

Binary Biopolymeric Beads of Alginate and Gelatin as Potential Adsorbent for Removal of Toxic Ni²⁺ Ions: A Dynamic and Equilibrium Study

Jaya Bajpai, Ruma Shrivastava, A. K. Bajpai

Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur 482 001, Madhya Pradesh, India

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ABSTRACT: Binary biopolymeric beads of alginate and gelatin were prepared and characterized by IR spectral and scanning electron micrograph techniques. On to the surfaces of the prepared beads were performed static and dynamic adsorption studies of Ni²⁺ ions at fixed pH and ionic strength of the aqueous metal ion solutions. The adsorption data were applied to Langmuir and Freundlich isotherm equations and various static parameters were calculated. The dynamic nature of adsorption was quantified in terms of several kinetic constants such as rate constants for adsorption (k_1), Lagergreen rate constant (k_{ad}),

interparticle diffusion rate constant (k_p), and pore diffusion coefficient (\bar{D}). The influence of various experimental parameters such as solid to liquid ratio, pH, temperature, presence of salts, and chemical composition of biopolymeric beads on the adsorption of nickel ions was investigated. Various thermodynamic parameters were also calculated. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2581–2590, 2007

Key words: nickel(II); adsorption; kinetics; alginate; gelatin; beads

INTRODUCTION

Metal ions are nonbiodegradable in nature, and their intake at a certain level are toxic.¹ Environmental contamination with heavy metal ions is of growing public concern because of health risks posed by human and animal exposure. The separation of metal ions, present as contaminants in water, is complicated because of the number of variables that must be considered, including the solution composition, salinity, pH, temperature, and the presence of organic substances. It is well known that heavy metal ions, which are toxic to most organisms, have found their way into the water system from different processes.² Therefore, there is great interest in recovering metal ions for both environmental and economic reasons.^{3,4}

A serious problem encountered in the removal of the metal ions is that the target species are usually in low concentration and in complex mixtures. Attempts to solve problems of removal of heavy metal ions have led to the development and application of several techniques such as precipitation, adsorption, extraction, and sorption or ion exchange.^{5–7} With respect to the low concentrations and handling of large volumes of

aqueous solution, extraction procedures are not economical, and precipitation procedures require the addition of relatively large amounts of chemicals, whereas applications of sorption or exchange on solids are preferable.⁸ This makes the use of exchangers for selective separation of heavy metal ions very attractive. The ion-exchange resins contain functional groups where the metal ions are covalently bound to an insoluble polymer, and hence, there is no loss of extractant into the aqueous phase.

One of the most widely studied biopolymers are polysaccharide-based biosorbents such as alginate, which have binding sites for divalent cations because of the presence of amino, carboxyl, phosphate, and sulfate functional groups within them.^{9,10} Alginate is a linear polyurinate obtained from marine algae and contains variable amounts of D-manuronic acid and L-guluronic acid, which can be crosslinked by using calcium ion. Other biopolymeric moieties capable of interacting with metal ions are proteins, which because of nitrogen atoms of the imidazole group of the histidine residue and the sulfur atom of the sulfhydryl group of the fine cysteine residue are potential adsorbent for metal ions.^{11–13}

Thus, the present work aims at investigating the removal of Ni(II) ions from aqueous solutions by adsorption onto a binary biopolymeric matrix composed of crosslinked sodium alginate and crosslinked gelatin in the form of spherical beads.

Correspondence to: A. K. Bajpai (akbmr1@yahoo.co.in).

EXPERIMENTAL

Materials

Sodium alginate was obtained from Loba Chemie, Mumbai, India and used as received. Gelatin (acid-processed) was purchased from Loba Chemie, India and used without further treatment. Other chemicals used, such as nickel sulfate (adsorbate), calcium chloride (crosslinking agent for alginate), glutaraldehyde (crosslinking agent for gelatin), etc., were of high purity grade. Triple distilled water was used throughout the experiments.

Methods

Preparation of binary biopolymeric beads

Biopolymeric beads employed as adsorbent were prepared in two steps. In the first step, a known solution of mixture of sodium alginate (4.0 g) and gelatin (1.0 g) was added dropwise into a 0.05M CaCl₂ solution with the help of a syringe and under constant stirring. The beads so produced were of almost identical spherical dimensions and allowed to harden by leaving them in CaCl₂ solution for 24 h and thereafter filtered and washed thrice with triple distilled water. The washed beads were further placed in a glutaraldehyde bath overnight and then filtered carefully and washed three times with triple distilled water. These binary biopolymeric beads were stored in triple distilled water at room temperature and used as such. A photograph of both dry and swollen biopolymeric beads is shown in Figure 1.

Scanning electron microscope

Morphological features of the prepared biopolymeric beads were studied by scanning electron micrograph technique (STEREO SCAN, 430, Leica SEM, USA).

Adsorption experiments

The adsorption was carried out by the contact method as described in our other communications.¹⁴⁻¹⁶ In brief, firstly the standard nickel sulfate stock solution was prepared by dissolving 0.448 g NiSO₄·6H₂O in 1 L dis-

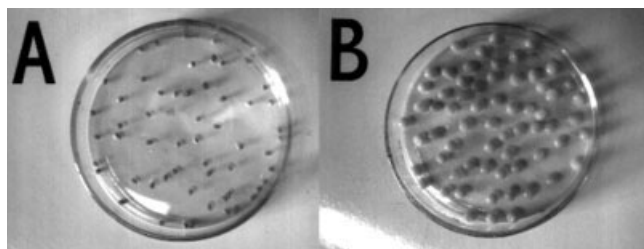


Figure 1 Photograph depicting dry and swollen binary biopolymeric beads of alginate and gelatin.

tilled water. Into 20 mL of diluted stock solution (1 : 1 v/v) were added 0.2 g of swollen biopolymeric beads at constant pH 8.0 and ionic strength (0.001M KNO₃). The suspension was shaken in a rotary shaker (Tempstar, India) for 2 h, which was found to be a sufficient time to attain equilibrium adsorption. After shaking, 1 mL of supernatant was taken and into this was added a reagent (200 mL distilled water, 25 mL 1N HCl, 5 mL bromine water, 10 mL conc. NH₄OH, 20 mL DMG, and 20 mL ethyl alcohol). The amount of nickel present in the colored solution was assayed spectrophotometrically.¹⁷ The amount of adsorbed Ni(II) was calculated by the following mass balance equation:

$$\text{Adsorbed amount (mg g}^{-1}\text{)} = \frac{(C_i - C_f)V}{m} \quad (1)$$

where C_i and C_f being the initial and final concentrations of NiSO₄ solution (mg mL⁻¹), V being the volume of adsorbate solution, and m is the weight of swollen beads, i.e., adsorbent.

