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Selective Separation of Thiocyanate Ion by Ion-Imprinted Polymer

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Abstract

Molecular imprinting is a emerging technology to create recognition sites in a polymeric matrix using a molecular template. The molecularly imprinted polymers (MIPs) are easy to prepare, stable, inexpensive and capable of molecular recognition. This manuscript describes a method for the selective binding behavior of SCN^- ions on surface imprinted polymers which were prepared using chitosan succinate-Zn(II) complex. This polymer was prepared in the presence of epichlorohydrin and was imprinted with SCN^- ions. After that, the template (SCN^- ions) was removed using 1 M KOH solution. Selective cavities for the SCN^- ions was obtained in the SCN^--imprinted chitosan-succinate beads. The effect of initial concentration of SCN^- ions, adsorption time and imprinting efficiency on adsorption selectivity for SCN^--imprinted polymer were investigated. The adsorption process was fast and equilibrium was reached at around 30 min. Maximum adsorption capacity was found to be 95 mg g^{-1}. The number of accessible binding sites (Q_{max}), relative selectivity coefficient (k') and binding ability were also evaluated. The observed adsorption order under competitive conditions was $SCN^- > F^- > Cl^- > PO_4^{3-}$ in mass basis.

INTRODUCTION

Thiocyanate (SCN^-) presents as a normal constituent in mammalian tissues and body fluids [1]. It also present in industrial wastewaters, pesticides residues and organism metabolites. Since thiocyanate is end product of detoxification of hydrogen cyanide included in cigarette smoke, its extraction in urine and human serum saliva can provide a useful probe for distinguishing between smokers and non-smokers [2]. If the content of thiocyanate is a little higher in the body than normal, the protein dialysis will be affected and it may even result in coma. Therefore, the determination of thiocyanate at low levels especially in food, biological and water samples is important [3].

Several methods have been developed for the determination of thiocyanate. These include application of spectrophotometry [4-6], spectrofluorimetry [7,8], amperometry [9-12], polarography [13], chromatography [14-16] and ion selective electrodes [17,18] for the determination of thiocyanate. However, some of these techniques are with high detection limits [19-24], of intricate chemometric treatments to analytical signals [6], which require toxic reagents [13], etc. It is essential to look for a new method with high sensitivity, simplicity and efficiency for the detection of thiocyanate.

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Molecular imprinting technology provides a promising alternative way to design artificial recognition sites within a synthetic polymer network via the template polymerization process. In this process, polymerizable functional monomers are pre-arranged around a template molecule in porogenic solvent. The resulting pre-polymer complexes are copolymerized with an excess of cross-linking monomer in the presence of a free radical initiator under thermal or photochemical conditions. After the removal of the template by extraction, binding sites complementary to the template molecule both in shape and chemical functionality are left within the polymer matrices that allow rebinding of the template with high specificity [25]. To date, molecularly imprinted polymers (MIPs) have been exploited extensively in many different applications including their use as separation materials [26,27], chemical sensors [28], reaction catalysts [29], enzyme mimics [30] and in particular, as solid-phase extraction (SPE) adsorbents [31,32].

In this study, SCN^--imprinted chitosan succinate has been proposed for the selective determination of thiocyanate specifically from synthetic water samples. The SCN^--imprinted bead was prepared from chitosan, succinic anhydride and epichlorohydrin avoiding a higher-level of cross-linking network. The effect of pH value in mobile phase has been determined, and binding capacity, repeated use and selectivity have also been evaluated.

EXPERIMENTAL

Materials

Chitosan, succinic anhydride and epichlorohydrin were supplied from Aldrich Chemical (USA). All other chemicals were analytical reagent grade and purchased from Merck (Darmstadt, Germany).

Instrumentation

Jenway 3100 pH-meter was used to mesaure pH values. Anions concentration was mesaured by unicam UV spectrometer. FTIR spectroscopy was used in the 4000-400 cm^{-1} range for the chemistry of functional monomer, pre-organized complex, and imprinted beads in the solid state (FTIR 100 series, Perkin Elmer, USA).

