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CHROMIUM (VI) REMOVAL FROM AQUEOUS SOLUTIONS BY PUROLITE BASE ANION-EXCHANGE RESINS WITH GEL STRUCTURE

The removal of Cr (VI) from aqueous solution using two strong base anionic resins with gel structure, purolite A-400 (styrene-divinylbenzene matrix) and purolite A-850 (acrylic matrix) was investigated using a batch technique. The sorption efficiency was determined as a function of phases contact time, solution pH, resin dose, temperature and initial Cr (VI) concentration. The percentage of Cr (VI) removed reached maximum values (up to 99%) in the pH range 4.0-5.3 at a resin dose of 6 g/L and Cr (VI) concentration up to 100 mg/L. An increase in temperature had a positive effect on the Cr (VI) sorption process. The equilibrium sorption data were fitted with the Freundlich, Langmuir and Dubinin-Radushkevich isotherm models, using both linear and nonlinear regression methods. The Langmuir model verified the experimental data very well and gave a maximum sorption capacity of 120.55 and 95.82 mg Cr (VI)/g for the A-400 and A-850 resins, respectively. The thermodynamic study and mean free energy of sorption values calculated using Dubinin-Radushkevich equation indicated the sorption is a chemical endothermic process. The kinetic data were well described by the pseudo-second order kinetic equation and the sorption process is controlled by external (film) diffusion and intraparticle diffusion.

Keywords: anion exchange resins, chromium (VI), isotherms, kinetics, removal.

Chromium is one of the major heavy metal pollutants, usually present in aqueous environment due to effluents discharged from various industries like mining, metallurgy, electroplating, leather tanning, textile dyeing, paint and pigment production, preservation of wood, etc. Under common environmental conditions of pH and Eh, chromium appears in two stable oxidation states, Cr (III) and Cr (VI), which have different physicochemical characteristics and biological reactivity. Generally, Cr (VI) compounds are more soluble, mobile and bioavailable in the environment compared with Cr (III) compounds. While Cr (III) at low concentrations is an essential nutrient for human, plant and animal metabolism, Cr (VI) is harmful in biological systems. Hexavalent chromium (Cr(VI)) is a strong oxidizing agent and can easily cross the cell membranes causing deleterious health problems such as dermatitis, ulcers, kidney and liver damage, respiratory problems, lung cancer, etc. [1,2]. Because of its highly toxicity and carcinogenic properties to living organisms, Cr (VI) has been considered an *a priori* pollutant. The permissible limit for Cr (VI) in drinking water is 0.05 mg/L [3].

Therefore, the removal of large amounts of Cr (VI) from industrial effluents before their discharge into aquatic ecosystems is of considerable concern. The methods commonly used for chromium (VI) removal are reduction and precipitation as Cr (III) hydroxide, ion exchange, adsorption, membrane filtration and electrochemical treatment; selection of the suitable method depends on the initial Cr (VI) concentration, environmental impact and operational cost of the process [4,5].

Sorption onto various materials, including ion exchange and adsorption, may be considered an ideal opportunity for the removal and recovery of Cr (VI). The sorption process involves a solid phase (sorbent) and a liquid phase (usually water) containing dissolved species to be sorbed. Due to the sorbent affinity, the sorbate species are attracted there and

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bounded by different mechanisms (van der Waals forces, electrostatic interactions, covalent bonding); the process continues until the equilibrium is established. Among the materials applied as effective sorbents for Cr (VI) removal are activated carbon, mineral oxides, various industrial and agricultural by-products biosorbents and polymer resins [2,5-9]. Because of their high chemical and mechanical stability, high ion exchange capacity and ion exchange rate, anion exchange resins are versatile sorbents used to remove Cr (VI) from different aqueous media [10]. Other major advantages of the use of ion exchange resins over conventional treatment methods include: minimization of chemical and/or biological sludge, regeneration of sorbent, possibility of metal recovery. Both strongly basic anion exchange resins (SBA) and weakly basic anion exchange resins (WBA) can be utilized, however the last are preferred due to their better regeneration efficiencies. The advantages of the gel type resins are greater operating efficiencies and a lower cost price, while macroporous resins have better physical stability and organic fouling resistance. Among the two basic types of the polymer matrix, styrene-DVB and acrylic, the acrylic resins have limited applications due to weaker physical and chemical stability. Some of various anion exchange resins (commercially or synthesized by authors) investigated for removal of Cr (VI) from aqueous media are listed in Table 1.

This paper describes the sorption of Cr (VI) from aqueous solutions on two strong base anionic resins, purolite A400 and purolite A850, using a batch method. The effects of process variables, such as phases contact time, pH, resin amount, temperature and concentration of Cr (VI) were investigated. The equilibrium sorption data were fitted with various isotherm and kinetic models to find the best fit model for the sorption system.

EXPERIMENTAL

Materials

The strongly basic anion-exchange resins were supplied from Purolite International Ltd.; their main characteristics from the guideline of manufacturer are given in Table 2. Both resins have similar functional groups and gel structure but differs by matrix chemical structure.

