

[Research]

## Adsorption of Strontium (II) on new ion-imprinted solid-phase support: determination, isotherms, thermodynamic and kinetic studies

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### ABSTRACT

An ion imprinted polymer (IIP) based on aniline-formaldehyde was synthesized and then modified with extra aniline as cross-linker in the presence and absence of Sr (II) as the template to produce ion imprinted poly(aniline-formaldehyde) (IIPAF) and non imprinted poly(aniline-formaldehyde) (NIPAF). The sorbent was characterized by Fourier Transform Infrared Spectroscopy and was used for solid phase extraction. The kinetics of the sorption was analyzed using the pseudo-first order and pseudo-second order kinetic models. The equilibrium adsorption data of Sr (II) on synthetic polymer were analyzed by Langmuir, Freundlich, Temkin and Redlich-Peterson models. The thermodynamic parameters were determined using the equilibrium constant values obtained at different temperatures. The results showed the negative values of  $\Delta G^{\circ}$  and positive  $\Delta H^{\circ}$  which indicated that the Sr (II) adsorption process is spontaneous and endothermic. The method was applied for strontium ions determination from Tap water samples.

**Keywords:** Adsorption, ion imprinted polymers aniline-formaldehyde, Strontium (II), Kinetic.

### INTRODUCTION

Strontium in its elemental form occurs naturally in many compartments of the environment, including rocks, soil, water, and air. Strontium is always present in air as dust, up to a certain level. Strontium concentrations in air are increased by human activities, such as coal and oil combustion. Dust particles that contain strontium will settle on surface water, soils or plant surfaces at some point. Strontium is non-toxic and a daily intake of about 0.8-5 mg through food is harmless, when it only contains non-radioactive strontium. The risk of radioactive strontium intake is mainly based on its carcinogenic and mutagenic mechanism, problems that occur in cell division, and possible increased infant mortality. Sr90 decays to radioactive yttrium, which accumulates in

hyp-ophysis and ovaries, and subsequently disrupts infant hormonal development, and infant growth. (Lenntech *et al.*, 2012).

Ion imprinting is a versatile technique for creating macromolecular matrices that display selective ion recognition behavior. This has shown remarkable promise as a technique for material of preparation with spatial recognition towards a target toxic metal ion by mimicking the key and lock principle. Ion imprinted polymers are prepared by the copolymerization of functional and cross linking monomers in the presence of toxic target inorganic species (the imprint ion) which act as an ionic template. The functional groups are held in position by the highly cross linked polymeric structure. Subsequent leaching of imprint ion reveals

binding sites that are complimentary in size and shape to the imprint ion. (Booking. 2007)

### MATERIALS AND METHODS

Aniline, formaldehyde, hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, acetic acid, sodium acetate, sodium dihydrogen phosphate, di-sodiumhydrogen phosphate, acetone, ethanol and other materials were products of Merck (Darmstadt, Germany).

All the solutions were prepared in deionized water using analytical grade reagents.

The stock solution (100 mgL<sup>-1</sup>) of Sr (II), was prepared by dissolving appropriate amounts of Sr(NO<sub>3</sub>)<sub>2</sub>, in deionized water. 0.1 M acetic acid - acetate buffer (pH= 3 - 6.5), 0.01 M phosphate buffer (pH= 6.5 - 9) was used to adjust the pH of the solutions, wherever suitable.

### Instruments

Strontium ion concentrations were measured using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) Varian, Vista-pro (Salt lake city, Australia). The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland) by the potassium bromide pellet method.

### Synthesis of aniline formaldehyde condensate (AFC)

Commercial grade aniline [C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>] for synthesizing polymers was purified by distilling obtain MIP. The non-imprinted polymer (NIP) was prepared following the same protocol in the absence of the template ion.

