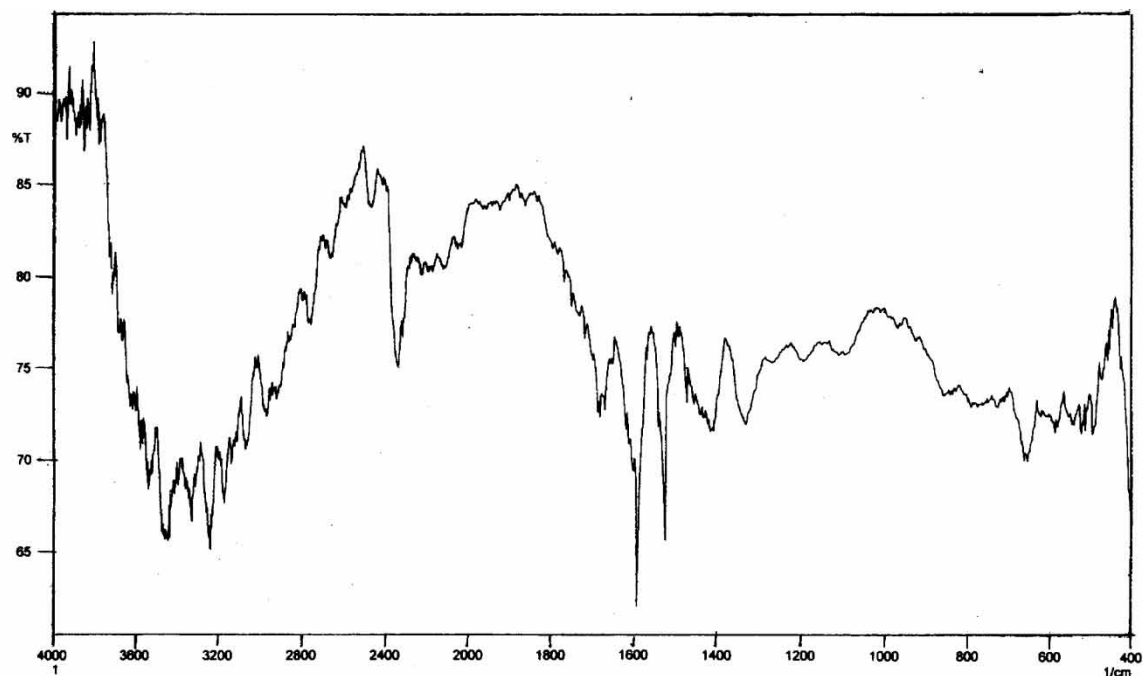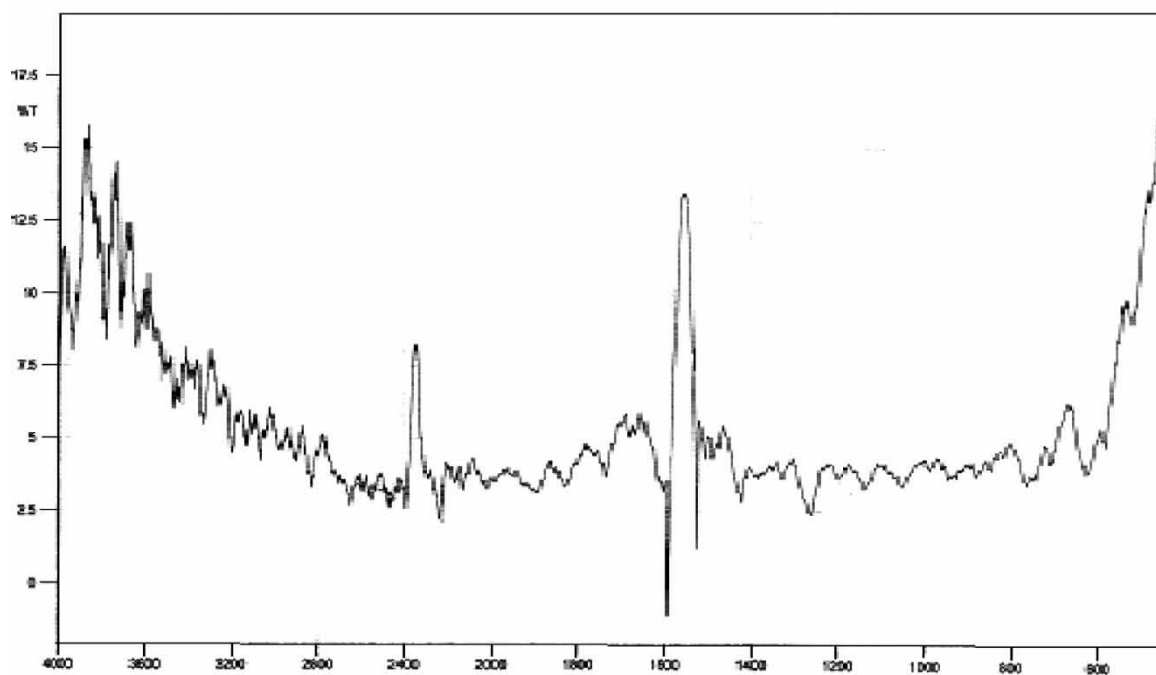
Fig. 1. (A) FTIR spectrum of co-polymer sample. (B) FTIR spectrum of Cu(II)-immobilized sample.

