

Sorption of Ni(II) on Acrylic Polymers Functionalized with Triethylenetetramine

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Abstract: A crosslinked acrylic copolymer functionalized with triethylenetetramine (TETA) was used for retention of Ni(II) prior to determination by flame atomic absorption spectrometry (FAAS). Batch method was used and the optimum conditions for nickel sorption (pH, contact time, metal ion concentrations, temperature) have been established. Ni(II) Sorption equilibrium data were better described by Freundlich isotherm models and kinetic data accurately fitted to pseudo second order model. In the Cu(II) ions presence Ni(II) ion sorption is drastically diminished.

Keywords: Nickel; Sorption; Acrylic copolymer; Triethylenetetramine.

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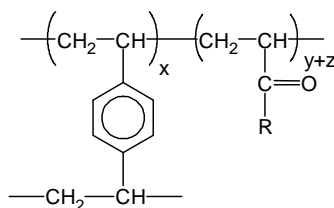
Introduction

Removal of heavy metals from industrial effluents is of primary importance because the contamination of wastewaters is a very serious health and environment problem. Nickel together with copper, cobalt and zinc are toxic and relatively accessible metals.¹ The low concentrations of metals in most seawaters, industrial wastewater, domestic effluents, rivers, sediments, etc. request selective and sensitive techniques of determination. These features beside speed and fairly low operational cost are performed by FAAS.² However preconcentration steps are often necessary for trace metals determination in various samples of complex matrices.

Various methods of preconcentration and separation procedures³ such as electrodeposition, coprecipitation, solvent extraction, evaporation and freeze-drying, membrane process can be used to increase the sensitivity and precision of analyte determination in a complex matrix. These methods have several disadvantages which include incomplete metal removal and toxic sludge generation. The sorption on solid phase has become an increasingly popular method because of its advantages: high preconcentration factor, high recovery, rapid phase separation, simplicity, and low cost.

The sorptive properties of very wide materials are exploited for Ni(II) preconcentration / separation: zeolites,⁴ clays,⁵ chitine,⁶ living⁷ or nonliving⁸ bacteria, biomass,⁹ silica-gel¹⁰ or cellulose¹¹ with different functional groups, activated carbon¹² or sludge,¹³ etc. Probably the most attractive due their selective fictionalizations capability are the synthetic resins. Ni(II) sorption /desorption on different chelating resins have been reported.¹⁴

This paper deals with a study of Ni(II) retention on an acrylic copolymer functionalized with triethylenetetramine (TETA) with crosslinking 2% DVB, As 14P, with the following structural unity:



Scheme 1



In order to establish the proper conditions for retention of Ni(II) at trace levels, the sorption behaviour of this metal ion in batch system has been investigated.

Experimental

Reagents

- Acrylic crosslinked copolymers-based on divinyl benzene (DVB) ethyl acrylate (EA) and acrylonitrile (AN) - functionalized with triethylenetetramine (TETA), with two crosslinked degrees: As-14P (2 wt % DVB) and As-25P (8 wt % DVB);

- standard solution of Ni(NO₃)₂ 0.1 M;
- HNO₃ and NaOH for adjusting the pH.

Methods

The effect of important parameters such as pH, contact time, initial metal ion concentration, adsorbent dose and temperature on the adsorptive retention of nickel ion was investigated in a series of kinetic and equilibrium experiments.

The adsorption experiments were performed by batch method suspending the copolymer (0.05 - 0.2 g) in 10 - 50 mL solution containing 5 - 100 mg L⁻¹ Ni(II) under precise experimental conditions (18 – 55 °C, pH = 1-8, 15 minutes - 24 hours contact time).

The pH was varied from 1 to 8 and it was adjusted by using diluted solution of HNO₃ and NaOH and measured with a RADELKIS pH - meter, OP 211/2.

The excess of Ni(II) has been determined in an aliquot of supernatant, by flame atomic absorption spectrometry on a PERKIN-ELMER 3300 spectrophotometer. For the calibration curve Merck standard solution with 1000 mg L⁻¹ Ni(II) and bidistilled water for dilution were used.

The sorption capacity of the resins was evaluated by the amount of metal ion adsorbent (Equation 1), by percent of metal ion removal (Equation 2) and by distribution constant (Equation 3).

$$q_e = (C_o - C_e) V 10^{-3} / m \quad (1)$$

$$R \% = (C_o - C_e) 100 / C_o \quad (2)$$

$$K_d = q_e / C_e \quad (3)$$

where: q_e is the amount of Ni(II) adsorbed per unit weight of adsorbent at equilibrium, mg g⁻¹; C_o and C_e are initial and equilibrium concentration of Ni(II) in solution, mg L⁻¹; m is the amount of adsorbent, g; V is the volume of solution, mL; K_d is the distribution constant, (mg g⁻¹) / (mg L⁻¹).