### Batch adsorption experiments

A sample solution (25 mL) containing (0.3 µg.mL<sup>-1</sup>) of Sr (II) was taken in a glass stoppered bottle, after adjusting its pH to the optimum value. The 0.05 g of ion imprinted aniline-formaldehyde was added to the bottle and the mixture was shaken for an optimum time. The resin was filtered and sorbet metal ion was eluted with 0.5 M HNO<sub>3</sub> (10 mL). The concentration of metal ion in the elute was determined by (ICP-AES). The wavelength of 216.596 nm was used for Strontium determination. Isotherm studies were carried out by adding a fixed amount of adsorbent (0.05 g) to a series of

over KOH pellets at 180 °C. Poly aniline-formaldehyde was synthesized by reacting formaldehyde (37% HCHO) with aniline (Kumar., A. et al., 2007). Strontium [Sr(NO<sub>3</sub>)<sub>2</sub>] was used as the source of Strontium. In a 100 mL reaction vessel, 5 mL of 37% formaldehyde was added to a mixture of 9.3 g of aniline and 3 mL of 37% HCl. Condensation was carried out at 100 °C for 2 h. The temperature was then decreased to 60 °C and the mixture was neutralized with 4 mL of 30% NaOH, resulting in an insoluble liquid resin. The resin was then washed with warm water three times and separated from the aqueous layer. The resin was kept at 80 °C under a reduced pressure of 10 kPa for 1 h to remove any unreacted aniline and/or formaldehyde.

### IIP preparation

The chemical polymerization of aniline was performed as described in the literature; (Kumar *et al.*, 2007; Abe *et al.*,1989; Liu *et al.*,1997) however, in this work, Ammonium persulfate was used as the initiator. In a 150 mL reaction vessel, AFC was dissolved in an optimum amount of 1 M HCl aqueous solution in varying ratios. Then 20 mL of a 100 ppm solution of Sr(II) was added drop wise to the solution as a template. Then 0.5 mL of aniline was added to the solution as a cross linker with vigorous stirring. After polymerization for 1 h at 25 °C, a dark polymer powder was obtained. The MIP was kept in a water bath at 0 °C for 2h. The powder was washed with 0.5 M HNO<sub>3</sub> to

beakers filled with 50 mL diluted solutions of Sr (II) (6-48 µg.mL<sup>-1</sup>). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (3 h) at 25 °C and optimum pH (8). pH adjustments have been done using 0.01 M phosphate buffer. The beakers were then removed from the shaker, and the final concentration of Sr(II) in the solution was measured by (ICP-AES). The amount of Sr (II) at equilibrium  $q_e$  (mg.g<sup>-1</sup>) on ion imprinted aniline-formaldehyde was calculated from the following equation:

$$q_e = (C_0 - C_e) V / W \quad (1)$$

Where  $C_0$  and  $C_e$  (mg.L<sup>-1</sup>) are the liquid phase concentrations of Sr (II) at initial and equilibrium,

respectively,  $V$  (L) the volume of the solution and  $W$  (g) is the mass of adsorbent used.

## RESULTS AND DISCUSSION

### Isoterm studies

The analysis of equilibrium data to monitor the adsorption process is quite important for design purposes. Adsorption isotherms express the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at a constant temperature. Sorption data for a wide range of adsorbate concentration are most conveniently described by sorption isotherms. The adsorption studies were carried out at 40, 50 and 60 °C to determine the adsorption isotherms and the isotherm parameters were evaluated using Langmuir, Freundlich, Temkin and Redlich-Peterson models. Four isotherm equations have been tested in the present study, namely, Langmuir, Freundlich, Temkin and Redlich-Peterson. The Langmuir equation was given in the following form; (Langmuir L., 1918),

$$q_e = q_{\max} \cdot K_L \cdot C_e / (1 + K_L \cdot C_e) \quad (2)$$

where  $q_{\max}$  is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface ( $\text{mg} \cdot \text{g}^{-1}$ ) and  $K_L$  is the Langmuir constant ( $\text{L} \cdot \text{mg}^{-1}$ ). The equation (2) can be rearranged to a linear form:

$$C_e / q_e = (1 / q_{\max} \cdot K_L) + (C_e / q_{\max}) \quad (3)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of  $C_e / q_e$  versus  $C_e$ .

Conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of ion imprinted aniline-formaldehyde surface. Langmuir parameters calculated from Equation (3) are listed in Table 1.

The four models are applicable in describing the data (for example,  $R^2$  adsorption isotherm coefficients) with the Redlich-Peterson model being more appropriate.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor,  $R_L$ , defined as: (Hall et al., 1966)

$$R_L = 1 / (1 + K_L \cdot C_0) \quad (4)$$

The values of  $R_L$  indicate the type of isotherm to be irreversible ( $R_L = 0$ ), favorable ( $0 < R_L < 1$ ), linear ( $R_L = 1$ ) or unfavorable ( $R_L > 1$ ). The  $R_L$  values were

found to be less than 1 and greater than 0 (Table 2) for all experiments carried out at different initial concentrations and temperatures. Thus, ion imprinted aniline-formaldehyde seems to have a good affinity for strontium ions removal.