Kinetics of adsorption

For monitoring the progress of the adsorption process, several adsorption experiments were run under identical conditions and amount of adsorbed Ni(II) was determined in each set one by one at different time intervals.

Zeta potential measurements

As the biopolymeric beads are made up of polyelectrolyte biomolecules, the surface charge vary with pH of the immersion medium. The surface charge were measured by suspending 0.2 g of swollen beads into aqueous medium of varying pH and measuring the surface charge by a pH/E.M.F. meter (Systronics μ pH system 362).

IR spectra

The IR spectra of unadsorbed (bare) and Ni(II)-adsorbed biopolymeric beads were recorded on a Perkin-Elmer spectrophotometer (FTIR Paragon, 1000).

RESULTS AND DISCUSSION

Characterization of beads

The prepared beads have been characterized by the following techniques.

IR spectra

The IR spectra of bare and Ni²⁺ ion-adsorbed beads are shown in Figure 2(a, b), respectively. The spectra not only provide clear evidences of presence of alginate and gelatin in the beads but also suggests for binding

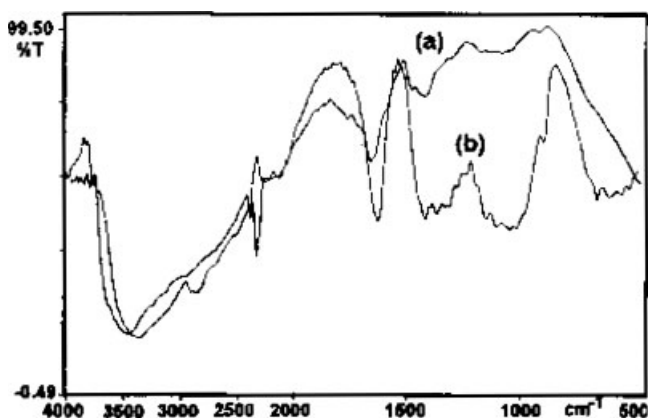


Figure 2 IR spectra of biopolymeric beads (a) without adsorption and (b) with adsorption.

of Ni^{2+} ions to the carboxylate ions of alginate and gelatin in the adsorbent beads. The spectra clearly mark the presence of alginate as confirmed by the O—H stretching of hydroxyls at 3426 cm^{-1} , C—O stretching of alcoholic OH at 1058 cm^{-1} , and C—O stretching of carboxylic acid at 1402 cm^{-1} . The spectra also present a strong asymmetrical stretching band at 1651 cm^{-1} due to carboxylate anion of both alginate and gelatin. The presence of gelatin is well confirmed by NH_3^+ stretching band at 2377 cm^{-1} .

A close examination of spectra (b) reveals a slight shift of carboxylate anion band from 1651 to 1637 cm^{-1} , which could be assigned to the electrostatic binding of Ni^{2+} ions to anionic sites. Similarly, two bands arising from C—O stretching and O—H bending appearing in the spectra (b) at 1427 and 1377 cm^{-1} clearly indicate the presence of some undissociated COOH groups in the beads. The spectra also mark the presence of methylene groups at 2906 cm^{-1} due to C—H stretching.

SEM analysis

The scanning electron micrograph (SEM) image of the blend surface is shown in Figure 3, which reveals that there is no phase separation between the alginate and the gelatin, thus indicating a homogeneous blending of the two natural polymers. The SEM image, however, indicates a heterogeneous nature of the surface as evident from the uneven morphology of the blend surface. This unevenness of the surface could be due to great structural dissimilarities between the alginate and the gelatin.

Concentration effect and adsorption isotherm

When the concentration of nickel sulfate solution is raised in the range of 0.0095 – $0.342\text{ (mg mL}^{-1}\text{)}$, the amount of adsorbed Ni^{2+} ions is found to increase. The observed increase is quite obvious, as on increasing the concentration of solute, greater number of metal

ions arrive at the swollen bead–solution interface and thus get adsorbed. This is a common finding and has been largely reported in the literature.¹⁸ However, for a better understanding of the metal ion–polymeric beads interaction, it is genuine to construct an adsorption isotherm, which is normally done by plotting the adsorbed amount of Ni^{2+} ions versus the equilibrium concentration of the metal ion solution. The following adsorption isotherms can be considered:

Langmuir isotherm

The Langmuir equation was basically derived for the sorption of gases on a solid surface. Nevertheless, it has been extended to include the sorption of solute at solid–liquid interface. A standard mathematical representation of linearized Langmuir equation is

$$\frac{C_e}{a} = \frac{1}{a_s k} + \frac{C_e}{a_s} \quad (2)$$

where a is the adsorbed amount of Ni^{2+} ions (mg g^{-1}) at any equilibrium concentration C_e , a_s is the adsorbed amount of metal ions at saturation (adsorption capacity), and k is the adsorption coefficient, i.e., equal to k_1/k_2 , where k_1 and k_2 are the rate constants for the adsorption and desorption, respectively.