Results and discussions

Testing of ion exchangers

The preliminary selection was made by suspending for 24 h ~ 0.05 g of acrylic copolymer functionalized with ethylenediamine (EDA) and triethylenetetramine (TETA), each with two degrees of crosslinkage (2% and 8%), in 25 mL Ni(II) solutions with 5 mg L^{-1} .

In the investigated conditions significant retention, up to 60%, was obtain for the copolymer functionalized with TETA and 2% DVB. By increasing the crosslinkage to 8% DVB the retention diminished until 40%.

The resin functionalized with EDA reached less than 20% retention. For efficiency reason future systematic studies were only done for As 14P.

Effect of pH

The investigated acrylic copolymer is a weak base and due the protonation and deprotonation of amine groups, its adsorption behaviour for metal ion is influenced by pH. The tests were limited to the pH range of 1.0 to 8.0 because the precipitation of Ni(II) in basic medium may occur.

25 mL solutions with pH being varied from 1.0 to 8.0 with 5 mg L^{-1} Ni(II) have been put together with 0.05 g resin and slowly stirred for 8 hours. The results (Figure 1) proved that the adsorption increases with the increase of pH until 6 and at higher values is relatively constant.

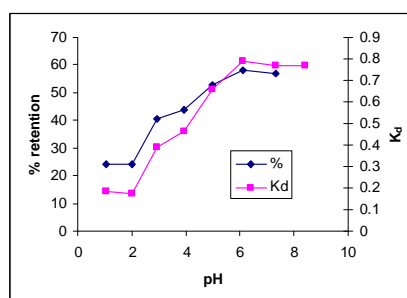


Figure 1. Effect of pH on Ni(II) sorption.

The low metal adsorption at low pH (<3) could be explained as a competition between protons and Ni(II) ions for the same active site. The pH values near neutrality are generally adequate to the sorption on resin functionalized with amine groups.

Influence of contact time and initial Ni(II) ion concentration

The experiments were carried out in aqueous solutions of pH = 6 with ~0.2 g resin and initial concentration of Ni(II) ion: 17 mg L⁻¹, 68 mg L⁻¹ and 100 mg L⁻¹ and with intermittent stirring. The results (Figure 2) proved that in 8 hours the sorption equilibrium was established for all solutions.

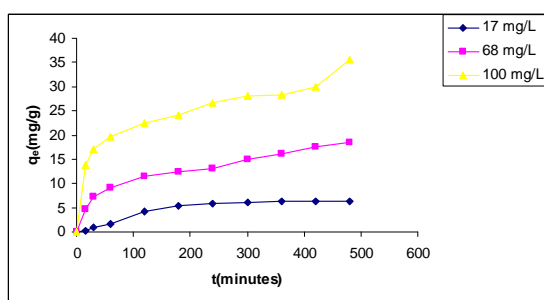


Figure 2. Effect of contact time and initial concentration on Ni(II) sorption.

In all cases, but especially for the highest concentration, the results obtained after 24 hours of sorbent-liquid phase contact indicate a supplementary lowering of Ni(II) solution concentration. In correlation with the increased pH, due to the sorption process, this may be attributed to a complementary process, probably precipitation on the resin granule surface.

Influence of temperature

The effect of temperature on Ni(II) sorption was investigated at three different temperatures, 8, 27 and 55 °C, respectively, using a constant

amount of adsorbent (0.15 g), for four Ni(II) concentrations and 24 hours of contact time.

The results showed that with increasing temperature the maximum percentage of Ni(II) removal increased very slowly for all the investigated concentrations only until 27 °C. The further decrease may suggest that the sorption is complex being the result of superposition of physical and chemical processes. Moreover, the Ni(II) – resin complex might have a higher stability at low temperature.

Sorption isotherms

The analysis of isotherm data is important to develop an equation which accurately represents the results and which could be used for design.

The adsorption behaviour of resin was determined by studying the amount of adsorbed metal as a function of metal concentration. The experiments were done by contacting ~ 0.15g resin with 25 mL solutions with 6 different concentrations for 10 hours, temperature of 27 °C, and pH = 6. In order to establish the best fit, two isotherm models were tested, the results being judged in terms of correlation coefficient and values of specific parameters.