The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity factor  $1/n$ . Hence, the empirical equation can be written as: (Freundlich, 1906)

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

where  $K_F$  is the Freundlich constant ( $\text{mg} \cdot \text{g}^{-1}$ ) ( $\text{L} \cdot \text{mg}^{-1}$ )<sup>1/n</sup> and  $1/n$  is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the Equation (5):

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (6)$$

Therefore, a plot of  $\ln q_e$  versus  $\ln C_e$  enables the constant  $K_F$  and exponent  $1/n$  can be determined. The Freundlich equation predicts that the Sr (II) concentration on the adsorbent will increase as long as there is an increase in the Sr(II) concentration in the liquid.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

The Temkin isotherm has been generally applied in the following form:

$$q_e = (RT/b) \ln(AC_e) \quad (7)$$

$$q_e = B \ln(A) + B \ln(C_e) \quad (8)$$

Where  $B = RT/b$  and  $b$  is the Temkin constant related to heat of sorption ( $\text{J} \cdot \text{mol}^{-1}$ ).  $A$  is the Temkin isotherm constant ( $\text{L} \cdot \text{g}^{-1}$ ),  $R$  the gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ) and  $T$  is the absolute temperature (K). Therefore the constants  $A$  and  $B$  can be determined by plotting  $q_e$  versus  $\ln C_e$ . Temkin parameters calculated from Equation (7 and 8) are listed in Table 1.

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$\ln(AC_e / q_e - 1) = g \ln(C_e) + \ln(B) \quad (9)$$

It has three isotherm constants, namely,  $A$ ,  $B$ , and  $g$  ( $0 < g < 1$ ), which characterize the isotherm. Three isotherm constants,  $A$ ,  $B$ , and  $g$  can be evaluated from the linear plot represented by Eq. (13) using a trial and error procedure, which is applicable to computer operation.

It was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination,  $R^2$ , for a series of values of A for the linear regression of  $\ln(C_e)$  on  $\ln[A(C_e/q_e)-1]$  and to obtain the best value of A which yields a maximum 'optimized' value of  $R^2$  using the solver add-in with Microsoft's spreadsheet, Microsoft Excel.

The Langmuir, Freundlich, Temkin and Redlich-Peterson isotherms for the adsorption of Strontium ion imprinted aniline-formaldehyde at different temperatures are presented in Fig.1.

The corresponding Langmuir, Freundlich, Temkin and Redlich-Peterson parameters along with Correlation coefficients are given in Table 1.

### Characterization of polymers in spectrum

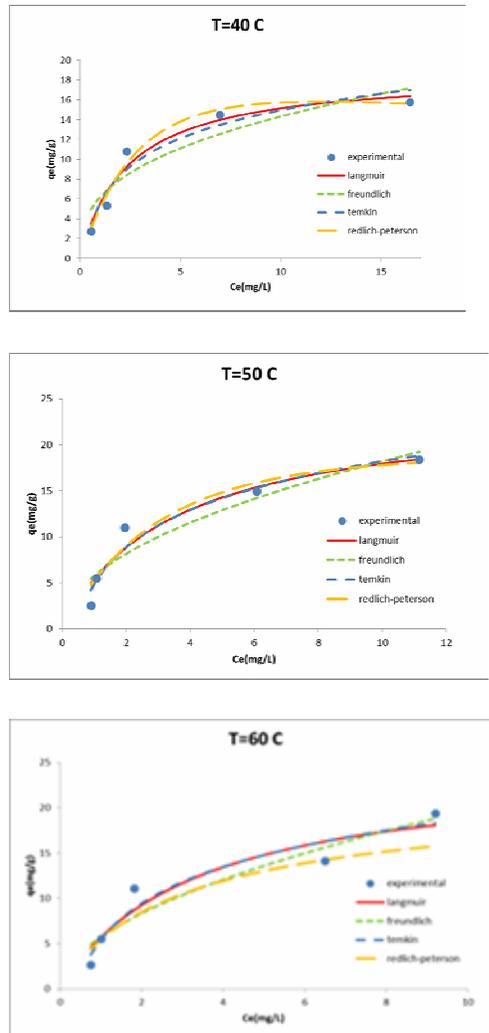
The structure of ion imprinted aniline-formaldehyde confirmed the existence of functional groups of (C-N) 1041, (C=C) 1463, 1627, (C-H) 2922, 2854, (OH) 3413 and (NH<sub>2</sub>) 1627, 3413. The IR spectrum of ion imprinted aniline-formaldehyde loaded Sr (II) demonstrates a structure similar to that mentioned above. But, the bands observed in the ion imprinted aniline-formaldehyde at 3413 and 1627 cm<sup>-1</sup> can be assigned to NH<sub>2</sub> and aromatic ring which are shifted to the lower frequency (Fig.2)