Preparation of Chitosan Succinate

Chitosan-succinate was synthesized according to the procedure reported in the Aiedeh and Taha’s work [33]. Chitosan (1.00 g, corresponding to approximately 6.20 mmol glucoseamine) was dissolved in acetic acid aqueous solution (1%, 100 mL) at ambient temperature, and a solution of the succinic anhydride (6.25 mmol) in pyridine (5 mL) was added dropwise with vigorous stirring. The reaction pH was maintained at 7.0 by the dropwise addition of NaOH solution (1.0 M). NaOH addition was continued till the pH was stabilized. After 40 min the reaction was terminated by the addition of NaCl aqueous solution (20%, 200 mL). The resulting precipitate was filtered, washed with acetone and diethyl ether, and desiccated to give chitosan-succinate conjugates. The IR spectra of the chitosan-succinate showed amide carbonyl band at 1650 cm^{-1}, carboxylic carbonyl band at 1735 cm^{-1}, indicating the formation of amide links with succinate [33].

Preparation of SCN^--Imprinted Chitosan Succinate

Chitosan succinate (1 g) was dissolved in the acetic acid (5%) and $Zn(NO_3)_2.4H_2O$ (2 g) was added slowly to this solution with continuous stirring at room temperature. Zn(II) ions was complexed the amide groups of chitosan-succinate. KSCN (1.85) was added to Zn(II)-chitosan-succinate mixture. Then, the mixture solution was slowly dropped into 150 mL of 1 M NaOH. The suspended solution was stirred at 200 rev min^{-1} for 12 h. After filtering this yellow suspended solution and drying in vacuum, the obtained thiocyanate-complexed chitosan succinate was crosslinked by 5 mL of epichlorohydrin in 250 mL of acetic acid solution (5 %) under refluxing conditions in an oil bath (ca. 110°C) for 1 h. Then, 250 mL of 0.1 M NaOH solution was added to complete the crosslinking reaction. After vacuum filtration, the clearly yellow product of crosslinked thiocyanate-complexed chitosan succinate was washed with 1 M KOH and deionized water several times. The whitely product was obtained, after the removing of SCN^- ions from the thiocyanate-complexed chitosan succinate using 1 M KOH .

The IR spectra of the SCN^--imprinted chitosan-succinate showed -OH band at 3435 cm^{-1}, SCN^- band at 2070 cm^{-1}, amide I carbonyl band at 1628 cm^{-1}, amide II -NH band at the 1574 cm^{-1}, aliphatic -CH band at 1384 cm^{-1}. The results indicated that, SCN^- was connected to Zn(II)-chitosan-succinate.

Adsorption/ Depsortion/ Reuse

Adsorption Studies

Effects of pH of the medium and the initial concentrations of SCN^- on the adsorption rate and capacity were investigated in batch adsorption-equilibrium experiments. The effect of pH on the adsorption rate of the SCN^--imprinted bead was investigated in the pH range of 2.0-12.0 at 25°C. Optimum pH was found as 3.0. The suspensions were brought to the desired pH by adding NaOH and HNO_3. The pH was maintained in a range of ± 0.1 until equilibrium was attained. In all experiments, polymer concentration was kept constant at 25 mg/25 mL. Anions was treated with the SCN^--imprinted bead at room temperature, in the flask stirred magnetically at 600 rpm.

The concentration of the ions in the aqueous phases after desired treatmant periods were measured by using UV spectrophotometer [34]. The effect of the initial ion concentration on the adsorption was investigated at a suitable pH as described above except that the concentration of thiocyanate ions in the adsorption medium was varied between 20 and 400 mg L^{-1}.

Competitive adsorption of SCN^-/Cl^-, SCN^-/PO_4^{3-} and SCN^-/F^- from their mixture was also investigated in a batch sysytem. A solution (25 mL) containing 25 mg L^{-1} from each anions was treated with the thiocyanate imprinted beads at a pH 3.0 at room temperature, in the flask stirred magnetically at 600 rpm. After the adsorption equilibrium reached, the concentration of anions in the remaining solution was mesaured by UV spectrometer.

The amount of adsorbed ions was obtained using the expression.

$$Q=[(C_o-C).V]/M \qquad (1)$$

Q is the amount of ions adsorbed onto the unit amount of the polymer (mg g^{-1}); C_o and C are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively (mg L^{-1}); V is the volume of the aqueous phase (mL); and M is the amount of polymer (g).

Desorption and Reuse

25 mg of the imprinted bead was placed in a 25 mL solution containing 25 ppm of thiocyanate ion for the adsorption process. Then, adsorbed thiocyanate anions were desorbed by the treatment of the imprinted bead with 1 M KOH solution stirring at 600 rpm for 30 min. Desorption ratio (DR) was calculated from the following expression.

$$DR= (C_{em}/C_{as}) X 100 \qquad (2)$$

where C_{em} and C_{as} are amount of ions desorbed to the elution medium and amount of ions adsorbed onto the sorbent.