the crosslinks M_c, volume fraction of swollen polymer ϕ, number of elastically effective chains V_e, crosslink density q, were determined for the three hydrogel samples prepared with varying amounts of crosslinker, namely 19.45×10^{-2}, 32.43×10^{-2} and 48.64×10^{-2} mM, respectively. Moreover, the dynamic water uptake data, obtained for the three samples (Figure 2) was used to calculate swelling exponent 'n', gel characteristic constant k, and various diffusion coefficients, i.e., initial, average and late time diffusion coefficients. A detailed calculation for all the parameters mentioned above, have been described in our previous work (10).
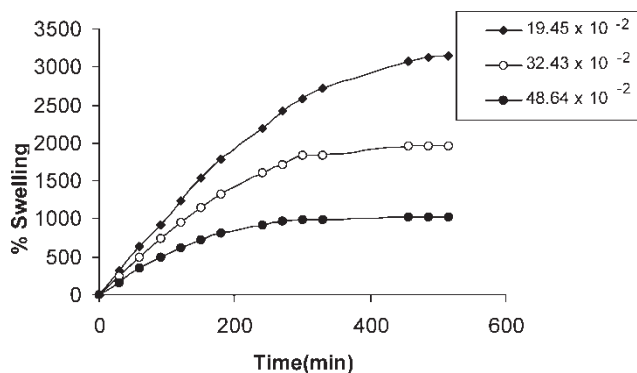
Bajpai and Pathak

Fig. 2. Dynamic uptake of water as a function of time for the hydrogel sample. HG (53) crosslinked with (◆)19.45×10^{-2} mM, (○) 32.43×10^{-2} mM and (●) 48.64×10^{-2} mM of crosslinker, in the buffer solution of pH 7.4 at 30°C.

Table 1 describes the various network and swelling parameters mentioned above. It is clear that the value of M_c decreases with the increase in crosslink density. Moreover, the number of elastically effective chains increases. It can also be seen that the values of swelling exponent 'n' for the three samples lie in the 0.6 to 0.8 range, thus indicating a non-Fickian or anomalous diffusion (11). This may be simply attributed to the fact that when gels are put in distilled water, the negatively charged -COO⁻ groups present along the macromolecular chains repel each other, thus causing the polymer chains to undergo relaxation, thus allowing more and more solvent (i.e. water) to enter into the swelling network. This is the most common phenomenon which occurs in the case of polyelectrolyte gels when they are put in a medium whose pH is more than the pK value of the ionizable groups (12). The data, displayed in Table 1 also includes various diffusion coefficients.

3.3 Effect of Salt Concentration on Swelling

When a swollen polymer polyelectrolyte gel is put in the salt solution, the gel undergoes sharp volume-phase transition owing to the decrease in the osmotic swelling pressure and occurrence of ion-exchange process between the free/counter ions in the swollen network and cations present in the external salt solution. It has been demonstrated that mono-valent-divalent cation exchange plays a significant role in the physiological processes such as nerve excitation and muscle contraction (13−15).

To investigate this effect, hydrogel samples, prepared with 19.45×10^{-2}, 32.43×10^{-2} and 48.6×10^{-2} mM of cross-linking agent, were allowed to equilibriate in distilled water and then the swollen samples were put in Cu^{2+} solutions of varying concentrations. The results, as depicted in Figure 3 clearly indicate that there is sharp decrease in percent mass swelling of three hydrogel samples in the 0−2 mM concentration range of Cu^{2+} solutions. In addition, the gel

Table 1. Swelling and network parameters

| Amount of crosslinker in hydrogels mM × 10²	Swelling exponet 'n'	Gel characteristic constant 'k' × 10³	Average molar mass between the crosslinks M_c × 10⁻⁴	Volume fraction of swollen polymer φ × 10²	No. of elastically effective chains V_e × 10⁻¹⁷	Crosslink density 'q' × 10⁵	Crosslinking ratio × 10⁴	Diffusion coefficients cm² min⁻¹ Average D_{av} × 10⁵	Initial D_i × 10⁵	Late time D_L × 10⁵
19.45	0.810	7.460	82.430	2.774	8.037	9.757	87.854	0.198	11.978	12.990
32.43	0.729	13.083	32.715	4.038	22.092	24.583	146.425	0.244	13.777	10.585
48.64	0.615	27.239	5.941	7.577	121.653	135.374	219.637	0.304	14.532	16.887
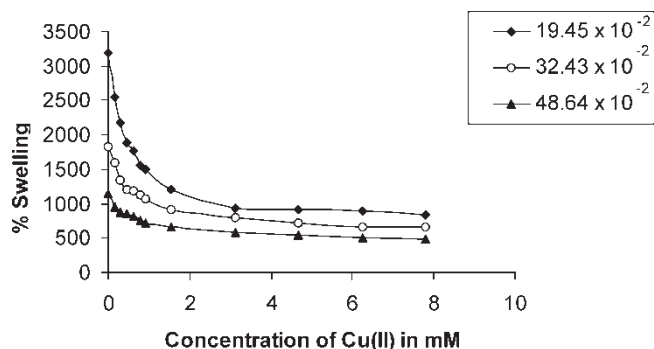
Fig. 3. Effect of concentration of Cu(II) ions on the percent mass swelling of hydrogel HG (53) crosslinked with ($\blacklozenge$) 19.45×10^{-2} mM, ($\circ$) 32.43×10^{-2} mM and ($\blacktriangle$) 48.64×10^{-2} mM of crosslinker at 30°C.

