Studies of the adsorption thermodynamics and kinetics of Cr(III) and Ni(II) removal by polyacrylamide

HASSAN ZAVVAR MOUSAVI[1]*, ABDORRAHMAN HOSSEINIFAR[2]
and VAHDAT JAHED[2]

[1]*Chemistry Department, College of Sciences, Semnan University, Semnan, Iran and*
[2]*Aja University of Medical Sciences, Tehran, Iran*

Abstract: Polyacrylamide (PAA) was investigated as an adsorbent for the removal of Ni(II) and Cr(III) metal ions from synthetic aqueous solutions. Different variables affecting the adsorption capacity of the adsorbent, *i.e.*, contact time, pH of the sorption medium, metal ion concentration and temperature of the solution, were investigated by batch sorption experiments. The adsorption equilibrium data was best fitted by the Langmuir isotherm model. The maximum adsorption capacities were found to be 84.03 and 32.67 mg g^{-1} polyacrylamide for Cr(III) and Ni(II), respectively. Three kinetic models, *i.e.*, the pseudo-first-order, pseudo-second-order and intra-particle diffusion equations, were selected to follow the adsorption process. The kinetic parameters, *i.e.*, rate constants, equilibrium adsorption capacities and related correlation coefficients, for each kinetic model were calculated and are discussed. It was indicated that the adsorption of both ions onto polyacrylamide could be described by the pseudo-second-order kinetic model. Various thermodynamic parameters, such as ΔH, ΔS and ΔG, were also evaluated and it was found that the sorption was feasible, spontaneous and exothermic.

Keywords: adsorption; polyacrylamide; Cr(III); Ni(II); kinetic.

INTRODUCTION

The presence of heavy metals in the aquatic ecosystem poses human health risks and causes harmful effects to living organisms in water and to their consumers. The wastewater from mining, painting and printing processes, plumbing, automobile batteries and petrochemical industries contains undesirable amounts of heavy metals ions. Heavy metal ions, such as lead, cadmium, mercury, chromium, nickel, zinc and copper, are non-biodegradable and can be toxic and carcinogenic, even at very low concentrations. Hence, they usually pose a serious threat

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to the environmental and public health.[1–3] Heavy metal containing effluents are generated in the following industrial processes: tanning, mining of chrome ore, production of steel and alloys, metal finishing, pigments manufacture, the photographic industry, glass manufacture, wood preservation, the use of chromium salts as corrosion inhibitor in industrial cooling water treatment, the textile industry and many others.[4–6]

Chromium is a highly reactive element. It exists in six oxidation states, of which Cr(III) and Cr(VI) are the two most stable states. Chromium forms stable complexes, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^- and $HCr_2O_7^-$. The fraction of these complexes varies with pH and at low pH, Cr exists as negatively charged dichromate ions. The chronic toxicity of nickel to humans and the environment is well documented. High concentrations of nickel cause cancer of lungs, nose and bone. At very high levels of exposure, nickel salts are known to be carcinogenic. In view of the toxic effects of nickel to human and animal life, it is important to treat industrial effluents polluted with Ni(II) ions before their discharge into the receiving water bodies.[7,8]

Due to the toxic and non-degradable nature of metallic species, the scientific community has worldwide carried out significant work on their removal from aqueous solutions and industrial effluents. Several treatment processes have been developed over the years to remove heavy metals dissolved in water and wastewaters: chemical precipitation,[9] membrane processes,[10] ion-exchange,[11,12] electrochemical,[13-15] membrane filtration,[16] reverses osmosis,[17] the employment of complexing agent[18] and ion flotation.[19] However, these techniques have disadvantages including incomplete metal removal, high consumption of reagents and energy, low selectivity, high capital and operational cost and the generation of secondary wastes the disposal of which is difficult. For these reasons, cost-effective alternative technologies for treatment of metal-contaminated waste streams are required. Adsorption[20–25] has proved to be one of the respective methods, which is a simple, selective and economical process for the removal of heavy metal ions from aqueous solutions.

Many researchers have studied on the feasibility of materials such as agricultural waste,[26] sawdust,[27,28] eggshell,[29] waste brewery yeast,[30] lichen,[31] waste tire rubber ash,[32] aliphatic polyamines,[33] orange peel,[34] zeolites,[35,36] poly(ethyleneglycol methacrylate),[37] poly(ethyleneglycol dimethacrylate-1-vinyl-1,2,4-triazole),[38] polybenzoxazine,[39] and zwitterionic hybrid polymer[40] for the removal of heavy metal ions from aqueous solutions.