In the present study, the typical Langmuir isotherm is shown in Figure 4, which clearly implies that the adsorption isotherm belongs to L2 type, which is one of the forms of Langmuir isotherms. It is also revealed that the adsorbed amount of Ni^{2+} increases with increasing concentration of the NiSO_4 solution and ultimately levels off indicating a saturation in the

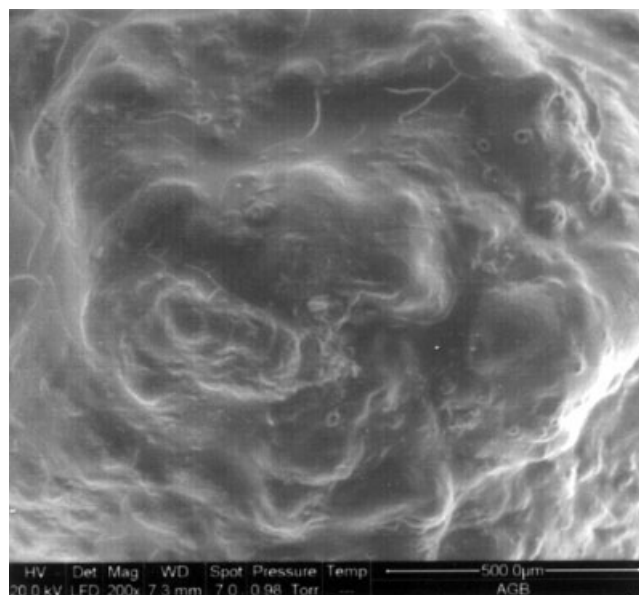


Figure 3 Scanning electron micrograph (SEM) image of biopolymeric bead.

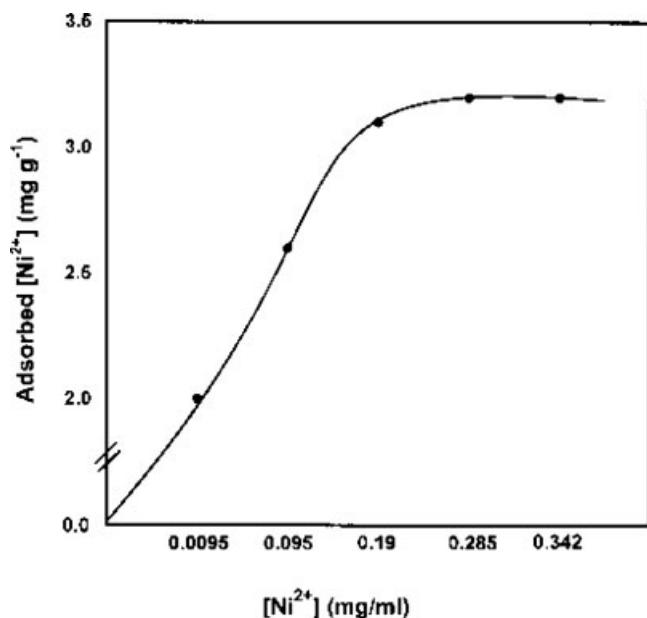


Figure 4 Langmuir adsorption isotherm drawn between adsorbed amount of Ni^{2+} ions and equilibrium concentration of nickel sulfate solution showing the adsorption of Ni^{2+} onto biopolymeric beads of definite composition; [alginate] = 4.0 g, [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [gluteraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

adsorbed amount. Similar types of isotherms have also been reported elsewhere.¹⁹ The values of k and a_s determined from eq. (2) are summarized in Table I, which clearly suggest for a favorable adsorption of Ni^{2+} ions.

Another essential characteristics of Langmuir isotherm equation can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is equal to $1/(1+KC_0)$, where K is the adsorption coefficient and C_0 is the initial metal ion concentration.²⁰ R_L value obtained in the present case is given in Table I, which is less than 1 and, therefore, indicates a favorable adsorption.²¹

Freundlich isotherm

The Freundlich isotherm equation has the following form

$$a = K_F C_e^{1/n} \quad (3)$$

or

$$\ln a = \ln K_F + (1/n) \ln C_e \quad (4)$$

where a is the adsorbed amount of Ni^{2+} ions, K_F is the predicted quantity of sorption per gram of the biopolymeric beads at unit equilibrium concentration of metal ion solution, and $1/n$ is the measure of the nature and strength of the adsorption process and the distribution of active sites. If $1/n < 1$, the bond

energies increase with the surface density; if $1/n > 1$, the bond energies decrease with the surface density; and when $n = 1$, all surface sites are equivalent.²² Alternatively, it has been shown using mathematical calculation that n values between 1 and 10 represent beneficial adsorption.²³ The sorption equation obtained in the present case may be written as

$$a = 46.9 C_e^{0.20} \quad (5)$$

The above equation can be used to determine the volume of effluent solution that could be treated for the removal of toxic metal ions.

Modified Freundlich isotherm

The biopolymeric beads are multi-functional in nature and, therefore, may be considered responsible to cause the adsorption process heterogeneous, i.e., not mono energetic.²⁴ Thus, the following modified Freundlich equation, originally deduced by Sposito²⁵ using statistical mechanics, may also be applied in the present case:

$$\log \frac{a}{(a_s - a)} = \beta \log C_e + \log \frac{A}{a_s} \quad (6)$$

where the terms involved have their own significance as mentioned in the preceding para, and β and A are empirical constants, which can be determined through linear regression analysis. These empirical constants provide a means for visualizing the general sorption process relative to the distribution of sorptive energies by the exchange surfaces.

In accordance with eq. (6), a plot was drawn (not shown) and the values of β and A were calculated and are summarized in Table I. It is clear from the numerical values of β and A that the distribution of the Ni^{2+} ions is not even over the active sites of the beads surfaces; rather, it is widely spread, thus indicating the heterogeneity of the beads surface.