Adsorption-desorption cycle was repeated ten times by using the same sorbent for the reusability of the SCN^--imprinted beads. The imprinted bead was washed several times with 1 M KOH solution and demineralized water after each use and then reloaded.

RESULT AND DISCUSSION

Adsorption Capacity of SCN^- Imprinted Bead

Adsorption Rate

Figure 1 shows adsorption rate of thiocyanate ions onto the SCN^--imprinted bead from aqueous solutions containing 200 mg L^{-1} of thiocyanate ions at a constant pH of 3.0. Note that the ordinate values on this figure were calculated by using the expression given Eq. (1). As seen here, thiocyanate adsorption increases with the time during the first 30 min and the levels off as equilibrium is most probably due to geometric shape memory between thiocyanate anions and created thiocyanate cavities in the beads structure. It is well known that removal of the template (thiocyanate) from the polymeric matrix leaves ionic cavities of complementary size, shape and chemical functionality to the template.

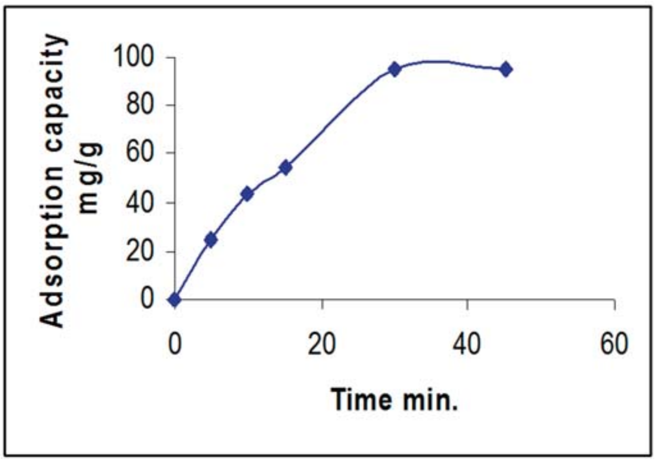

Figure 1. Adsorption rate of thiocyanate ions on the SCN-imprinted polymer; pH: 3.0; T: 25°C.

Several experimental data on the adsorption of various ions by chitosan have shown a wide range of adsorption rates. For example, Inukai et al. have investigated adsorption of germanium(IV) on the 2,3-dihydroxypropyl chitosan beads and reported 5 h equilibrium adsorption time [35]. Guo et al. used molecularly imprinted chitosan beads for separation of hemoglobin and found 10 h as an equilibrium time [36].

Adsorption Capacity

Figure 2 shows effects of initial concentration of thiocyanate ions onto the adsorption capacity of the SCN^--imprinted bead. For this purpose, the experiment was applied within the range of 20-400 mg L^{-1} initial concentration. As seen from the figure, the amount of thiocyanate ions adsorbed per unit mass of the polymer (i.e., adsorption capacity) increased with the initial concentration of thiocyanate ions. The maximum adsorption was found to be 95 mg thiocyanate/g polymer for 200 mg L^{-1} thiocyanate ion initial concentration.

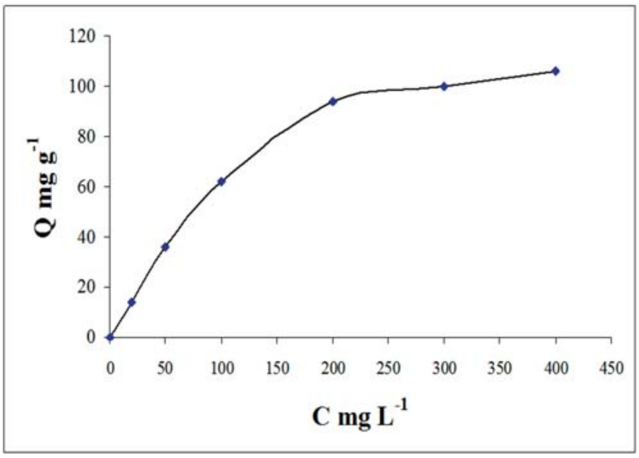

Figure 2. Adsorption capacity of thiocyanate anions on the SCN-imprinted particles; pH, 3.0; T, 25°C.

Namasivayam and Sangeetha were investigated adsorption of thiocyanate onto $ZnCl_2$ activated carbon from coir pith, an agricultural solid waste, and they reported 14.98 mg g^{-1} as adsorption capacity [37].