Polyacrylamide is one of the most widely used polymers for several purposes. Three-dimensional polyacrylamide networks can absorb large amounts of water compared with other water absorbing materials. They can also show stimuli-responsive properties to various external parameters such as temperature, pH, solvent composition, and salt composition depending on the type of func-

tional groups in the structure. Polyacrylamide is a polymer with large numbers of amide side groups. It has been successfully grafted onto the surfaces of various matrices as selective sorbents for the removal of pollutants, such as dyes and heavy metals from aqueous solutions.[41–43]

The aim of the present batch adsorption study was to study the adsorption capacity of PAA for Ni(II) and Cr(III) metal ions. The effect of variable factors, such as contact time, initial concentration of the metal ions, adsorbent dose, pH and temperature, on the removal of both ions was investigated. Langmuir and Freundlich models were used to describe the adsorption isotherms. The adsorption kinetics of both ions with PAA was studied.

EXPERIMENTAL

Materials and apparatus

All employed reagents were of analytical grade. Test solutions of heavy metal ions were prepared from their nitrate salts (Merck, Darmstadt, Germany) by serial dilution of stock nickel and chrome ion solution (1000 mg L^{-1}) using deionized distilled water (Milli-Q, Milipore). Blank solution of deionized distilled water was analyzed by atomic absorption spectroscopy (AAS) to ensure that it did not contain nickel or chromium ions. Polyacrylamide was obtained from Guangzhou Chemical Reagent Factory, Guangzhou, China. A Shimadzu AA-680/G (Japan) atomic absorption spectrophotometer equipped with single-element hollow cathode lamps and an air–acetylene burner was used for the determination of the metal ions. A Metrohm E-632 pH meter (Switzerland) with a glass combination electrode was used throughout this study.

Preparation of the adsorbent

Polyacrylamide (PAA) was immersed in distilled water for three hours. The swollen gels were taken out of the solution at regular time intervals, wiped superficially with filter paper, weighed and replaced in the same solution until a state of equilibrium swelling was obtained.

Batch adsorption studies

The batch studies were conducted by mixing PAA with Ni(II) and Cr(III) metallic solutions prepared in the laboratory. The samples were stirred at room temperature at 100 rpm and after the required time their content was filtered through 0.45 µm membrane filter using a vacuum pump. The progress of adsorption was assessed by determining the residual concentration of both ions in the sample solution by AAS.

The removal percentage of metallic cations from aqueous solution was calculated using the following equation:

$$R = 100\frac{c_i - c_e}{c_i} \tag{1}$$

where c_i and c_e are the initial and final concentration of both ions in the solution respectively. The adsorption capacity of an adsorbent, which is obtained from the mass balance on the sorbate, in a system with solution volume V is often used to acquire experimental adsorption isotherms. Under the experimental conditions, the adsorption capacities of the adsorbent at equilibrium (q_e) for each concentration of Ni(II) and Cr(III) ions were calculated using Eq. (2):

$$q_e \ (\text{mg g}^{-1}) = \frac{V(c_i - c_e)}{M} \qquad (2)$$

where V is the volume of solution (L) and M is the mass of adsorbent (g) used.

The reported value of metal ions adsorbed by the adsorbent in each test was the average of at least three measurements.