Fig. 4. Effect of concentration of sodium acrylate in the feed mixture on the amount of Cu(II) sorbed (mg g^{-1}) from 50 ppm copper(II) solution at 30°C.

prepared with minimum crosslinking agent i.e., 19.45×10^{-2} mM demonstrates the highest degree of deswelling, while the decrease is not much pronounced in two other swollen hydrogel samples which contain a relatively higher amount of crosslinking agent.

The observed deswelling may simply be attributed to the ion-exchange process between Cu^{2+} ions of external solutions and Na^+ ions (i.e. counter ions) present in the gel phase. This occurs due to the strong tendency of Cu^{2+} ions to form complex with charged carboxylate groups. These divalent ions also serve as additional crosslinks within the polymer network. In addition to this, since for a single Cu^{2+} ion entering the swollen network, two Na^+ ions are required to diffuse out to maintain the electroneutrality, the resulting decrease in osmotic swelling pressure also contributes towards observed deswelling.

Finally, the highest degree of deswelling, observed with the minimum crosslinked gel may be attributed to higher flexibility of macromolecular chains due to a fewer number of crosslinking junctions as compared to two other samples. The highest value of M_c (i.e., molecular mass between the two successive crosslinks) for this hydrogel sample (Table 1) also supports our arguments.

From the above discussion, it is crystal clear that Cu^{2+} ions are strongly sorbed into the swollen copolymer network, thus causing it to deswell. Now, in the forthcoming sections we shall discuss the sorption behavior of Cu(II) into the copolymeric hydrogels. For the purpose of studying sorption behavior, the gels prepared were ground and sieved to yield different micrometer sized particles.

3.4 Effect of Composition of Sorbent on Cu(II) Uptake

In order to obtain the composition of copolymeric sorbent, which could exhibit maximum Cu^{2+} sorption from aqueous solution, we synthesized a number of hydrogels with varying sodium-acrylate percent mole fraction in the 0 to 55.7 range. The completely dried.
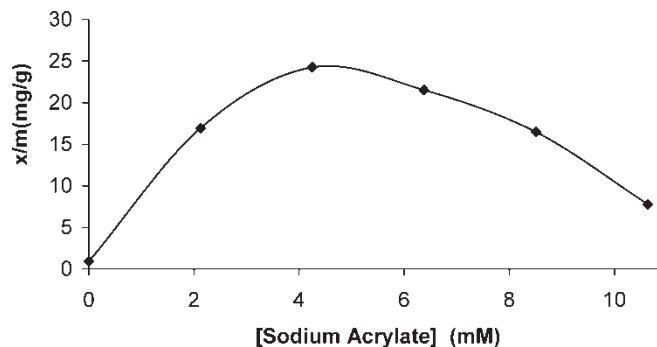
Pre-weighed, ground gels (particle sizes 710 μm) were put in 50 ppm Cu^{2+} solutions till the attainment of equilibrium. The constant stirring was also provided during the sorption process. The results, as obtained by plotting x/m (i.e., amount of Cu(II) sorbed in mg per g of sorbent) against a concentration of sodium-acrylate, depicted in Figure 4, clearly indicate that the amount of Cu(II) sorbed increases with an increase in percent mole fraction of sodium-acrylate up to 20.1 and then it begins to decrease with a further increase in sodium-acrylate content. It means that for the gel, synthesized with 20.1% mole fraction of sodium acrylate, maximum Cu(II)-uptake is observed. The initial increase in metal ion uptake with sodium-acrylate content up to 20.1% mole fraction may be attributed to the fact that Na^+ ions, present within the gel as counter/free ions undergo ion-exchange process with the Cu^{2+} ions that are present in the external solution. In this way, the presence of $-COO^-Na^+$ groups along the macromolecular network in the swollen gel is mainly responsible for the metal ion uptake. However, when percent mole fraction of sodium-acrylate is increased beyond 20.1 Cu(II) uptake begins to decrease. The observed decrease may be attributed to the counter ion condensation or the limited extensibility of the network (16). In other words, when percent mole fraction of sodium-acrylate is further increased beyond 20.1, the Na^+ ions begin to condense around the charged $-COO^-$ groups and screens the negative charges causing a decrease in the chain relaxation process. Therefore, due to strong electrostatic attraction between Na^+ counter ions and $-COO^-$ groups, the Na^+ ions are no longer free and they prefer to remain condensed around the carboxylate groups rather than to diffuse out through ion-exchange with external Cu^{2+} ions. The limited extensibility of macromolecular chains also enhances the electrostatic attraction between $-COO^-$ groups and Na^+ ions, thus discouraging the entrance of Cu^{2+} ions through ion-exchange mechanism. Therefore, an increase in percent mole fraction of sodium-acrylate beyond 20.1 results in a decrease in uptake of Cu(II). In this way, it can be concluded from the above study that copolymeric hydrogel, prepared with 20.1% mole fraction of sodium-acrylate, shall demonstrate

maximum metal ions uptake. Therefore, the rest of the sorption studies were carried out with the above mentioned copolymeric sorbent.