TABLE I
Static and Kinetic Parameters for Adsorption of Ni^{2+} Ions on to Biopolymeric Beads

Parameter	Value
Adsorption coefficient (K)	$2 \times 10^3 \text{ mg}^{-1} \text{ dm}^3$
Adsorption capacity (a_s)	$5 \times 10^{-3} \text{ mg g}^{-1}$
Separation factor (R_L)	(0.161–0.877)
Predicted sorption (K_F)	$46.9 \text{ (mg g}^{-1}\text{)}$
Freundlich constant (n)	5.0
β	0.79
A	3.30
Rate constant for adsorption (K_1)	$9.25 \times 10^{-5} \text{ s}^{-1}$
Rate constant for desorption (K_2)	$4.62 \times 10^{-8} \text{ (mg dm}^{-3} \text{ s}^{-1}\text{)}$
Lagergreen rate constant (K_{ad})	$4.33 \times 10^{-4} \text{ (mg g}^{-1} \text{ s}^{-1}\text{)}$
Interparticle diffusion rate constant	$9 \times 10^{-3} \text{ (mg g}^{-1} \text{ s}^{-1/2}\text{)}$
Pore diffusion constant (D)	$3.0 \times 10^{-7} \text{ (cm}^2 \text{ s}^{-1}\text{)}$

Adsorption kinetics

The progress of the adsorption process monitored at different time intervals is shown in Figure 5, which clearly reveals that the adsorbed amount of Ni²⁺ ions constantly increases with increasing time and then levels off after 3 h. It is also notable that the rate of adsorption is almost constant up to 2 h and then it slows down. Thus, in the existing framework, the following kinetic scheme proposed by Bajpai and Bajpai²⁶ may be applied to evaluate the rate constant for adsorption:

$$\frac{1}{C} = k_1 \frac{t}{C_0} + \frac{1}{C_0} \quad (7)$$

where C and C_0 are the concentrations of metal ion solution at any time t and at zero time (i.e., initial concentration) and k_1 is the rate constant for adsorption. Obviously, from the plot drawn between $1/C$ and t , the value of k_1 may be calculated as summarized in Table I. Once K and k_1 values are known, the value of k_2 (rate constant for desorption) may also be calculated. It is to be noted here that the constant k has been determined from the linearized Langmuir equation.

The dynamics of the sorption of Ni²⁺ may also be quantified in terms of the Lagergreen²⁷ equation as given below

$$\log(a_s - a) = \log a_s - \frac{k_{ad}}{2.303} t \quad (8)$$

where the terms involved have their own significance and k_{ad} is the Lagergreen rate constant for

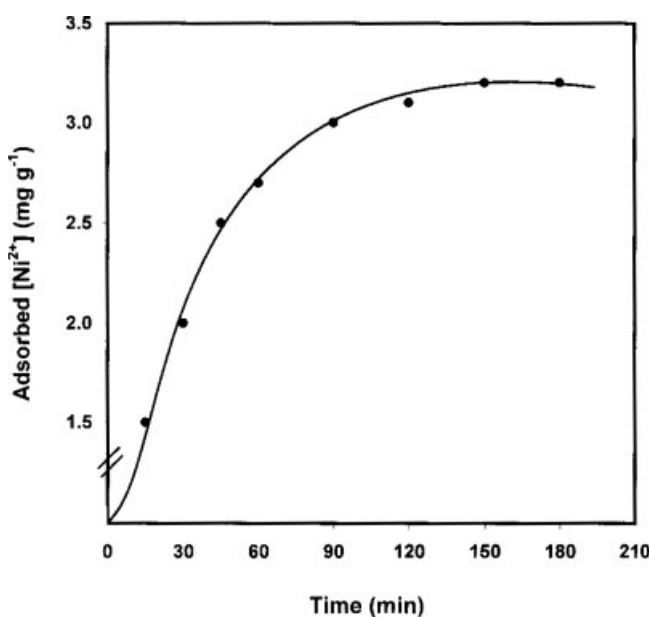


Figure 5 Variation in the adsorbed amount of Ni²⁺ ions with time for fixed composition of beads; [alginate] = 4.0 g, [gelatin] = 1.0 g, [CaCl₂] = 0.05M, [gluteraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, [KNO₃] = 0.001M, Temperature = (35 ± 0.2)°C.

adsorption. The calculated value of k_{ad} is also given in Table I.

The adsorbed amount versus time data can be used to study the rate-limiting step in the adsorption process as shown elsewhere.²⁸ Since the biopolymeric beads are constantly agitated during the adsorption process, it is probably reasonable to assume that the rate is not limited by mass transfer from the bulk liquid to the bead's external surface. One might then postulate that the rate-limiting step may either be film or interparticle diffusion. As they act one after the other, the slower of the two will be the rate-determining step. The rate constant for intraparticle diffusion is obtained using the equation

$$a = K_p t^{1/2} \quad (9)$$

where K_p is the intraparticle diffusion rate constant. The value of K_p determined from the plot drawn between a and $t^{1/2}$ is summarized in Table I.

The pore diffusion coefficient for the intraparticle transport of Ni(II) was calculated assuming spherical geometry of the bead using the following equation²⁹

$$t_{1/2} = \frac{0.03 r_o^2}{\bar{D}} \quad (10)$$

where r_o is the radius of the dry unadsorbed bead, \bar{D} is the pore diffusion constant, and $t_{1/2}$ is the time for half sorption. The calculated value of \bar{D} is given in Table I.