RESULTS AND DISCUSSION

Effect of contact time

The rate of removal of Ni(II) and Cr(III) from solution is shown in Fig. 1, from which it can be seen that the adsorption of Ni(II) and Cr(III) reached equilibrium after a contact time of 90 min, while the removal efficiency for Ni and Cr at equilibrium was 68.0 and 94.2 %, respectively. The rate of the removal of Ni and Cr gradually decreased with increasing contact time. Initially, the uptake rate was higher because all sites on the PAA were vacant and the concentration was high, but the decrease of sorption sites reduces the uptake rate. As is shown Fig. 1, desorption occurred after saturation. Therefore, considering technical and economic aspects, a contact time of 90 min was chosen for nickel and chromium removal from aqueous solution by adsorption by PAA.
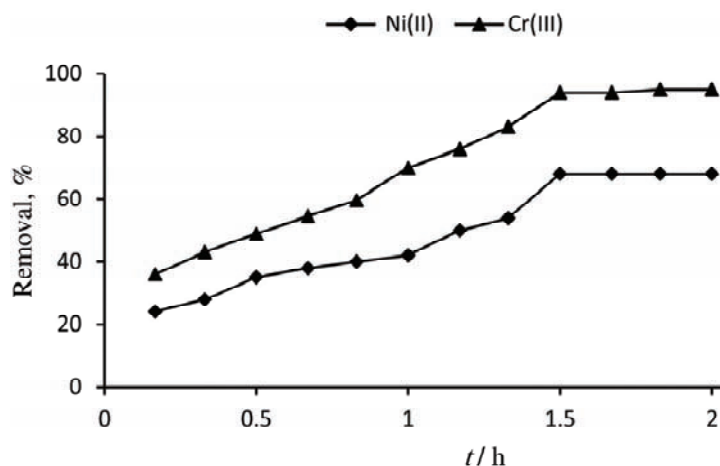

Fig. 1. Effect of contact time on the adsorption of Cr(III) and Ni(II) onto PAA. Conditions: 0.7 g L^{-1} PAA, pH 5, 100 mL 50 mg L^{-1} metal ions solution, contact time 1.5 h, temperature 298 K, agitation speed 100 rpm.

Effect of the amount of adsorbent

The effect of adsorbent dosage on the removal of Ni(II) and Cr(III) is shown in Figs. 2 and 3, respectively. It is clear from the figures that the percentage removal of the metal ions increased with increasing weight of the adsorbent. This is an expected result because as the amount of adsorbent increased, the available

surface area increased, thereby exposing more active sites for the binding of metal ions. A similar trend of the effect of the adsorbent concentration was observed and is discussed in the literature.[44]
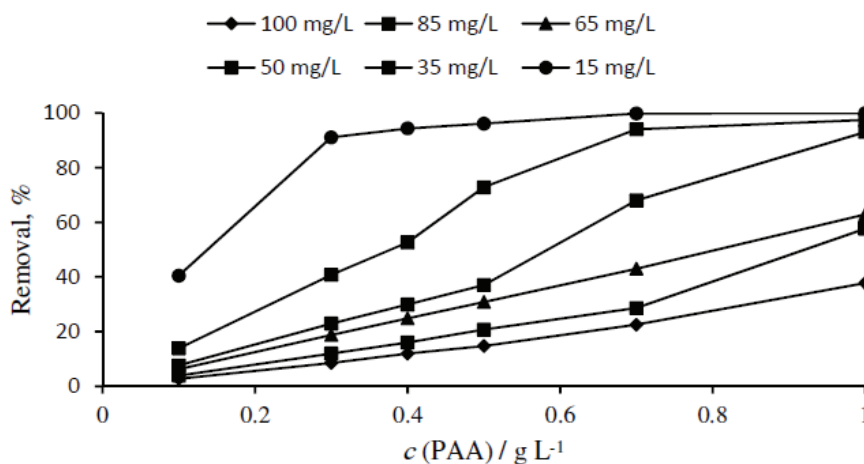

Fig. 2. Effect of adsorbent dose on the adsorption of Ni(II). Conditions: 100 ml 50 mg L^{-1} Ni(II), agitation speed: 100 rpm; contact time 1.5 h, pH 5, temperature: 298 K.
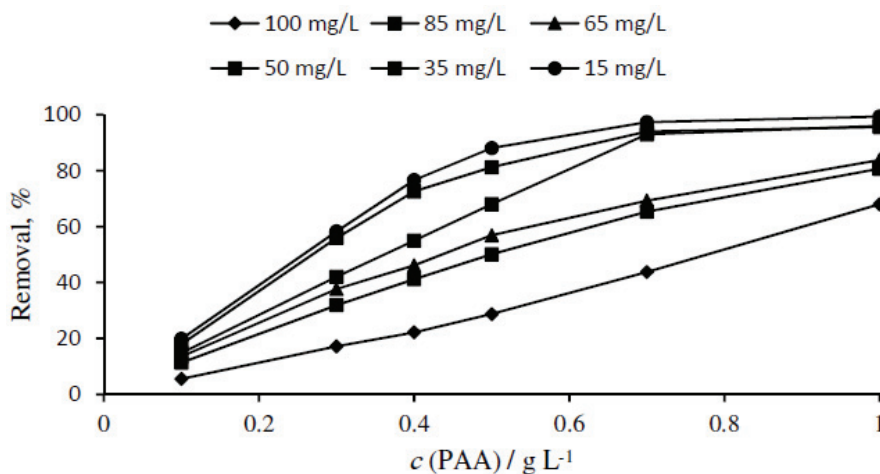