3.5 Sorption Isotherm

The sorption isotherm shows how the sorbate molecules are distributed between the liquid phase, C_e (mg L^{-1}) and the solid phase, q_e (mg g^{-1}). The analysis of the isotherm data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purpose (17).

The Langmuir model (18), assumes that the uptake of sorbate occurs on a homogenous surface by monolayer sorption without any interaction between the sorbed ions. The linear form of the Langmuir isotherm is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max.}b} + \frac{C_e}{Q_{max.}}$$

Where, C_e is the equilibrium concentration of the sorbate (mg L^{-1}), q_e is the amount of metal ions (i.e. sorbate) sorbed at equilibrium (mg g^{-1}) and Q_{max} (mg g^{-1}) and b (L mg^{-1}) are the Langmuir constants related to the sorption capacity and energy of sorption, respectively. The linear plot of C_e/q_e vs. C_e (Figure 5) shows that sorption of Cu(II) into the copolymeric sorbent obeys the Langmuir isotherm model ($R^2 = 0.98$). The values of constants Q_{max} and b were determined using the slope and intercept of the linear plot and were found to be 38.46 mg g^{-1} and 0.10 L mg^{-1}, respectively.

According to Hall et al. (19), the essential characteristics of the Langmuir isotherm can be explained in terms of a dimensionless separation factor (R_L) which is defined as:

$$R_L = \frac{1}{1 + bC_o}$$

Where, b (L mg^{-1}) is the Langmuir constant and C_o (mg L^{-1}) is the initial concentration of Cu(II) ions. The parameter R_L shows the type of isotherm as shown in the Table 2.

In the proposed study, the different values of R_L obtained for various initial concentrations have been summarized in Table 3. It is clear that R_L values lie between 0 and 1, thus
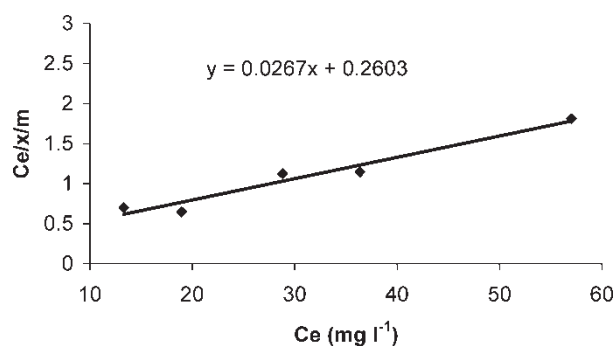
Table 2. Effect of separation factor R_L on type of isotherm

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 3. R_L values, based on Langmuir model for sorption of Cu(II) into polymeric sorbent

Initial concentration C_o (mg L^{-1})	Value of R_L
20	0.333
40	0.200
60	0.142
80	0.111
100	0.090
120	0.076

indicating the favorable sorption of Cu(II) into the copolymer. We also fitted the experimental sorption data in a Freundlich sorption model. However, the value of R^2 (0.84) indicated that the model did not fit satisfactorily as compared to the Langmuir model. To summarize, it can be concluded that sorption of Cu(II) into poly(acrylamide-co-sodium-acrylate) follows the Langmuir model and the dimensionless separation factor R_L also indicates favorable sorption.

3.6 Initial Sorbate Concentration Effect

The dependence of Cu(II) uptake on the initial sorbate concentrations (0.625 to 2.343 mM) has been shown in the Figure 6. It is clear that as the initial concentration of Cu^{2+} ion increases, the percent Cu(II)-uptake decreases. This may simply be attributed to the fact that for low concentration, the ratio of surface area available to number moles
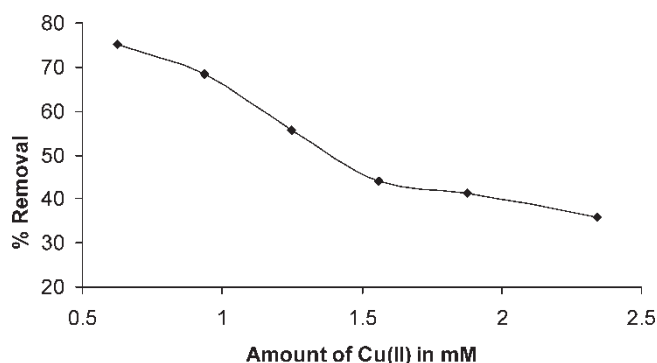

Fig. 5. Langmuir isotherm for the sorption of Cu(II) ions into the copolymer sorbent at 30°C.

Fig. 6. Effect of initial concentration of Cu(II) ions on the percent removal.

1085

Cu(II)-Immobilized Co-polymer for Urea Removal

of metal is quite high. However, at higher concentrations, the available sites for sorption become fewer and subsequently the percent Cu(II)-uptake decreases. Similar results have also been reported with other metal ions (20).