The pseudo-first and the second-order kinetic models were used to test the mechanism of adsorption process [38]. A comparison of the experimental adsorption capacity and the theoretical values are presented in Table 1. The pseudo-first-order kinetic of the experimental data for the SCN$^-$-imprinted bead is shown in Figure 3. The theoretical Q value estimated from the pseudo-first-order kinetic model is more close to the experimental value and the correlation coefficient. Thus, obtained results suggested that the pseudo-first order adsorption mechanism is predominant for the SCN$^-$-imprinted adsorbent system and that overall rate of the SCN$^-$ adsorption process appeared to be controlled by chemical reaction.

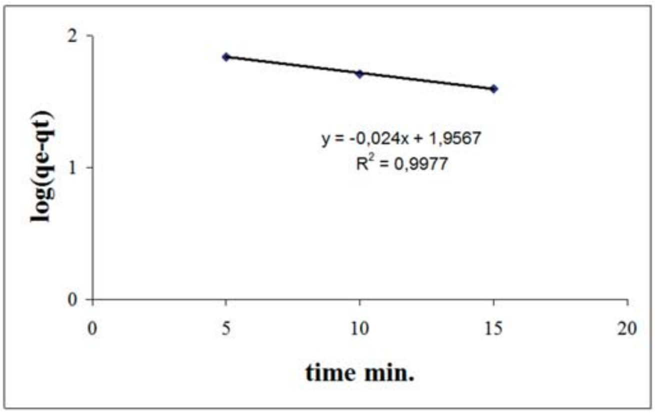

Figure 3. The seudo-first-order kinetic of the experimental data for the SCN-imprinted polymer.

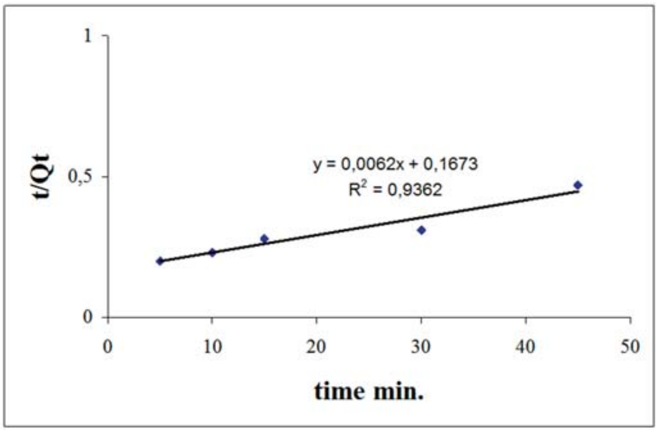

Figure 4. The pseudo-second-order kinetic of the experimental data for the SCN-imprinted polymer.

The correlation coefficient for the linear plot of t/Q_t versus t for the pseudo-second-order equation was 0.93. Since the theoretical Q_e value was slightly more different from the experimental value, this adsorbent system was not so well described by the the pseudo-second-order kinetic model. The pseudo-second-order kinetic of the experimental data for the SCN$^-$-imprinted bead is shown in Figure 4.

Adsorption Isotherms

Adsorption of SCN$^-$ from aqueous solutions was investigated in batch experiments. When adsorption data of SCN$^-$ were fitted against Langmuir and Freundlich isotherms, satisfactory fits were found with the Langmuir isotherm. The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites. The Langmuir constant was calculated as 0.018 L mg^{-1}, maximum adsorption capacity, Q_{max}, was calculated as 147 mgg^{-1} from this plot and the R^2 value of Langmuir plot was found as 0.9873. On the other hand the R^2 value of Freundlich plot was found as 0.9074. Langmuir adsorption isotherm of SCN$^-$ binding by the imprinted beads is shown in Figure 5.

Effects of pH

The effect of pH on the SCN$^-$ ions adsorption using the SCN$^-$-chitosan succinate beads is shown in Figure 6. As can be seen in Figure 6, the SCN$^-$-imprinted bead exhibited a high affinity in acidic conditions (pH=3.0 and 4.0) for thiocyanate ions. Therefore high efficiency in acidic medium can be attributed to the gradual increase in attractive forces and low efficiency in alkaline medium can be explained by the repulsion between the polymeric surface and thiocyanate.

Table 1. Kinetic constants for the SCN$^-$-imprinted polymer.