**Table 1.** Isotherm parameters obtained using the non-linear method

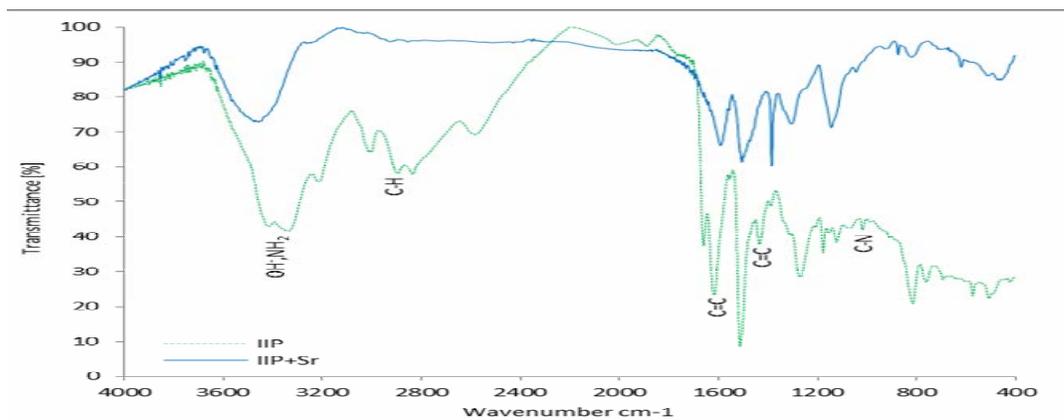
Isotherm		Temperatures		
		40 (°C)	50 (°C)	60 (°C)
Langmuir	$q_m$	18.756	24.121	24.626
	$K_l$	0.420	0.290	0.300
	$R^2$	0.956	0.934	0.913
Freundlich	$K_f$	6.154	5.797	5.784
	$n$	2.721	2.012	1.881
	$R^2$	0.853	0.891	0.900
Temkin	$B_t$	4.089	5.791	5.789
	$A_t$	3.884	2.322	2.569
	$R^2$	0.938	0.952	0.934
Redlich-Peterson	$A_r$	5.806	6.029	7.767
	$B_r$	0.139	0.146	0.359
	$g$	1.289	1.213	0.947
	$R^2$	0.975	0.938	0.913

**Table 2.** The values of  $R_L$  based on the Langmuir isotherm for strontium ions adsorption with respect to temperatures

$C_0$ (mg.L <sup>-1</sup> )	Temperatures		
	40 (°C)	50 (°C)	60 (°C)
6	0.284	0.365	0.357
12	0.165	0.223	0.217
24	0.090	0.125	0.122
36	0.062	0.087	0.085
48	0.047	0.067	0.065



**Fig.1.** Isotherms obtained using the non-linear method for the sorption of Sr (II) onto the imprinted polymer at various temperatures.



**Fig. 2.** FT-IR spectrum of the ion imprinted polymer (IIP) and the ion imprinted polymer loaded Sr(II).

### Effect of initial pH on metal sorption

The degree of metal sorption at different pH values was determined by batch equilibration technique. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Strontium content (by ICP-AES) in the supernatant liquid and in the eluate obtained by desorbing the metal ion from ion imprinted aniline- formaldehyde with 0.5 M nitric

acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Fig.3. The maximum recovery was 87% at pH= 8. The degree of metal desorption with different eluting agents after Sr (II) adsorption at optimum pH value was determined in batch experiments. Nitric acid at 0.5 M provided the best recovery.