3.7 Effect of Presence of Co-ions on Cu(II)-Uptake

It is normally expected that the presence of other co-ions in the sorbate solution does influence its sorption capacity. In order to investigate this, sorption studies were carried out in 80 ppm Cu^{2+} solutions, containing varying amounts of Ni^{2+} and Ca^{2+} ions (in the 0–150 ppm range). The results, as depicted in Figure 7 clearly indicate that as the concentration of co-ions in the solution increases, the uptake of Cu(II) decreases. This may simply be attributed to the fact that these ions, namely Ni^{2+} and Ca^{2+} compete with Cu^{2+} ions for sorption at available binding sites. As a result, the amount of Cu(II) sorbed begins to decrease with an increase in the concentration of co-ions in the solution. Here, it is also interesting to see that the decrease in Cu(II)-uptake is more prominent in the case of Ni^{2+} ions. This may be explained on the basis of the fact that Ni(II), being a transition metal, has a greater tendency to bind with the carboxylate groups present along the macromolecular chains within the sorbent. On the other hand, Ca^{2+} ions, being alkaline earth metal, has a relatively weaker tendency to get complexed with -COO$^-$ groups in the sorbent. In this way, the presence of other co-ions does effect the uptake of Cu(II) ions.

3.8 Effect of pH on Cu(II)-Uptake

The pH of the medium affects the process of sorption significantly as it changes the charge profile of the sorbent surface that finally results in the alteration in the extent of sorption (21). If the sorbent is a polyelectrolyte then dissociation/protonation of functional groups present within the matrix at different pH of the sorption system yield interesting results (22–23).

In order to study the effect of pH on the Cu(II)-uptake, pH of the 100 ppm Cu^{2+} solution was varied by addition of
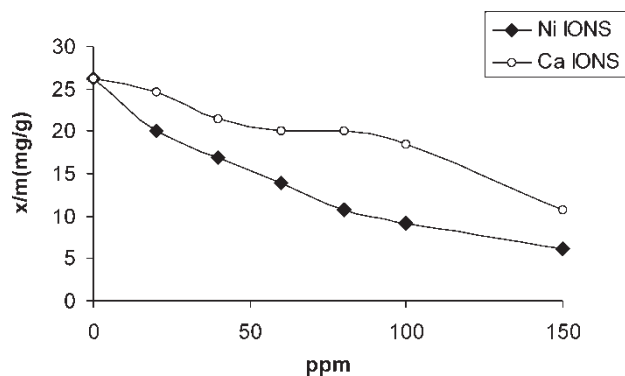
NaOH/HCl and the final volume of all the resulting solutions was made equal by adding distilled water. In this way, 72 ppm Cu(II) solutions of different pH, in the range 2.2 to 6.4 were obtained. The results of sorption study as depicted in Figure 8 clearly indicate that maximum Cu^{2+} uptake is observed at the pH 5.2 of the sorbate solution which was the self pH of the 72 ppm Cu(II) solution. Interestingly, the metal uptake is found to decrease with pH. It means that the addition of HCl results in a decrease in the Cu(II)-uptake by the copolymeric sorbent. The observed results may be explained as below.

When the pH of the sorbate solution (self pH 5.2) is decreased by the addition of HCl, the carboxylate groups present along the macromolecular chains in the sorbent begin to get protonated to yield uncharged -COOH moieties, which do not contribute towards the ion-exchange process which is mainly responsible for the uptake of Cu^{2+} ions. As the pH is further decreased by addition of HCl, more and more carboxylate groups undergo protonation and therefore extent of sorption decreases continuously. Finally, when the pH of the Cu(II) solution was increased slightly beyond 5.2 (i.e., self pH), the Cu(II)-uptake remained almost the same. However, as soon as the pH of the Cu(II) solution was further increased beyond 6.0, slight turbidity was observed due to formation of $Cu(OH)_2$ (24). Therefore, we did not study the Cu(II)-uptake beyond pH 6.0. In this way, it may be concluded that self pH of the copper(II) solution is the optimum pH for metal ion uptake.

3.9 Crosslinking Effect

In order to see whether the degree of crosslinking of co-polymeric sorbent influences the metal ion uptake, we synthesized a number of hydrogels with different amount of crosslinker, in the range 6.48×10^{-2} to 22.70×10^{-2} mM, and studied their Cu(II)-uptake capacity in 50 ppm Cu^{2+} ions solutions. The results, as depicted in Figure 9, indicate that as the amount of crosslinker, used in the hydrogel synthesis, increases, the Cu(II)-uptake also increases and for 19.45×10^{-2} mM of crosslinker, maximum Cu(II)-uptake is
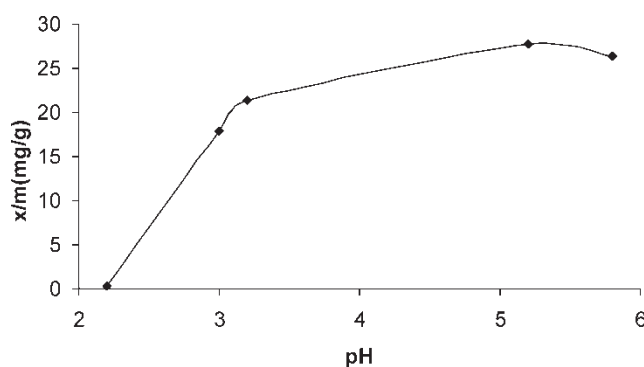

Fig. 7. Amount of Cu(II) sorbed (mg g^{-1}) as a function of concentrations of Ni^{2+} ions and Ca^{2+} ions present in the 50 ppm Cu(II) solutions at 30°C.

Fig. 8. Effect of pH of 72 ppm Cu(II) solutions on the amount of Cu(II) sorbed (mg g^{-1}) at 30°C.