Factors affecting adsorption

Solid to liquid ratio

The solid to liquid ratio in an adsorption systems exerts a great effect on the amount of adsorbed solute. A change in solid to liquid ratio not only changes the number of active sites available on the solid but also brings about a change in the number of ions of the solute invading the solid surface for adsorption. In the present study, the solid to liquid ratio has been varied in the range of 0.05–0.30 (g mL⁻¹) and the respective results are shown in Figure 6, which clearly reveals that the amount of adsorbed Ni²⁺ ions decreases with increasing solid to liquid ratio. The results may be explained on the basis of the fact that due to the increasing amount of solid (beads) in the adsorption system, their larger surfaces remain inaccessible to the adsorbing Ni²⁺ ions, thus lowering the amount of adsorbed Ni²⁺ ions. Similar type of results have been published elsewhere.²⁹

Effect of pH

Effect of pH in adsorption investigations where a charged ion adsorbs on a charged surface has cre-

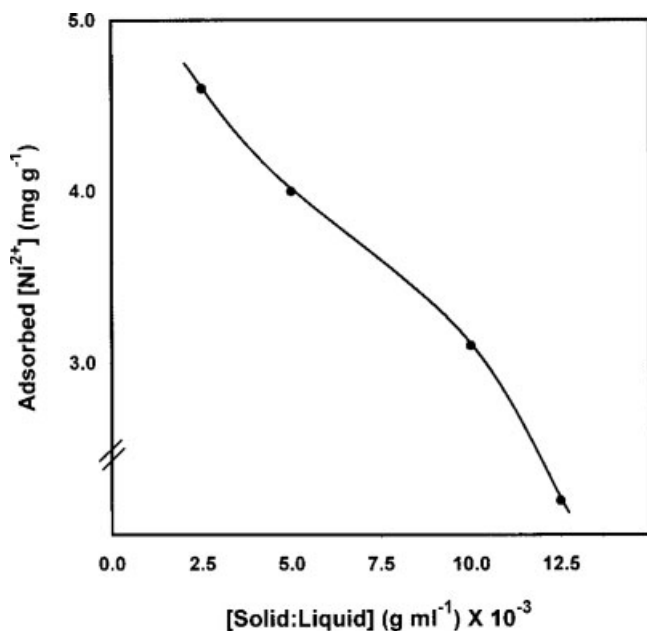


Figure 6 Effect of solid to liquid ratio on the adsorption of Ni^{2+} onto biopolymeric beads of alginate and gelatin of definite composition; [alginate] = 4.0 g, [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [gluteraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

ated much interest in recent past, not only because of the chemistry involved but also due to the practical utility of the subject. The pH of the solution is one of the prime factors that drastically influence the adsorption behavior of a system. In the present case, the role of pH is much prominent as a variation in pH of the solution differently alters the charged profile of both the adsorbate ions and adsorbent beads, respectively. In this study, gelatin (Type A) has been employed as one of the components of the bead, which is well known for exhibiting varying charge over its macromolecules with changing pH of the solution. In this way, a change in pH must also bring about a change in the type and extent of effective charge over the gelatin molecule. Realizing the above point, we have measured surface charge of the prepared beads at various pH of the solutions and data are summarized in Table II. It is clear from the table that as the pH of solution increases, there is a reduction in positive potential over the beads, which ultimately attains a large negative value (-212 mV) at a higher pH of 11.3.

The effect of pH on the adsorbed amount of Ni^{2+} ions have been investigated in the range of 2.0–12.0. The results are shown in Figure 7 that clearly reveals that the adsorption initially increases with increasing pH and becomes optimum at pH 8.0. However, upon further increasing the pH beyond 8.0, a fall in adsorption is noticed. The results may be explained as below

TABLE II
Variation of Surface Potential (mV) of the Biopolymeric Beads with pH of the Solution

pH	E.M.F. (mV)
1.87	262
4.89	140
5.10	100
11.33	-212

- i. At very low pH, i.e., when the suspension is highly acidic in nature, biopolymeric beads possess a high positive potential, which is well evident from Table II. This positive charge results from the prominence of positively charged groups such as $-\text{NH}^+$, $-\text{NH}_3^+$, etc. due to gelatin over the negatively charged groups such as carboxyl, sulfate, and phosphate due to both gelatin and alginate macromolecules. In this situation, the negatively charged sites may be mostly occupied by H^+ ions via electrostatic attraction in comparison to Ni^{2+} ions. Thus, resulting in a lower adsorption of Ni^{2+} ions.
- ii. However, as the pH of the solution is increased in the acidic range, the positive charge significantly decreases as presented in Table II. This, in other way, indicates for increasing negative charge over the biopolymeric beads. Thus, in the existing experimental conditions, less number of H^+ ions adsorb onto ionic sites, while more number of Ni^{2+} ions adsorb favorably onto the nega-

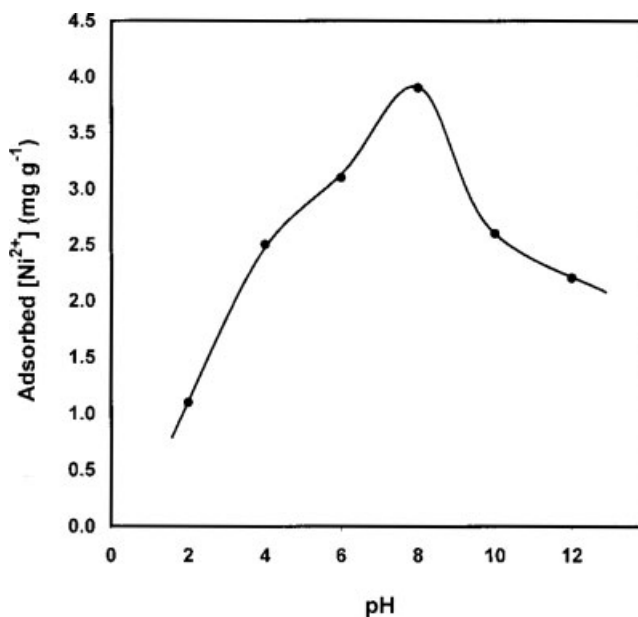


Figure 7 Effect of pH on the adsorption of Ni^{2+} onto biopolymeric beads of alginate and gelatin of definite composition; [alginate] = 4.0 g, [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [gluteraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

tively charged sites. This increase continues up to pH 8.0, which is quite near to the isoelectric point of the gelatin. At this pH, the biopolymer molecules acquires a net zero charge and consequently offers minimum resistance to the invading Ni^{2+} ions. This obviously explains the optimum adsorption at pH 8.0

- iii. However, on increasing the pH in the alkaline range, a fall in adsorbed amount of Ni^{2+} ions is noticed. The observed decrease in adsorption may be attributed to the reason that in alkaline medium Ni^{2+} ions get hydrolyzed forming $\text{Ni}(\text{OH})_2$ species and thus less number of Ni^{2+} ions will be available for adsorption. This, obviously, results in a lower adsorption at alkaline pH.