Fig. 3. Effect of adsorbent dose on the adsorption of Cr(III). Conditions: 100 ml 50 mg L^{-1} Cr(III), agitation speed: 100 rpm; contact time 1.5 h, pH 5, temperature: 298 K.

Effect of temperature

To study the thermodynamic properties of adsorption, experiments were performed at 298, 308, 318 and 328 K. The adsorption of Cr(III) and Ni(II) by PAA as a function of temperature is illustrated in Fig. 4. The results showed that the adsorption capacity for Ni(II) and Cr(III) decreased from 81.4 to 21.0 % and from

64.1 to 11.3%, respectively, with increase temperature, indicating that the process is exothermic.
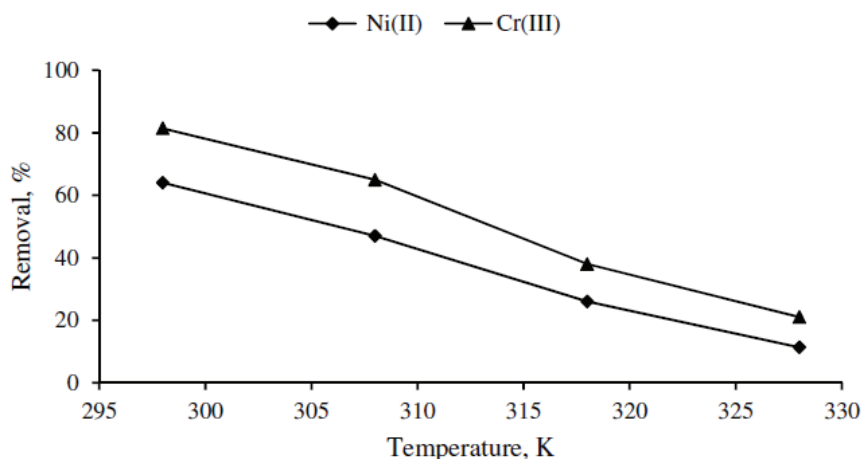

Fig. 4. Effect of temperature on the adsorption of Cr(III) and Ni(II) onto PAA. Conditions: 0.7 g L^{-1} PAA, pH 5, 100 mL 50 mg L^{-1} metal ions solution, contact time 1.5 h, temperature 298 K, agitation speed 100 rpm.

Effect of pH

The variation in the adsorption of the both ions was studied in the pH range of 2–6, at which values chemical precipitation was avoided. It is clear from the results shown in Fig. 5 that the removal was low at lower pH values; however, with increasing pH, a significant enhancement in the adsorption was recorded. The optimum pH for the removal of both ions was found to be in the range 4.0– –6.0. The variation of adsorption with pH can be explained by considering the charge of the ions and the electro–kinetic behavior of PAA. At lower pH values, more protons are available to protonate the amino groups of PAA, therefore, the attractions of both cationic ions decreased. Under strongly basic conditions, the negatively charged phenolic hydroxyl groups become potential active sites (NH$_2$) and could be attracted by the ammonium groups in the absorbents. At pH value higher than 6, both ions precipitated as hydroxides, which decreased the rate of adsorption and consequently the percent removal of the metal ions).

Isotherm studies

Equilibrium data, commonly known as adsorption isotherms, are the basic requirements for the design of a sorption system. The linear form of the Langmuir and Freundlich models are given by Eqs. (3) and (4), respectively:

$$\frac{c_e}{q_e} = \frac{1}{Q_m b} + \frac{c_e}{Q_m} \tag{3}$$

$$\log q_{e} = \log K_{F} + \frac{1}{n}\log c_{e} \qquad (4)$$

where q_{e} is the amount adsorbed at equilibrium (mg g^{-1}) and c_{e} is the equilibrium concentration of metal ions in solution (mg L^{-1}). The other parameters are isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation, Q_{m} (mg g^{-1}) is a measure of adsorption capacity under the experimental conditions and b is a constant related to the energy of adsorption (L mg^{-1}). Freundlich treatment gives the parameters, n, indicative of the bond energies between the metal ion and the adsorbent and K_{F} (mg^{1-n} L^{n} g^{-1}) related to the bond strength.