Polymer	Experimental	Pseudo- first order			Pseudo- second-order		
	Q (mg g^{-1})	K_1	Q_e	R^2	K_2	Q_e	R^2
SCN$^-$-imprinted bead	95	0.05	90.51	0.9977	$2.29.10^{-4}$	161.29	0.9362

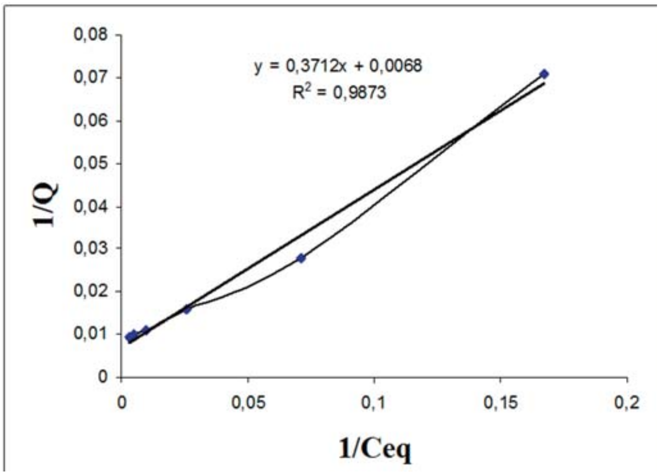

Figure 5. Langmuir adsorption isotherm of SCN^- binding by the imprinted beads.

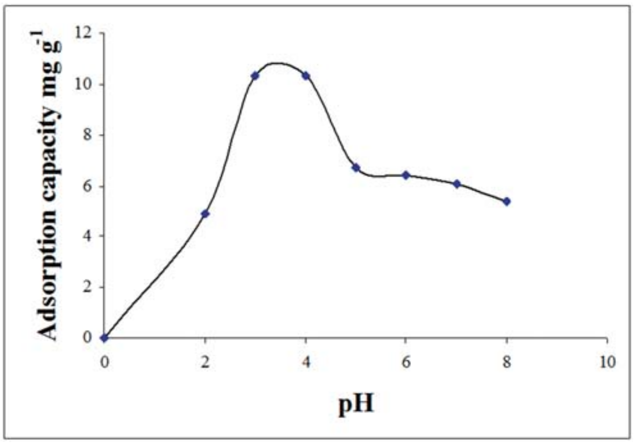

Figure 6. Effects of pH on SCN^- adsorption; thiocyanate initial concentration, 25 mgL^{-1}; T, 25°C.

Selectivity Studies

Competitive adsorption of SCN^-/Cl^-, SCN^-/PO_4^{3-} and SCN^-/F^- from their couple mixture was also investigated in a batch system. Thiocyanate adsorption capacity of the SCN^--imprinted beads was higher than the other ions. The competitive adsorption capacity of the SCN^--imprinted beads for thiocyanate ions was also higher than non-imprinted beads. When they exist in the same medium, a competition will start for the same attachment sites. It can be concluded that the thiocyanate imprinted beads show the following metal ion affinity order under competitive conditions: $SCN^- > PO_4^{3-} > Cl^- > F^-$. It should be noted that the imprinted beads showed excellent selectivity for the target molecule (thiocyanate ions) due to molecular geometry. Distribution and selectivity coefficienet of thiocyanate with respect to F^-, Cl^-, PO_4^{3} and SCN^- were calculated as explained below.

$$K_d = [C_i - C_f/C_f] \times (V/m) \qquad (3)$$

where K_d, C_i, C_f, V, and m represent the distribution coefficient, initial and final solution concentrations, volume of the solution (mL) and mass of beads (g), respectively. The selectivity coefficient for the binding of a anion in the presence of competitor species can be obtained from equilibrium data according to the Eqn.4;

$$k = K_{d,\text{template ion}} / K_{d,\text{interferent ion}} \qquad (4)$$

where k is the selectivity coefficient. A relative selectivity coefficient k' (Eqn. 5) can be defined [39,40];

$$k' = k_{\text{imprinted}} / k_{\text{control}} \qquad (5)$$

k' that results from the comparision of the k values of the imprinted beads to non-imprinted beads, allows an estimation of the effect of imprinting on selectivity. A comparison of the selectivity coefficient of SCN^--imprinted beads with the selectivity coefficient of non-imprinted beads showed that the imprinted matrix for SCN^-/F^-, SCN^-/Cl^- and SCN^-/PO_4^{3-} were 79.7, 7.23, and 2.2 times greater than the non-imprinted beads, respectively (Table 2).