Effect of salts

Inorganic salts play a key role in influencing the adsorption on charged surfaces as their presence in the system exerts multiple effects on adsorbate-adsorbent interaction. In a system containing a macromolecule and charged surfaces, the ions present can either bind to the macromolecular functional groups, adsorb preferentially on the surface, or cause screening of coulombic potential produced due to macro ion and charged surfaces.

Addition of inorganic salts to the adsorption system is an effective way of influencing adsorption. The situation becomes much more significant when both the adsorbate and adsorbent are charged bodies. In fact, added salts affect adsorption via two mechanisms, (i) either by screening the coulombic potential between the adsorbing ion and the charged adsorbents, or (ii) by adsorbing preferentially on the active sites of the adsorbent.

In the present study, the effect of salts on adsorbed amount of Ni^{2+} ions has been investigated in two ways. In the first experiment, KCl was added to nickel sulfate solution in the concentration range of 0.005–0.1M and the results are shown in Figure 8, which reveals that the adsorbed amount of Ni^{2+} ions constantly decreases with increasing concentration of added salt. The results may be explained by the fact that increased ionic strength of the medium results in an enhanced electrostatic repulsion between the nickel ions and added ions as well as with fixed ionic centers lying along the constituents polymer molecules of the biopolymeric beads. This obviously results in a fall in the adsorbed amount of nickel ions. It is also likely that the added ions get preferably adsorbed onto the biopolymeric beads and thus exhaust available active sites. This will also lower the adsorbed amount of Ni^{2+} ions. Similar types of results have also been obtained elsewhere.³⁰

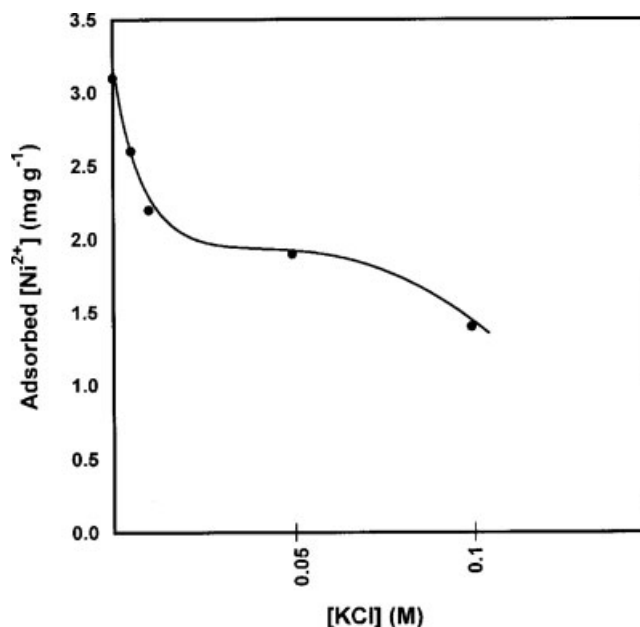


Figure 8 Effect of addition of salts on the adsorption of Ni^{2+} ions onto biopolymeric beads of alginate and gelatin of definite composition; [alginate] = 4.0 g, [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [gluteraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

Specific ion effect

The effect of various halide ions on the adsorbed amount of Ni^{2+} ions has been observed by adding 0.1M concentration of potassium salts of halides. The results have been expressed as variation in the adsorbed amount of metal ion with radii of the added ions as shown in Figure 9. It is clearly indicated by the Figure 9 that the adsorption of Ni^{2+} ions decreases with increasing radii of the added ions and the added halide ions obey the following increasing order of effectiveness: $\text{Cl}^- < \text{Br}^- < \text{I}^-$

The observed decrease in adsorption of Ni^{2+} ions may probably be attributed to the fact that the added anions may form complex species with the Ni^{2+} ions, thus, preventing them to become available for adsorption. In the case of a larger anion, its greater size can hinder the excess of complex anion to the pores of the adsorbent, which may result in a fall in the adsorbed amount. Moreover, due to negatively charged potential of biopolymers, they show a small tendency to adsorb the anions, which have been complexed to Ni^{2+} ions.

Effect of temperature

The effect of temperature on adsorption of Ni^{2+} ions has been studied by performing adsorption experiments in the temperature range of 5–50°C. The results are shown in Figure 10, which clearly indicates that the adsorption increases in the temperature range of 5–35°C, while beyond 35°C, a sudden

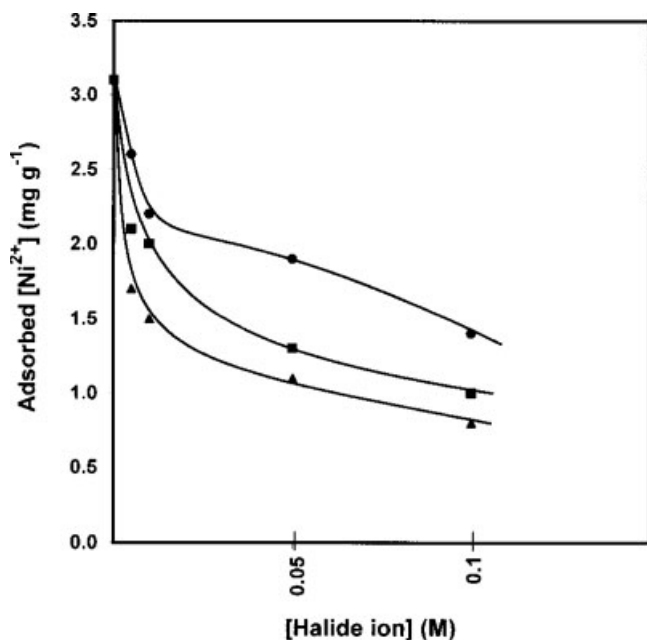


Figure 9 Effect of addition of halide ions on the adsorption of Ni^{2+} ions onto biopolymeric beads of alginate and gelatin of definite composition; [alginate] = 4.0 g, [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [gluteraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