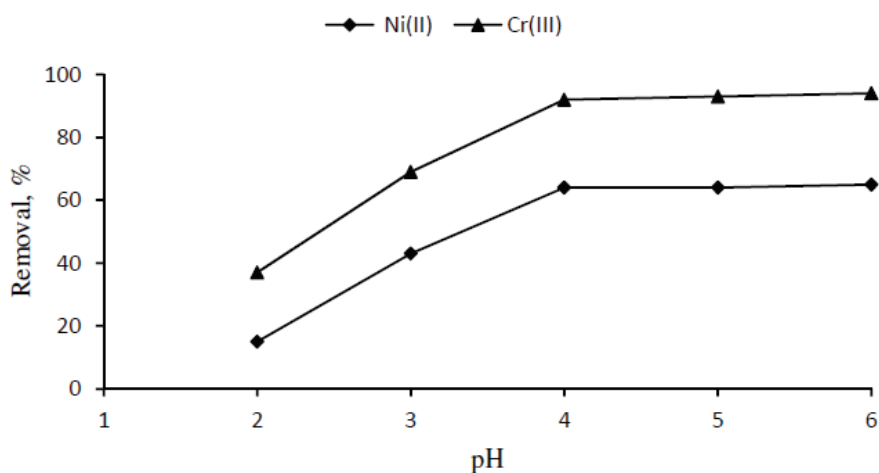Fig. 5. Effect of pH on the adsorption of Cr(III) and Ni(II) onto PAA. Conditions: 0.7 g L^{-1} PAA, 100 mL 50 mg L^{-1} metal ions solution, contact time 1.5 h, temperature 298 K, agitation speed 100 rpm.

The plot of c_{e}/q_{e} as a function of c_{e} allows the calculation of the Q_{m} and b values. From the adsorption parameters, the maximum adsorption capacity of the both ions by the adsorbent and the Langmuir constant can be evaluated. Values of K_{F} and n may be calculated by plotting $\log q_{e}$ *vs.* $\log c_{e}$. The slope is equal to *1/n* and the intercept to $\log K_{F}$. As mentioned above, the isotherm constants for both models at specific pH values were determined from the respective plots and are presented in Table I. Regression values (R^{2}) presented in Table I indicate that the adsorption data for Ni(II) and Cr(III) removal are fitted well by the Langmuir isotherm for both metal ions.

TABLE I. Values of the Langmuir and Freundlich constants for the adsorption of Ni(II) and Cr(III)

Ion	Langmuir			Freundlich		
	Q_m / mg g^{-1}	b / L mg^{-1}	R^2	K_F / mg^{1-n} L^n g^{-1}	n	R^2
Cr(III)	84.03	0.05	0.99	13.65	2.75	0.92
Ni(II)	32.67	1.03	0.98	5.38	1.62	0.79

A comparison of adsorption capacity of PAA with some previously used adsorbents is provided in Table II. The results show that PAA is very effective for the removal of Ni(II) and Cr(III) from aqueous solutions and the removal efficiencies of Ni(II) and Cr(III) obtained by PAA were comparable with literature data.

TABLE II. Comparison of the Langmuir constants for Ni(II) and Cr(III) adsorption onto PAA

Adsorbent	Adsorbent capacity, mg g^{-1}		
	Ni(II)	Cr(III)	Reference
Ilgın lignite	13.0	–	45
Synthesized zeolite	–	75.5	46
Gum kondagogu	50.5		47
Peat	–	22.36	48
Black gram husk	19.56	–	49
PAA	32.67	84.03	This study

Adsorption kinetics

In order to investigate the controlling mechanism of the adsorption process such as mass transfer and chemical reaction, the pseudo-first-order, pseudo-second-order kinetics and the intra-particle diffusion models were used to test the experimental data of the adsorption of chromium and nickel ions by PAA.