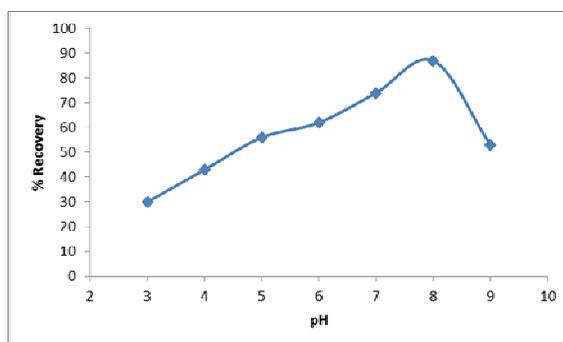


Fig. 3. Effect of pH on sorption of Sr(II) by ion imprinted polymer

### Effect of temperature

The 0.05 g of ion imprinted aniline-formaldehyde resin beads were stirred for 4 h. with 25 mL solution containing 6-48 mg.L<sup>-1</sup> of strontium, at optimum pH and different temperatures 40, 50 and 60 °C. The metal ion concentration in the supernatant liquid was estimated before and after the washing by ICP. The sorption capacity of the resin for the metal ion was ascertained from the difference between the metal ion concentrations in

solution before and after the sorption. Fig. 4 indicates the effect of initial concentration of the Sr(II) in the solution and the temperature on capacity sorption of Sr (II) by ion imprinted aniline-formaldehyde resin. An adsorption capacity of 19.4 mg.g<sup>-1</sup> was obtained with an initial concentration of 48 mg.L<sup>-1</sup> of Sr (II) at optimum pH and 60 °C .

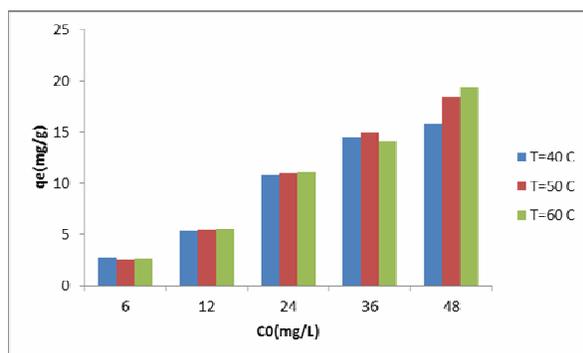


Fig. 4. Effect of initial Sr(II) concentrations on sorption capacity at different temperatures

### Optimization of sorption time of Sr (II)

Optimum sorption time of strontium ions was obtained according to the following procedure: Ion imprinted aniline- formaldehyde (0.05 g) was

shaken with 25 mL of solution containing 0.3 mg.L<sup>-1</sup> of strontium at different sorption times (10, 30, 45, 90, 180, 240 and 300 min) under optimum pH. After filtration of the sorbent, the concentration of

strontium ions in solution was determined with ICP-AES using the recommended batch method.

The Sr (II) sorption as a function of contact time is shown in Fig.5.

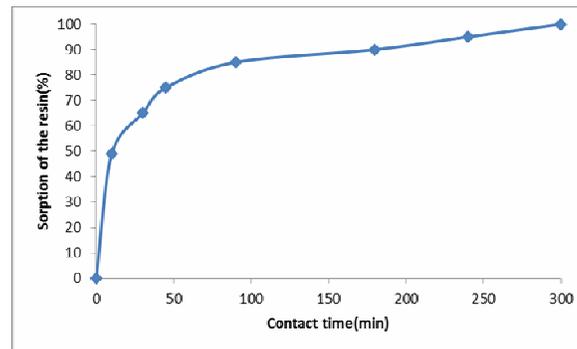


Fig.5. Kinetics sorption of Sr (II) on imprinted polymer

This figure reveals that saturation of the sorbent with Sr(II) takes about 300 min and halftime for saturation of the polymeric sorbent is less than 10 min. The profile of strontium uptake on this sorbent reflects good accessibility of the chelating sites in the ion imprinted aniline- formaldehyde.