fall in adsorption is noticed. The observed increase in adsorption may be attributed to the fact that with increasing temperature, greater number of active sites may be generated on the biopolymeric beads because of enhanced rate of protonation/deprotonation of functional groups on the beads. This will clearly bring about an increase in the adsorption of Ni^{2+} ions. Increased adsorption at higher temperature also suggests for the possibility of formation of some coordinate type of bond between the nickel atom and electron-rich donor atoms of the adsorbent beads.

The observed decrease in the adsorption of Ni^{2+} ions at much higher temperature ($> 35^\circ\text{C}$) could be attributed to the weakening of the binding forces between the nickel ions and active sites on the biopolymeric beads. The decrease observed may also be attributed to the reason that at higher temperature, the viscosity of the metal ion solution decreases due to which the transport of metal ions from the internal force of the adsorbent into the bulk solution is facilitated. This obviously brings about a fall in the adsorbed amount.

Several thermodynamic parameters³¹ have also been evaluated as follows:

- i. The standard free energy, ΔG^0 (kcal mol^{-1}) was calculated using the equation

$$\Delta G^0 = -RT \ln K \quad (11)$$

where K is the adsorption coefficient. Here ΔG^0 was calculated to be -7.60 kJ. A negative value of ΔG^0 clearly suggests for a spontaneous process, which is obviously desirable for the removal of toxic metal ions by adsorption. The observed lower value of ΔG also implies that there is an electrostatic type of attraction between the adsorbing Ni^{2+} ions and charged active sites of the biopolymeric adsorbent. This also suggests for a physical adsorption.

- ii. The apparent heat of reaction ΔH (kcal mol^{-1}) was estimated by using the equation

$$\ln \frac{k_2}{k_1} = \frac{\Delta H^0}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (12)$$

and has been calculated to be 60.19 kJ mol^{-1} , which implies that the process is endothermic in nature.

- iii. The entropy change, ΔS^0 of the adsorption process was calculated by the equation

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (13)$$

and the value was found to be 0.225 $\text{kJ deg}^{-1} \text{mol}^{-1}$.

The observed positive value of ΔS shows that the freedom of metal ions is not too restricted in the biopolymer, confirming a physical type of adsorption, which has also been supported by lower value of ΔG^0 .

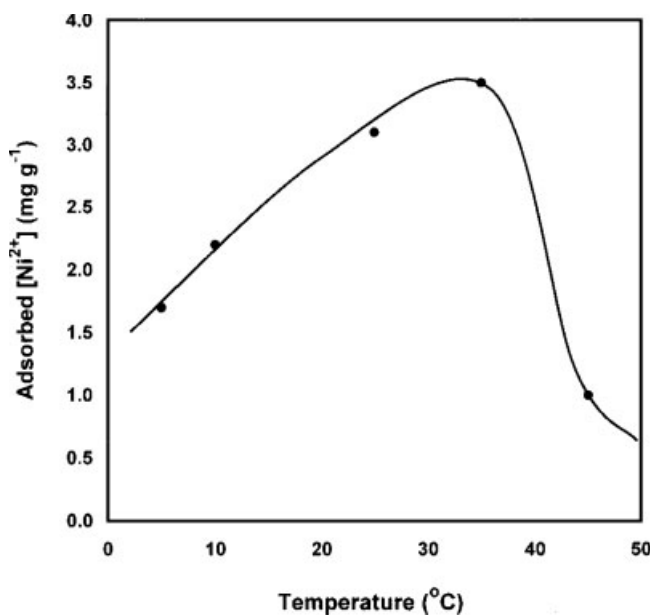


Figure 10 Influence of temperature on the adsorption of Ni^{2+} ions onto biopolymeric beads of alginate and gelatin of definite composition; [alginate] = 4.0 g, [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [gluteraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M.

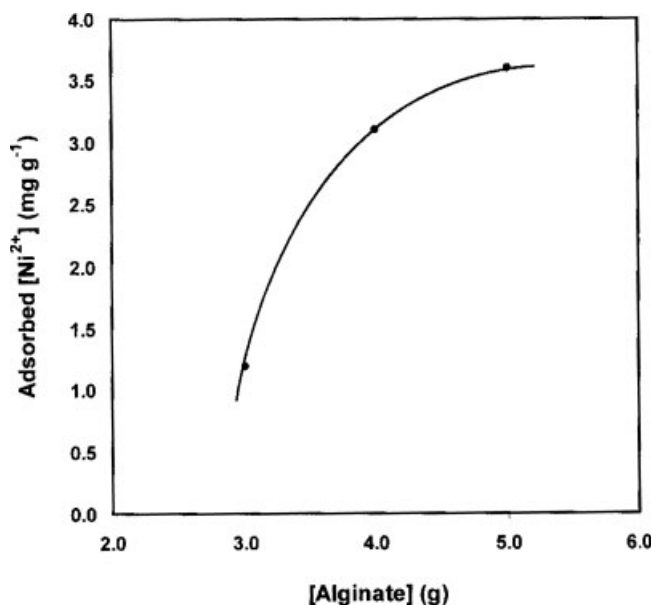


Figure 11 Effect of alginate content of the beads on the adsorption of Ni^{2+} ions; [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [glutaraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

Effect of beads composition

The chemical composition of biopolymeric beads might have a significant effect on the adsorption of nickel ions, because upon variation in the amount of biopolymeric components in the beads, the number and nature of the active sites will be largely affected which, in turn, will influence adsorption.