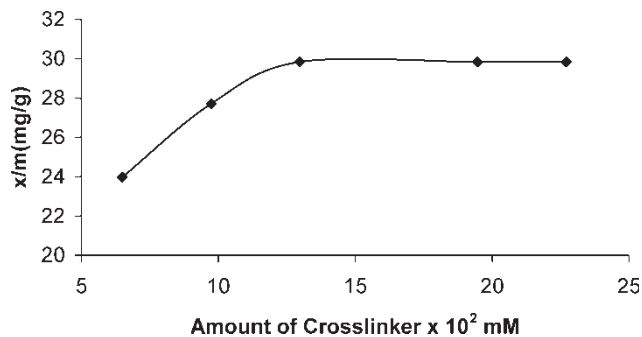

Fig. 9. Effect of crosslinker concentration used to prepare polymeric sorbent on the Cu(II) uptake (mg g^{-1}) from 50 ppm aqueous Cu(II) solution at 30°C.

observed. With further increase in the amount of crosslinker, there is no noticeable change in the amount of Cu(II) sorbed i.e., saturation value is obtained. The observed finding may be attributed to the fact that when the gels are synthesized with the concentration of the crosslinker below 19.45×10^{-2} mM, the network formation is insufficient (25). Moreover, due to extremely low degree of crosslinking soluble portion of polymer is also formed. These ultimately result in the formation of co-polymer sorbent with less number carboxylate groups (i.e., concentration of sodium-acrylate is relatively small). As a consequence of this, less Cu(II)-uptake is noticed. The insufficient polymer network formation is usually confirmed by gravimetric measurements (26).

3.9.1 Mechanism of Cu(II)-Uptake

In order to establish the mechanism of Cu(II) uptake by copolymer, we recorded FTIR of Cu(II)-immobilized copolymer and compared it with that of plain polymer (Figure 1 (A) and (B)). A comparison of the two spectra revealed following points:

1. The C=O stretching band, appearing in plain polymer was almost absent in the Cu(II)-immobilized copolymer. Moreover, the bending of CO acid, obtained at 659 cm^{-1} shifted to 629 cm^{-1} in the Cu(II)-immobilized polymer. This indicates binding of Cu(II) with oxygen atom as shown below:
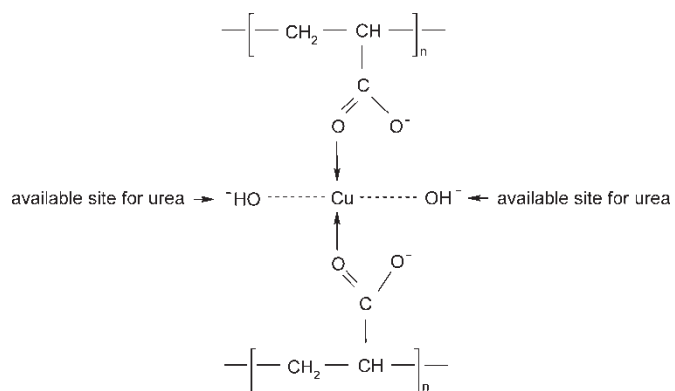
2. It was also found that NH stretching band, appearing at nearly 3444 cm^{-1} in the plain copolymer was almost disappeared in the spectrum of CIC, thus suggesting the coordination of Cu(II) with 'N' atom of acrylamide as shown below:
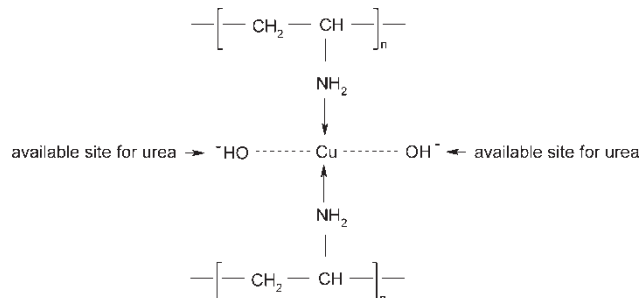
In this way, we find that in both the cases, two co-ordination sites at Cu(II) are still unoccupied and hence, can be used by 'O' atoms of urea molecules for coordination. Almost similar mechanism has been proposed by M. Rhazi et al. (27) to explain binding of Cu(II) with nitrogen atoms present in the chitosan molecules.

3.9.2 Effect of Temperature on Cu(II) Uptake

The effect of solution temperature on the Cu(II)-uptake was investigated by carrying out sorption studies in 50 ppm of Cu^{2+} solutions at various temperatures, in the 15°C–55°C range.

The results, as depicted in Figure 10, indicate that the amount of Cu(II) sorbed per g polymer increases with increase in temperature and it attains optimum value of 28.21 (mg/g) at 55°C. This can be explained on the basis of the fact that as the binding of Cu^{2+} ions with oxygen atoms present in sorbent molecules is chemical in nature, the higher temperature favors the uptake process. In addition, at high temperature sorbate ions diffuse into the polymer network at faster rate, thus enhancing the sorption process. Therefore, optimum temperature for Cu(II)-uptake is found to be 55°C.
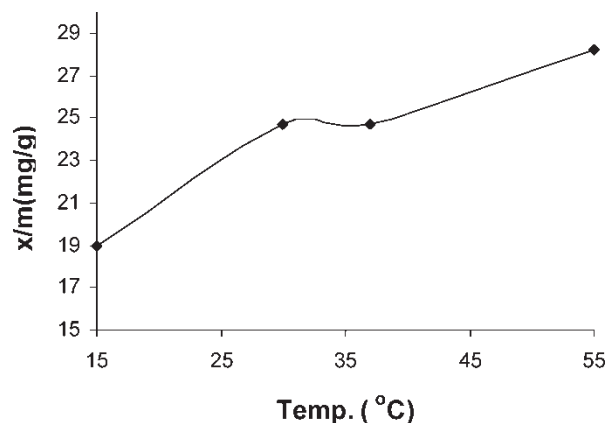