#### Adsorption kinetic models

In order to investigate the controlling mechanism of the adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo second- order equations are applied to model the kinetics of strontium adsorption onto ion imprinted aniline-formaldehyde. A simple

kinetic analysis of adsorption is the pseudo-first-order equation in the form

$$dq_t/dt = k_1 (q_e - q_t) \quad (10)$$

Where  $k_1$  is the rate constant of pseudo-first-order adsorption and  $q_e$  represents adsorption capacity (i.e. the amount of adsorption corresponding to monolayer coverage). After definite integration by applying the initial conditions  $t=0$  to  $t$  and  $q_t=0$  to  $q_t$ , Eq. (11) becomes:

$$\ln (q_e - q_t) = \ln(q_e) - k_1.t \quad (11)$$

Where  $q_e$  and  $q_t$  are the amount of Sr (II) adsorbed ( $\text{mg.g}^{-1}$ ) at equilibrium and at any time  $t$ ,  $k_1$  is the constant ( $\text{min}^{-1}$ ). The plot of  $\ln(q_e - q_t)$  versus  $t$  gives a straight line for the pseudo-first-order adsorption kinetics (Fig.6).

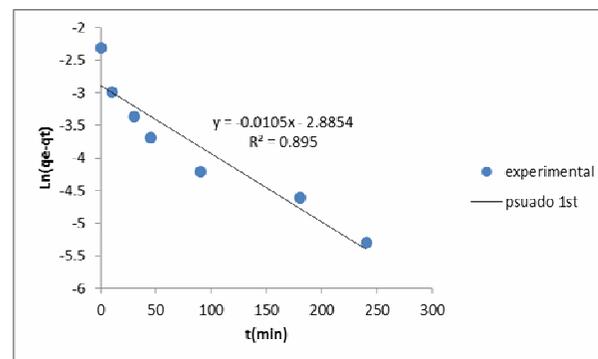


Fig.6. Pseudo-first-order kinetic onto Ion imprinted aniline-formaldehyde at different concentrations

The value of the pseudo-first-order rate constant  $k_1$  was obtained from the slope of the straight lines ( $k_1 = 13.91 \times 10^{-3}$ ) the  $q_e$  value could be calculated from the intercept ( $q_e = 0.1029$ ).

The pseudo-second-order model can be represented in the following form.

$$dq_t/dt = k_2 (q_e - q_t)^2 \quad (12)$$

Where  $k_2$  is the rate constant of pseudo-second-order adsorption. Integration of Eq. (12) and applying the initial conditions, we have:

$$t/q_t = (1/k_2)q_e + (1/q_e) t \quad (13)$$

Fig.7 shows the pseudo-second-order plots for Sr(II) onto Ion imprinted aniline-formaldehyde at pH 8. The pseudo-second-order rate constant  $k_2$  could be calculated from the intercept ( $k_2=0.74883$ )

and  $q_e$  could be calculated from the slop ( $q_e=0.0558$ ). Both correlation coefficients for the pseudo-first-order ( $R^2=0.895$ ) and pseudo-second-order ( $R^2=0.9975$ ) kinetic plots are high.

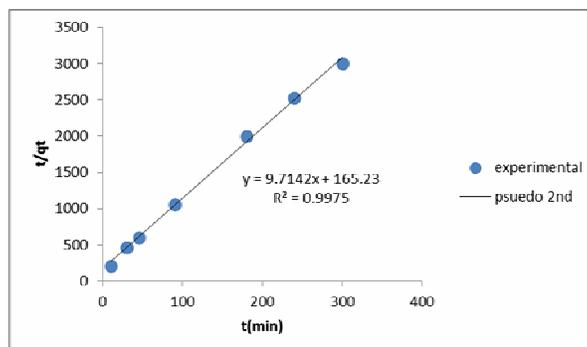


Fig. 7. Pseudo-second-order kinetic onto Ion imprinted aniline-formaldehyde at different concentrations

### Adsorption thermodynamics

To study the nature of adsorption, the thermodynamic parameters for adsorption processes, such as the standard Gibbs free energy change ( $\Delta G^\circ$ ), the standard enthalpy change ( $\Delta H^\circ$ ), and the standard entropy change ( $\Delta S^\circ$ ), were calculated with the following equations:

$$K_c = C_{A_e} / C_e \quad (14)$$

$$\Delta G^\circ = -RT \ln(K_c) \quad (15)$$

$$\ln(K_c) = \Delta S^\circ / R - \Delta H^\circ / RT \quad (16)$$

where  $C_e$  is the equilibrium concentration in solution ( $\text{mg.L}^{-1}$ ),  $C_{A_e}$  is the solid-phase concentration at equilibrium ( $\text{mg.L}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ ).  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are changes in Gibbs free energy ( $\text{kJ.mol}^{-1}$ ), enthalpy ( $\text{kJ.mol}^{-1}$ ), entropy ( $\text{J.mol}^{-1}.\text{K}^{-1}$ ),  $T$  (K) the absolute temperature and  $K_c$  ( $\text{L.g}^{-1}$ ) is the standard thermodynamic equilibrium constant defined by  $q_e / C_e$ . By plotting a graph of  $\ln(K_c)$  versus  $1/T$  (Fig. 8) the values  $\Delta H^\circ$  and  $\Delta S^\circ$  can be estimated from the slopes and intercepts. Table 3 shows the negative values of  $\Delta G^\circ$  and Positive  $\Delta H^\circ$  obtained which indicates that the Sr (II) adsorption process is spontaneous and endothermic. The positive value of  $\Delta S^\circ$  suggests that increased randomness at the solid/solution interface occur in the internal structure of the adsorption of Sr (II) onto Ion imprinted aniline-formaldehyde.

It has been reported that  $\Delta G^\circ$  up to  $-20 \text{ kJ.mol}^{-1}$  are consistent with electrostatic interaction between sorption sites and the metal ion (physical adsorption), while  $\Delta G^\circ$  values more negative than -

$40 \text{ kJ.mol}^{-1}$  involve charge sharing or transfer from the solid-phase surface to the metal ion to form a coordinate bond (chemical adsorption) (Horsfall *et al.*, 2004). The  $\Delta G^\circ$  values obtained in this study for the  $\text{Sr}^{2+}$  ions are  $< -10 \text{ kJ.mol}^{-1}$ , which indicates that physical adsorption was the predominant mechanism in the sorption process (Abdel Ghani *et al.*, 2007).

### Effect of foreign ions on sorption of Sr(II)

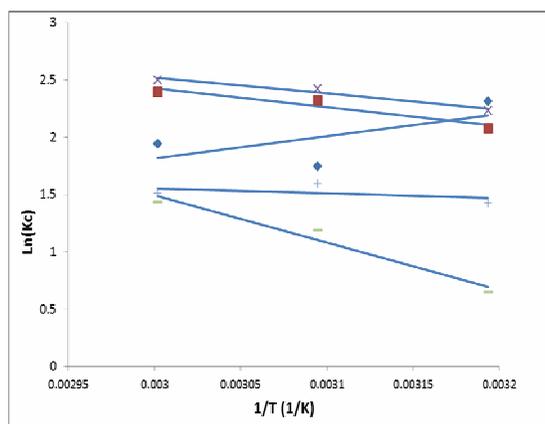
The sorption comparison of Sr(II) on Ion imprinted aniline-formaldehyde and non-Ion imprinted aniline-formaldehyde was investigated (with each ion having the concentration of  $10 \text{ mg.L}^{-1}$ ). The extraction percentage (E %) and the distribution ratio (D) was calculated from the following equations:

$$Q = (C_0 - C_e) V / W \quad (17)$$

$$\%E = (C_0 - C_e) / C_0 \times 100 \quad (18)$$

$$D = Q / C_e \quad (19)$$

where  $Q$  represents the adsorption capacity ( $\text{mg.g}^{-1}$ ),  $C_0$  and  $C_e$  represent the initial and equilibrium concentration of Sr ion ( $\mu\text{g.mL}^{-1}$ ),  $W$  is the mass of sorbent (g),  $V$  is the volume of metal ion solution (L),  $E\%$  is the extraction percentage and  $D$  is the distribution ratio ( $\text{mL.g}^{-1}$ ). The results in Table 4 demonstrate that the percentage of Sr(II) sorption by Ion imprinted aniline-formaldehyde is 31% higher than the non- Ion imprinted aniline-formaldehyde (Table 4).



**Fig.8.**  $\ln(K_c)$  vs.  $1/T$  for adsorption of Sr (II) onto Ion imprinted aniline-formaldehyde. The symbols refer to the experimental data:  $\blacklozenge$ ,  $C_0=6$ ;  $\blacksquare$ ,  $C_0=12$ ;  $\times$ ,  $C_0=24$ ;  $+$ ,  $C_0=36$ ,  $-$ ,  $C_0=48$  (concentration is  $\text{mg}\cdot\text{L}^{-1}$ ).