When alginate is varied in the range of 3–5 g in the feed mixture of the beads, an increase is observed in the adsorbed amount of Ni^{2+} ions as shown in Figure 11. The results may be explained by the fact that with increasing concentration of alginate, the number of active sites on the beads increases, which obviously results in an increased adsorption. It is worth mentioning here that below 3 g of alginate, no beads formation could be noticed.

In the case of gelatin, the amount was varied in the range of 0.5–2.0 g in the feed mixture of beads and the results are shown in Figure 12, which reveals that the adsorption of Ni^{2+} increases with increasing gelatin concentration up to 1.0 g, a further increase in gelatin results in a significant fall in adsorption. The observed increase in the initial range may be due to the fact that with increasing gelatin, the number of active sites on biopolymeric beads also increase and consequently the adsorption increases. However, beyond 1.0 g of gelatin concentration, the decrease obtained may be due to the reason that at much higher concentration of gelatin, the beads become morphologically compact and as a result diffusion of nickel ions may be hindered. This clearly lowers the adsorbed amount of Ni^{2+} ions. When the concentra-

tion of glutaraldehyde solution (crosslinker of gelatin) increases in the range of 25–100%, the amount of adsorbed Ni^{2+} ions is found to increase constantly in the studied range as shown in Figure 13. The observed increase may be due to reason that because of increasing degree of crosslinking of beads, their size gets smaller and this results in an increase in external as well as internal surface area of biopolymeric beads. This clearly results in increasing adsorption.

CONCLUSIONS

Biopolymeric beads composed of crosslinked sodium alginate and crosslinked gelatin prove to be an effective adsorbent for removal of nickel ions from their aqueous solutions. The adsorption of nickel ions follows Langmuir equation with adsorption coefficient (K) equal to $2 \times 10^3 \text{ mg}^{-1} \text{ dm}^3$, which clearly suggests for a much greatly favored adsorption process. The adsorption attains isoelectric point of gelatin (acid-processed). Presence of electrolytes such as halides of nickel results in a fall in the adsorption of Ni^{2+} ions and a decrease is observed with increasing radii of the added halide ions. Temperature also has a favorable effect on adsorption when varied in the range of 10–50°C. While beyond 35°C, a decrease in adsorption is noticed. Thermodynamic parameters suggest for endothermic nature of the adsorption process.

Chemical composition of beads greatly influences the adsorption capacity of beads. It is found that the adsorption of Ni(II) increases with increasing

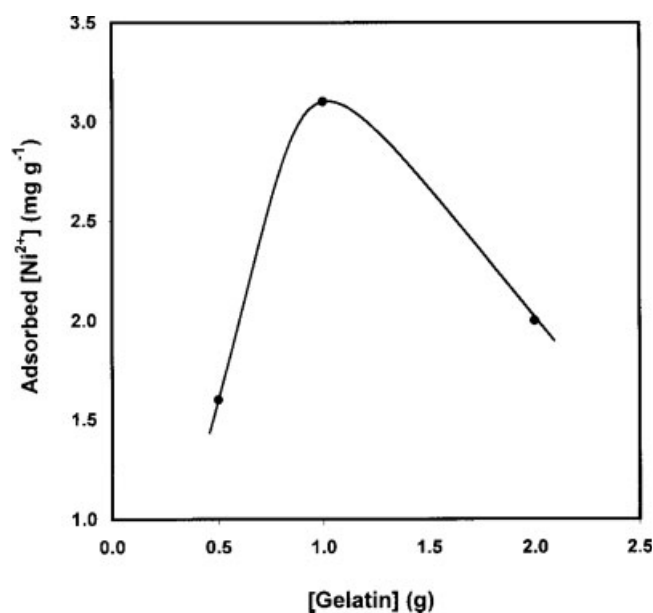


Figure 12 Effect of gelatin content of the beads on the adsorption of Ni^{2+} ions; [alginate] = 4.0 g, $[\text{CaCl}_2]$ = 0.05M, [glutaraldehyde] = 100% (v/v), [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

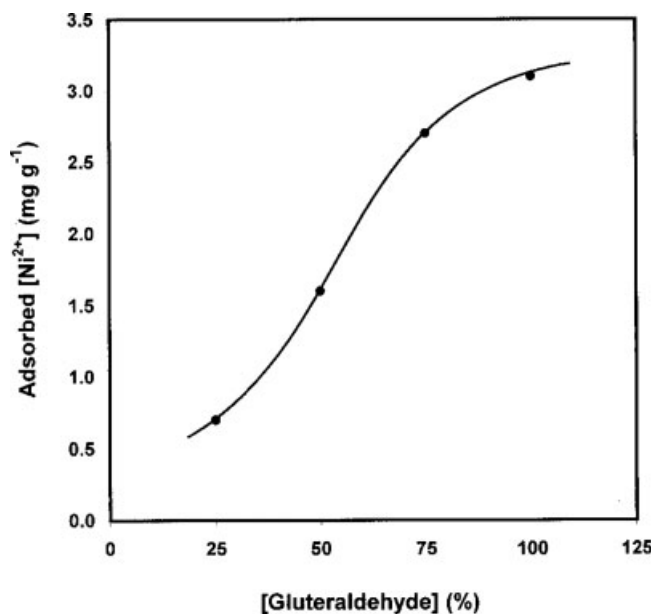


Figure 13 Influence of crosslinker (glutaraldehyde) content of the beads on the adsorption of Ni^{2+} ions; [alginate] = 4.0 g, [gelatin] = 1.0 g, $[\text{CaCl}_2]$ = 0.05M, [beads] = 0.2 g, pH = 8.0, $[\text{KNO}_3]$ = 0.001M, Temperature = $(35 \pm 0.2)^\circ\text{C}$.

concentrations of sodium alginate, gelatin, and glutaraldehyde. In the case of gelatin, however, a lower adsorption is noted at higher concentration.

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