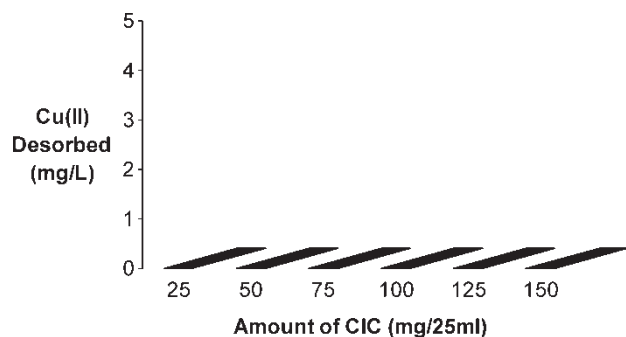**Fig. 10.** Effect of solution temperature on Cu(II)-uptake.

Fig. 11. Effect of increase in amount of CIC sorbent on Cu(II) desorption.

3.9.3 Desorption Studies of Cu(II) from Sorbent

The results of the desorption study, as depicted in Figure 11, clearly suggest that the amount of Cu(II) desorbed is nil in all the solutions. This clearly suggests that the increase in the amount of CIC sorbent in the solutions does not cause any desorption of Cu(II) species. This also confirms that binding of Cu(II) to the co-polymer is purely chemical in nature as discussed in the previous section.

3.9.4 Urea Sorption Study

In order to investigate urea uptake behavior of Cu(II)-immobilized copolymer (CIC), a series of urea solutions in the concentration range 60 to 180 mg per 100 ml, were prepared in physiological fluid (as mentioned in the Experimental section) and these pre-weighed quantities of grinded CIC sorbent (particle diameter 100 μm) were added and agitated for 4 h under constant stirring. The results, as depicted in Figure 12 clearly indicate that urea uptake increases with the increase in initial urea concentration. Therefore, the newly developed CIC sorbent seems to have potential to remove urea from aqueous solutions.

3.9.5 Effect of Agitation Speed on Urea Uptake

To investigate this, pre-weighed amounts of CIC sorbent were added to two urea solutions (urea concentration 90 mg/dL) and were agitated with different speeds, i.e., 40 rotations/
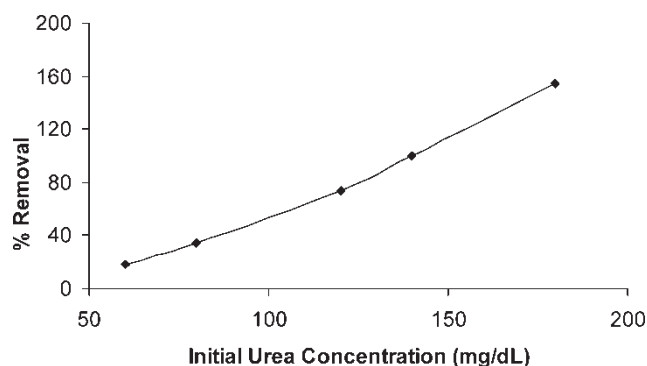

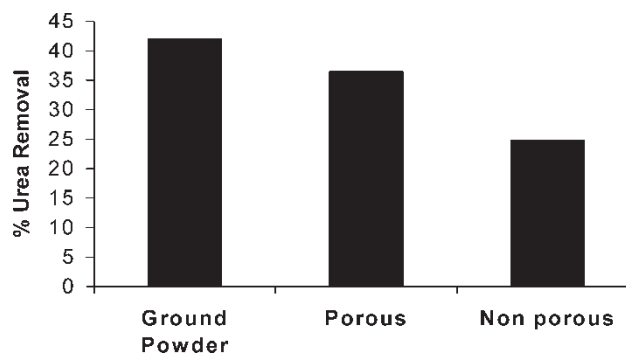**Fig. 12.** Effect of urea concentration on its uptake.

Fig. 13. Bar diagram showing percent urea removal by porous and non-porous films and ground powder (100 μm).

15 sec and 60 rotations/15 sec, respectively. The amount of urea sorbed per gram of CIC was found to be nearly 11.540 mg/g and 34.613 mg/g polymer, respectively. This suggests that agitation speed influences the urea removal rate significantly and higher agitation speed will favor the urea removal. This may simply be attributed to the fact that the higher agitation speed provides greater opportunity for urea molecules to contact with the CIC sorbent, thus enhancing the urea sorption.