**Table 3.** Thermodynamic parameters for the adsorption of Sr (II) onto Ion imprinted aniline-formaldehyde at different temperatures

$C_0$ ( $\text{mg}\cdot\text{L}^{-1}$ )	$\Delta G^0$ ( $\text{kJ}\cdot\text{mol}^{-1}$ )			$\Delta H^0$	$\Delta S^0$
	40 °C	50 °C	60 °C	( $\text{kJ}\cdot\text{mol}^{-1}$ )	( $\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
12	-5.49	-6.10	-6.72	13.76	61.46
24	-5.86	-6.42	-6.98	11.56	55.65

**Table 4.** Effect Ion imprinted on sorption

method	Amount of adsorbed Sr	Extraction percentage	Distribution
	(II) ( $\text{mg}\cdot\text{L}^{-1}$ )	(%)	ratio
Ion imprinted	3.52	35.2	0.18
Non-Ion imprinted	2.41	24.1	0.32

**Table 5.** Results obtained for Sr (II) ion determination in water samples: (I), (II) and (III)

Analyte	(I)	(II)	(III)
Found (without spiking of Sr (II))	0.21	0.21	0.21
Added Sr ( $\mu\text{g}\cdot\text{mL}^{-1}$ )	0.24	0.36	0.48
Found Sr (II), after preconcentration ( $\mu\text{g}\cdot\text{mL}^{-1}$ )	3.1	4.5	6.1
Preconcentration factor	10	10	10
Recovery %	68.9	78.9	88.4
Standard deviation	0.11	0.07	0.15
Relative standard deviation (%) a	3.41	1.64	2.48

a: For three determinations

### Analysis of real samples

Ion imprinted aniline- formaldehyde was used for pre-concentration and determination of Sr (II) ions in tap water (Tehran, Iran). The pH of water sample was adjusted to the optimum pH=8. Solid phase extraction with Ion imprinted aniline-formaldehyde coupled with ICP-AES was applied to determine the Sr (II) in water sample. The results are shown in Table 5.

### CONCLUSION

A new ion imprinted chelating sorbent is prepared by polymerization of aniline-formaldehyde. The synthesis of the resin is simple and economical. The Sr(II) adsorption was due to same size cavity in the polymer with amino groups. The polymeric sorbent also present the advantage of high adsorption capacity, good reusability and high chemical stability. The application of sorbent for the sorption of the Sr(II) from aqueous solutions has been demonstrated in batch techniques. The sorption of the investigated metal ions increases by increasing the contact time. The experimental results were analyzed using four adsorption isotherm models, the Freundlich, Langmuir, Temkin and Redlich-Peterson, isotherm models. Pre-concentration by this sorbent combined with ICP- AES can be applied to the determination of trace Sr(II) in water with satisfactory results.

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## استخراج دربستر جامد و پیش تغلیظ استرانسیم با جاذب حفره ای پلیمر مولکولی (MIP) در نمونه های زیست محیطی و اندازه گیری آن توسط (AES-ICP)

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### چکیده:

جاذب حفره ای مولکولی پلیمر (MIP) بر اساس آنیلین-فرمالدئید تولید شده و پس از آن با آنیلین اضافی در حضور و عدم حضور فلز استرانسیم رفتار جذب سطحی آن مورد مطالعه قرار گرفت. آزمایش ها با روش batch انجام شد و تاثیر غلظت فلز و زمان تماس بر راندمان جذب در pH بهینه در تحت دما های مختلف برای بررسی رفتار سینتیک و ترمو دینامیکی (تغییرات انرژی آزاد، آنتالپی و آنتروپی) مورد مطالعه قرار گرفت. رفتار جذب استرانسیم توسط چهار مدل همدمای مانند لانگمویر، فروندلیش، تمکین و ردلیچ-پترسون مورد تجزیه و تحلیل قرار گرفت. بررسی های ضرایب همبستگی نشان داد همدمای جذب ردلیچ-پترسون بهتر از بقیه مدل ها داده ها را پردازش می کند. مطالعات سینتیکی نشان داد واکنش جذب سطحی این فلز از محیط آبی بر روی جاذب سنتز شده از معادله مجازی مرتبه دوم تبعیت می کند. همچنین روش مذکور برای تعیین یون ها استرانسیم در نمونه های زیست محیطی با نتایج رضایت بخش مورد استفاده قرار گرفت.

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