Langmuir isotherm

For the AS-14P resin the equilibrium results at different concentrations were graphically represented (Figure 3) and analyzed (Table 1) based on the linearized Langmuir equation:¹⁵

$$1/q_e = 1/C_e b q_0 + 1/q_0 = 1/C_e K_L + 1/q_0 \quad (4)$$

where C_e is the equilibrium concentration of Ni(II) in solution, mg L^{-1} , b is a constant related to the energy of adsorption, L mg^{-1} , and q_0 , mg g^{-1} ,

represents the practical limiting adsorption capacity when the surface is fully covered with metal ions; K_L , $L g^{-1}$, is the Langmuir constant.

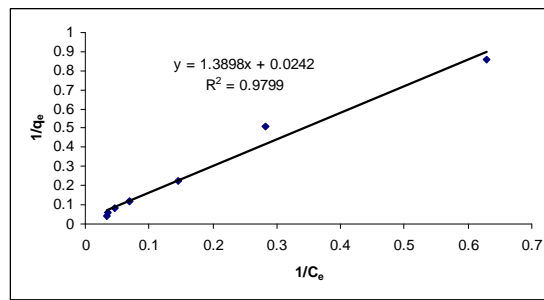


Figure 3. Linearized Langmuir isotherm for Ni(II) sorption onto As 14P resin.

The absorption performance in terms of q_0 value is 41.32 mg g^{-1} and for the studied experimental range reaches its full saturation.

The separation factor, R_L , was calculated with:

$$R_L = 1 / (1 + bC_0) \quad (5)$$

where C_0 is the highest initial Ni(II) concentration, mg L^{-1} .

The R_L values (0.493), in the range $(0 \div 1)$, confirmed that the adsorption behaviour of As 14P resin was favourable for Ni(II) ions.

Freundlich isotherm

The equilibrium experimental data were analyzed and fitted using the Freundlich model¹⁶ written in linearized form as:

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

where K_F , $L g^{-1}$, and n are the Freundlich constants that point to relative capacity and adsorption intensity, respectively. The values of K_F and $1/n$ (Table 1) were evaluated from the intercept and slope, respectively, of the linear plot of $\log q_e$ vs. $\log C_e$ (Figure 4).

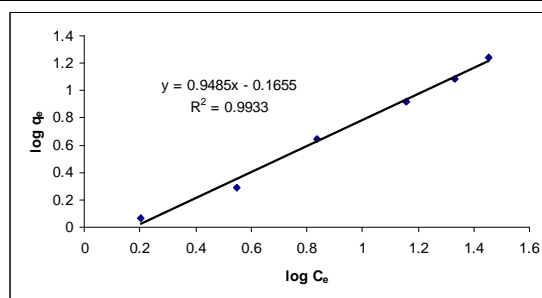


Figure 4. Linearized Freundlich isotherm for Ni(II) sorption onto As 14P resin.

The obtained n value of 1.059 ($1 < n < 10$) indicates that Ni(II) sorption is favourable.

Table 1. Characteristic parameters of Langmuir and Freundlich isotherms.

Langmuir					Freundlich		
K_L	q_0	b	R_L	R^2	K_F	n	R^2
$L g^{-1}$	$mg g^{-1}$	$L mg^{-1}$			$L g^{-1}$		
0.719	41.32	0.0174	0.493	0.98	0.165	1.054	0.993

In terms of correlation coefficient the best fits for the experimental data over the experimental range studied is for Freundlich model since it presents the greater coefficients of correlation.

Adsorption kinetics

Three different kinetic models were used to analyze kinetics data of sorption process, models divided in two main types: reaction-based models (first and second) and the diffusion-based model (the last one).

Pseudo first order model

The kinetics of adsorption was firstly analyzed by the pseudo-first order equation given by Lagergren¹⁷ as:

$$\log (q_e - q) = \log (q_e) - (k_1 / 2.303) t \quad (7)$$

where q_e and q - are the amount of Ni(II) adsorbed on resin at equilibrium and at time t , mg g^{-1} ; k_1 , min^{-1} is the rate constant of adsorption.

The k_1 values were calculated from the plots of $\log (q_e - q)$ vs. t , for different concentrations of Ni(II) (Table 2). The experimental q_e values do not agree with the calculated values obtained from the linear plots. The missing agreement with this model is also sustained by the correlation coefficient ($R^2 < 0.97$) obtained for the linearized form.

Table 2. Pseudo first and pseudo second order model parameters for the sorption of Ni(II).