3.9.6 Urea Removal by Porous CIC Film

We have seen that ground CIC powder (particle diameter 100 μm) seems to be an effective urea sorbent. However, we also prepared a porous film of CIC (as described in the Experimental section) and investigated its urea removing capacity by putting a pre-weighed piece of film in the urea solution (90 mg/100 ml) and agitating for 4 h under constant stirring. For comparison, we also put a non-porous film of the same composition in urea solution. The results as depicted in Figure 13 clearly indicate that the porous film shows greater tendency for urea uptake (i.e. nearly 36.4%) as compared to the non-porous one. This may be simply attributed to the fact that due to presence of pores, a greater surface area becomes available for the uptake of urea molecules. It is also worth mentioning here that 100 μm sized ground CIC particles removed nearly 42% urea under similar conditions. In this way, the urea removal capacity of the CIC sorbent follows the order:

Particle >Porous film > Non-porous film.

4 Conclusions

From this study, it can be concluded that poly(acrylamide-co-sodium acrylate) has a strong tendency to bind chemically with copper (II). The Cu(II)-uptake depends upon the degree of crosslinking of polymeric sorbent, composition of polymer, pH of the sorption medium. The higher temperature favors the Cu(II)-uptake. The sorption process is best interpreted by the Langmuir sorption model. The Cu(II)-

immobilized co-polymer(CIC) does not show any sign of desorption and it shows a fair tendency to remove urea from its aqueous solution. Also, the higher agitation speed favors the urea removal. Moreover, porous film demonstrates a greater tendency to take up urea as compared to the nonporous film. However, a detailed investigation is still needed to further establish the suitability of this Cu(II)-immobilized copolymer(CIC) as an alternative material for the fabrication of membrane to remove urea in hemodialysis. Particularly, the proposed CIC must be investigated for its mechanical strength, hemocompatibility, interaction with blood proteins and tendency not to induce compliment activation. The suitability of the proposed material can then be established.

5 Acknowledgements

6 References

1. Kim, S.H., Song, K.I., Chang, J.W., Kim, S.B., Sung, S.A., Jo, S.K. and Cho, W.Y. (2006) *Kidney Int.*, **69**, 161.

2. Yoshie, F. and Susumu, O. (1990) *Nippon Kaguka Kaishi*, **4**, 352.

3. Chen, X., Li, W.J. and Wu, T.Y. (1997) *Chin. J. Biomed. Eng.*, **16**, 284.

4. Shi, L.Q., Zhang, Y.Z. and He, B.L. (1999) *Poly. Adv.Technol.*, **10**, 69.

5. Bajpai, S.K. and Johnson, S. (2005) *React. Funct. Polym.*, **62**, 271.

6. Liu, Y., Velada, J.L. and Huglin, M.B. (1999) *Polymer*, **40**, 4299.

7. Wan, Y.Z., Yang, Y.L., Yao, K.D. and Chang, G.X. (2005) *J. Appl. Poly. Sci.*, **75**, 994.

8. Yoe, John H. *Photometry Chemical Analysis*; John Wiley and Sons Publications: New York; Vol. 1, pp. 182−183, 1928.

9. Gan, L.H., Deen, G.R., Gan, Y.Y. and Tam, K.C. (2001) *Eur. Poly. J.*, **37**, 1413.

10. Bajpai, S.K. and Singh, S. (2005) *Reactive and Functional Polymers*, **66**, 431−440.

11. Ritger, P.L. and Peppas, N.A. (1987) *J. Cont. Rel.*, **5**, 37.

12. Caykara, T. (2004) *J. Appl. Polym. Sci.*, **92**, 763.

13. Tasaki, I., Nakaye, T. and Byrne, P.M. (1985) *Brain Res.*, **331**, 363.

14. Tasaki, I. and Byrne, P.M. (1988) *Brain Res.*, **475**, 173.

15. Tasaki, I. (1999) *Jpn. J. Phys.*, **49**, 125.

16. Hasa, J., Illavsky, M. and Dusek, K. (1975) *J. Polym. Sci. Phys. Ed.*, **13**, 253.

17. Abdel-Halim, E.S., Abou-Qkeil, A. and Hashem, A. (2006) *Polym. Plast. Technol. Eng.*, **45**, 71.

18. Bayat, A. and Hazard, J. (2002) *Mater.*, **895**, 275.

19. Hall, R., Eaglton, L.C., Acrivos, A. and Vermevlem, T. (1966) *Ind. Eng. Chem. Fundam.*, **5**, 212.

20. Jamode, A.V., Sapkal, V.S. and Jamode, S. (2004) *J. Indian Inst. Sci.*, **84**, 163.

21. Bajpai, S.K. (2001) *Sep. Sci. Technol.*, **36**(3), 399.

22. Unnithan, M.R., Vinod, V.P. and Anirudhan, T.S. (2002) *J. Appl. Polym. Sci.*, **84**, 2541.

23. Igwe, J.C., Nwokernaya, E.C. and Abia, A.A. (2005) *African J. Biotechnology*, **4**(10), 1109.

24. Guclu, G., Kele, S. and Guclu, K. (2006) *Polymer-Plast. Techn. Engg.*, **45**(1), 55−59.

25. Sen, M., Yakar, A. and Guven, O. (1999) *Polymer*, **40**, 2969.

26. Bajpai, S.K. and Sonkusley, J. (2001) *J. Macromol. Sci. Pure Appl. Chem.*, **A38**(4), 365.

27. Rhazi, M., Desbrieres, J., Tolaimate, A., Rinaudo, M., Vottero, P. and Alagui, A. (2002) *Polymer*, **43**, 1267−1276.