Desorption and Repeated Use

The regeneration of the adsorbent is likely to be a key factor in improving process economics. Desorption of the adsorbed thiocyanate ions from the imprinted beads was also studied in a batch experimental set up.

When KOH is used as a desorption agent, the adsorbed ions are released from the thiocyanate templates into desorption medium. In order to show the reusability of the SCN^--imprinted beads,

Table 2. Effect of the imprinting on selectivity.

Polymer	SCN^- (mg L^{-1})	F^- (mg L^{-1})	K_D (SCN^-)	K_D (F^-)	k	k’
Non-MIP	25	25	1661.07	22607.18	0.07	79.29
SCN^--Imprinted beads	25	25	12532.53	2257.50	5.55	

Polymer	SCN^- (mg L^{-1})	PO_4^{3-} (mg L^{-1})	K_D (SCN^-)	K_D (PO_4^{3-})	k	k’
Non-MIP	25	25	2538.17	5145.53	0.49	2.27
SCN^--Imprinted beads	25	25	10995.01	9903.22	1.11	

Polymer	SCN^- (mg L^{-1})	Cl^- (mg L^{-1})	K_D (SCN^-)	K_D (Cl^-)	k	k’
Non-MIP	25	25	1199.08	91626.90	0.013	7.23
SCN^--Imprinted beads	25	25	10995.59	116980.17	0.094	

adsorption-desorption cycle was repeated 10 times by using the same imprinted beads. Figure 7 shows the adsorption-desorption cycle of SCN^--imprinted bead. The adsorption capacity of the recycled double imprinted beads can still be maintained at 95% of its original value at the 10th cycle. The results showed that the SCN^--imprinted affinity beads can be used repeatedly without loosing significantly their adsorption capacities.

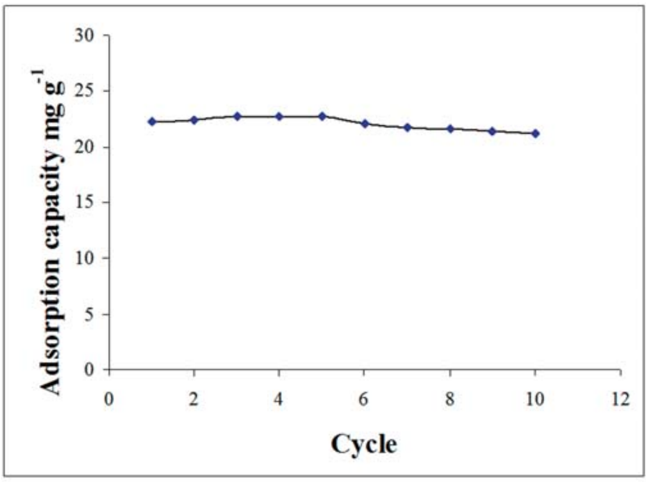

Figure 7. Adsorption-desorption cycle of SCN^--imprinted bead.

CONCLUSIONS

MIPs are materials that can be readily tailored with selectivity and afinity for guest molecules. Accordingly, MIPs have been utilized in many analytical applications that require molecular recognition, including sensors, adsorbents, immuno-type assays, and chromatographic stationary phases. In the present work, SCN^--imprinted beads are synthesized by molecular imprinting techniques in aqueous solution of epichlorohydrin, in the presence of SCN^-, chitosan-succinate-Zn(II). The effects of initial concentration of SCN^- ions, adsorption time and imprinting efficiency on adsorption selectivity for SCN^--imprinted beads was investigated.

The binding was relatively fast and the time required to reach equilibrium conditions was about 30 min. This fast binding equilibrium is most probably due to high complexation and geometric affinity between SCN^- ions and SCN^- cavities in the beads structure. The binding values increased with increasing concentration of SCN^- ions, and a saturation value is achieved at ion concentration of 200 mg L^{-1}, which represents saturation of the active binding cavities on the SCN^--imprinted beads. The relative selectivity coeficient is an indicator to express the binding affinity of recognition sites to the imprinted SCN^- ions. The results showed that the imprinted beads for SCN^-/F^-, SCN^-/Cl^- and SCN^-/PO_4^{3-} were 79.7, 7.2 and 2.2 times greater than nonimprinted matrix, respectively. The SCN^--imprinted beads can be used many times without decreasing their binding capacities signicantly. The obtained result indicate that the prepared MIP beads has high selectivity and affinity for the target molecule (SCN^-).

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