C_o mg L^{-1}	q_{exp} mg g^{-1}	Lagergren			Ho			
		k_1 min^{-1}	q_e mg g^{-1}	R^2	k_2 $\text{g mg}^{-1} \text{min}^{-1}$	q_e mg g^{-1}	h min^{-1}	R^2
17	6.2	0.0047	8.974	0.949	0.00195	6.283	0.1037	0.994
68	18.11	0.0099	16.106	0.928	0.00179	18.99	0.3175	0.991
100	27.97	0.0138	22.029	0.98	0.00146	27.777	1.1277	0.99

Pseudo second order model

The sorption data were also analyzed in terms of pseudo-second order mechanism given by Ho,¹⁸ in linearized form:

$$(t/q) = (1/k_2 q_e^2) + (1/q_e)t = 1/h + (1/q_e)t \quad (8)$$

where k_2 , $\text{g mg}^{-1} \text{min}^{-1}$, is the rate constant of pseudo-second-order adsorption and h , $\text{g mg}^{-1} \text{min}^{-1}$, is the initial sorption rate. Values of h , k_2 and q_e (Table 2) were calculated from the intercept and slope of the linear plots of t/q vs. t .

The correlation coefficients are higher than 0.99 for As14P and the estimated values of q_e also agree with the experimental ones. Both facts

suggest that Ni(II) sorption on As14P follows a second order kinetic model which relies on the assumption that this mechanism is predominant and that over all rate constant chemisorption process might be the rate limiting step.¹⁹

Intraparticle diffusion

Intraparticle diffusion model based on the theory proposed by Weber and Morris⁴⁰ was tested to identify the diffusion mechanism. The rate constant for the intraparticle diffusion, k_{id} , is calculated by the following equation:

$$q = k_{id} t^{1/2} \quad (9)$$

where q is the amount of Ni(II) adsorbed on resin, mg g^{-1} , at time t , min; k_{id} is the rate constant for intraparticle diffusion, $\text{mg g}^{-1} \text{min}^{-1/2}$. The k_{id} values were calculated using the slope of the linear plots of q_t vs. $t^{1/2}$. There are three gradual adsorption stages but the second part is attributed to the intraparticle diffusion.

Table 3. Intraparticle diffusion model parameters for the sorption of Ni(II).

C_o mg L^{-1}	k_{id} $\text{mg g}^{-1} \text{min}^{-1/2}$	R^2
17	0.559	0.961
68	1.073	0.972
100	1.03	0.977

The variation of k_{id} values are not consistent as solution concentration increases, the straight line obtained from Equation 9 does not pass through the origin and correlation coefficients are not good enough to suggest a strong relationship between the parameters. Consequently, the

intraparticle diffusion is not the controlling mechanism during Ni(II) adsorption.

Cu(II)+ Ni(II) competitive sorption

Because nickel is generally found in the combined state, usually in copper mineralization, additional experiments of sorption were made in binary mixture. For this purpose 0.1 g sorbent was stirred with 35 mL solution with 100 mg L^{-1} Cu(II) and 10 mg L^{-1} Ni(II) ($\text{pH} = 5$, $t = 25 \text{ }^\circ\text{C}$, for 600 minutes). The results (Figure 5) show that for Ni(II) the quantity and rate are drastically decreased in binary mixture. This might be explained by the fact that Cu(II) ions are quickly adsorbed on the external active sites, the surface becomes more hydrophobic and Ni(II) ions diffuse more slowly and hardly to the free internal active sites.

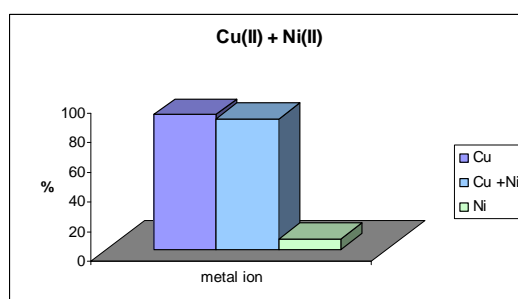


Figure 3. Competitive Cu(II) and Ni(II) sorption onto As 14P resin.

The Cu(II) – resin complex is more stable than Ni(II)-resin complex, the Ni(II) sorption being diminished until 6.8% in the investigated conditions.

Conclusions

The acrylic copolymer functionalized with TETA (2 % DVB) is a relatively good sorbent for Ni(II) removal from diluted solution, the sorption being affected by experimental parameters like pH, initial metal ion concentration, contact time, temperature. The maximum adsorption capacity, determined from Langmuir isotherm, has a value of 41.32 mg g⁻¹. The best fittings for the experimental data were found for Freundlich isotherm model and pseudo-second order kinetic model. The presence of Cu(II) ion diminished drastically the Ni(II) sorption.

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