Pseudo-first order model

The pseudo-first order model is one of the most widely used procedures for the adsorption of a solute from an aqueous solution.[50] The pseudo-first order equation can be expressed as follows:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where q_t is the amount of metal ions adsorbed at time t (mg g^{-1}), q_e (mg g^{-1}) is equilibrium solid phase concentration and k_1 is first order rate constant for adsorption (L min^{-1}). The plot of ln (q_e-q_t) *vs.* t should result in a straight line. The rate constant can be calculated from the slope of the straight line.

Pseudo-second order model

The pseudo-second order equation is based on the adsorption capacity of the solid phase. Contrary to other models, it predicts the behavior over the whole

range of adsorption.[51] Pseudo-second order model based on the equilibrium adsorption capacity may be expressed in the form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

(6)

where k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second order adsorption. The plot of t/q_t *vs.* t should yield a straight line (Fig. 6), which allows the computation of k_2.
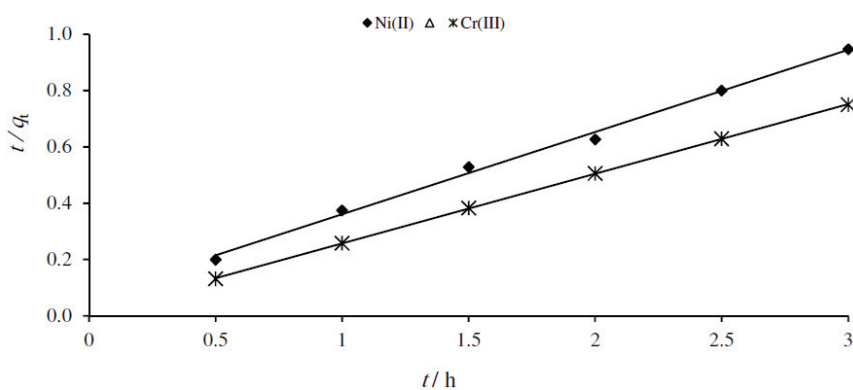

Fig. 6. Pseudo second-order sorption kinetics of Cr(III) and Ni(II) onto PAA.

Intra-particle diffusion

Intra-particle diffusion was explored using the intra-particle diffusion model given in Eq. (7)

$$q_t = k_{id} t^{1/2}$$

(7)

where k_{id} is the intra-particle diffusion rate constant and the meanings of the other terms have already been defined. This model predicts that the plot of q_t *vs.* $t^{1/2}$ should be linear if intra-particle diffusion is involved in the sorption process. Intra-particle diffusion is the rate-controlling step if the line passes through the origin.[52]

The application of the different kinetic models unveiled some interesting features regarding the mechanism and rate-controlling step of the overall sorption process. The kinetic parameters of both ions onto PAA under different conditions were calculated and are given in Table III. To quantify the applicability of each model, the correlation coefficient, R^2, was calculated for these plots. The linearity of these plots indicates the applicability of the three models. However, the correlation coefficients, R^2, showed that the pseudo-second-order model, an indication of a chemisorptions mechanism, fits better the experimental data ($R^2 \geq$ ≥ 0.998) than the pseudo-first-order and the intra-particle diffusion kinetic models (Table III and Fig. 5).

Thermodynamic parameters

The thermodynamic parameters, *i.e.*, the Gibb's free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) change of adsorption, can be evaluated from the following equations:[53]

$$K_c = \frac{c_{Ae}}{c_e} \tag{8}$$

where K_c is the equilibrium constant, c_{Ae}, and c_e (both in mg L^{-1}) are the equilibrium concentrations for the solute on the sorbent and in solution, respectively.

TABLE III. Kinetic parameters for the adsorption of Ni(II) and Cr(III) onto PAA

Parameter	Cr(III)	Ni(II)
Pseudo-first-order model		
k_1 / 10^{-2} min^{-1}	8.2	7.6
R^2	0.942	0.881
q_e (experimental), mg g^{-1}	19.25	7.54
q_e (kinetic plot), mg g^{-1}	16.35	5.37
Pseudo-second-order model		
k_2 / 10^{-4} g mg^{-1} min^{-1}	5.7	1.6
R^2	0.999	0.998
q_e (experimental), mg g^{-1}	19.25	7.54
q_e (kinetic plot), mg^{-1} g	19.21	7.38
Intra-particle diffusion model		
k_{id} / mg g^{-1} min$^{-1/2}$	5.347	1.873
R^2	0.923	0.903

To determine ΔG, the K_c values were used in Eq. (9):

$$\Delta G = -RT \ln K_c \tag{9}$$

K_c may also be expressed in terms of ΔH (kJ mol^{-1}) and ΔS (J mol^{-1} K^{-1}) as a function of temperature:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

A plot of ln K_c as a function of $1/T$ yields a straight line. The ΔH and ΔS parameters were calculated from the slope and intercept of the plot, respectively.

The Gibbs free energy change (ΔG) was calculated to be –7.10, –5.05, –3.16, and –2.34 kJ mol^{-1} for Ni(II) adsorption and –5.83, –3.79, –2.60, and –1.34 kJ mol^{-1} for Cr(III) adsorption at 298, 308, 318 and 328 K, respectively. The negative ΔG values indicate the thermodynamically feasible and spontaneous nature of the adsorption. The decrease in ΔG values shows a decline in the feasibility of the adsorption with increasing temperature. The ΔH parameter was found to be −57.44 and −76.13 kJ mol^{-1} for Ni(II) and Cr(III) adsorption, respectively. The ne-

gative ΔH values indicate the exothermic nature of the adsorption processes. The ΔS parameter was found to be 0.21 kJ mol^{-1} K^{-1} for Ni(II) and 0.25 kJ mol^{-1} K^{-1} for Cr(III) adsorption. The positive value of $\Delta S°$ suggests increased randomness at the solid/solution interface during the adsorption of Ni(II) and Cr(III) onto PAA.

CONCLUSIONS

The experimental results indicated that polyacrylamide could be successfully used for the removal of Ni(II) and Cr(III) ions from aqueous solutions. The developed adsorption studies demonstrated that the optimum pH values for Ni(II) and Cr(III) ions were in the range 4.0–6.0. The equilibrium adsorption data were very well fitted by the Langmuir model. The maximum adsorption capacities for Ni(II) and Cr(III) ions were found to be 32.67 and 84.03 mg g^{-1}, respectively. The adsorption of both ions obeyed pseudo-second-order equations with good correlations. Different thermodynamic parameters, *i.e.*, ΔH, ΔS and ΔG were also evaluated and it was found that the sorption is feasible, spontaneous and exothermic in nature. The positive value of the entropy change suggests increased randomness. The results show that polyacrylamide may be used effectively for the removal of Cr(III) and Ni(II) ions from aqueous solutions for environmental cleaning purpose.

И З В О Д

ИСПИТИВАЊЕ АДСОРПЦИОНЕ ТЕРМОДИНАМИКЕ И КИНЕТИКЕ УКЛАЊАЊА Cr(III) И Ni(II) ПОЛИАКРИЛАМИДОМ

HASSAN ZAVVAR MOUSAVI[1], ABDORRAHMAN HOSSEINIFAR[2] и VAHDAT JAHED[2]

[1]Chemistry Department, College of Sciences, Semnan University, Semnan u
[2]Aja University of Medical Sciences, Tehran, Iran

Испитиван је полиакриламид (PAA) као адсорбент при уклањању металних јона Ni(II) и Cr(III) из водених раствора. На бази шаржне сорпције испитиване су променљиве које утичу на адсорпциони капацитет адсорбента као што је време контакта, pH сорпционог медијума, концентрација металних јона и температура раствора. Подаци о адсорпционој равнотежи најбоље су апроксимирани моделом Ленгмирове изотерме. Нађено је да су максимуми адсорпционих капацитета 84,03, односно 32,67 mg g^{-1} полиакриламида за Cr(III), односно Ni(II). За праћење адсорпционог процеса одабрана су три модела и једначине: псеудо-први ред, псеудо-други ред и интра-честична дифузија. За сваки модел израчунати су кинетички параметри као што су константе брзина реакција, равнотежни адсорпциони капацитети и одговарајући корелациони коефицијенти. Показало се да су адсорпције оба јона на полиакриламиду могле бити описане моделом кинетике псеудо-другог реда. Одређено је неколико термодинамичких параметара као што су ΔH, ΔS и ΔG, те је закључено да је сорпција изводљива, спонтана и егзотермна.

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