The stock solution of Cr (VI) (1040 mg/L) was prepared using analytical reagent grade potassium dichromate ($K_2Cr_2O_7$) (Sigma) in doubly distilled water. All working solutions were prepared by appropriate dilutions of the stock solution.
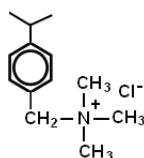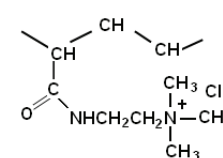
Chromium sorption experiments

Batch sorption experiments were performed in 250 mL conical flasks by shaking the required amount of dry anion exchange resin with 50 mL aqueous solutions of Cr (VI) of a known concentration, at a constant temperature (thermostat Grant Instrument of OLS 200 model). The initial pH of the solutions was adjusted to the desired value by the addition of HCl diluted solutions. After a specified phases contact time, the resin was separated by filtration and the

Table 1. Anion exchange resins used for removal of Chromium (VI)

Resin name	Main characteristics of the resin	Ref.
Lewatit MP64	Macroporous styrene-DVB matrix, WBA type, tertiary and quaternary amine groups	[10,11]
Lewatit MP500	Macroporous styrene-DVB matrix, SBA type, quaternary amonium group	[10]
Lewatit 610	Macroporous styrene-DVB matrix, SBA type, tertiary amine (dimethyl aminoethanol) group	[12]
Lewatit MP62	Macroporous styrene-DVB matrix, WBA type, tertiary amine group	[12]
Lewatit FO36	Macroporous, polystyrene-based, monodispersed, SBA type, doped with a nano-scaled film of iron oxide	[13]
Amberlite IRA-400	Macroporous styrene-DVB matrix, SBA type, quaternary amine group	[14]
Amberlite IRA 410	Gel, styrene-DVB matrix, SBA resin, quaternary amine group type 2	[15]
Amberlite IRA 910	Macroreticular crosslinked polystyrene matrix, SBA, quaternary amine group type 2	[16]
Amberlite IRA96	Styrene-DVB matrix (macroreticular), WBA type, tertiary amine group	[17]
Dowex 1x8	Styrene-DVB, fine mesh, SBA type, quaternary amine group	[17]
Dowex 1x8	Gel, styrene-DVB matrix, SBA type, quaternary amine group	[18]
D301, D354	Macroporous styrene-DVB matrix, WBA type, tertiary amine group	[19]
D314	Macroporous polyacrylic matrix, WBA type, tertiary amine group	[19]
RQA	Glycidyl methacrylate matrix, SBA type, quaternary amine group	[20]
701 (China)	Propylene oxide - polyethylene polymer, gel, epoxy WBA resin	[21]
PyR1, PyR2	Gel (pyr1) and macroporous (pyr2) 4-vinyl-pyridine-DVB matrix, SBA type, quaternary nitrogen atom	[22]
SBAB	Acrylic copolymer, SBA type with tertiary amine, quaternary ammonium and ketone groups	[23]

Table 2. Physicochemical properties of purolite anion exchange resins

Characteristic	A400	A850
	Matrix structure	
	Polystyrene - DVB	Polyacrylic - DVB
Functional group	Quaternary ammonium	Quaternary ammonium
Ionic form	Cl⁻	Cl⁻
Porosity	Gel	Gel
Particle size range, mesh	16-50	16-50
Total capacity, eq/L; eq/kg dry mass	1.3; 3.7	1.25; 4.23
Moisture retention, %	48-54	57-62
Shipping weight, g/L	680-695	720
pH range, stability	0-13	No limitations
Maximum operating temperature, °C	100	40

residual concentration of Cr (VI) in solution was analyzed. The effect of the operating process parameters was investigated according to the conditions listed in Table 3.

Analysis

The residual concentration of Cr (VI) was determined through atomic absorption spectrometry. The absorbance measurements were performed using a GBC Avanta 2007 atomic absorption spectrometer; the operational parameters of the device were: flame air-acetylene, Cr-hollow cathode lamp at 4 and 6 mA current setting and wavelength, 357.9 nm.

All samples were read three times at FAAS and the mean value of chromium concentration was calculated.

The efficiency of Cr (VI) removal was assessed by percentage removal of Cr (VI), R (%), by the sorbed amount of Cr (VI) per unit weight of the resin beads, q_e (mg/g), and by fractional attainment of equilibrium, F, calculated using following equations:

$$R = \frac{(C_0 - C_e)}{C_0} 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)}{m} V, \text{ mg/g} \tag{2}$$

$$F = \frac{(C_0 - C_t)}{(C_0 - C_e)} \tag{3}$$

where C_0, C_t and C_e are the Cr(VI) concentration (mg/L) in solution at the initial moment, at time t and at the equilibrium, respectively, m is the amount of dry resin (g) and V is the solution volume (L).

The pH of the solutions was measured with a pH-meter Inolab pH/ion analyzer 735.

Infrared spectroscopic analysis of anion exchange resins before and after Cr (VI) sorption was performed on a FT-IR BioRad spectrometer FTS2000 with 4 cm⁻¹ resolution for 32 scans, using KBr pellets.

RESULTS AND DISCUSSION

Effect of phases contact time

The effect of phases contact time on the amount of Cr (VI) sorbed on Purolite A400 and Purolite A850 resins (2 g/L) from solutions of pH 5.3 and initial concentration of 104 mg/L, at 20 °C is presented in Figure 1.

Table 3. Experimental conditions in Cr (VI) removal by anion exchange resins

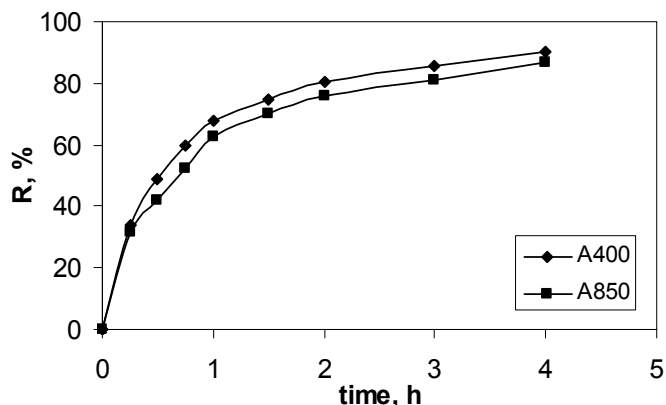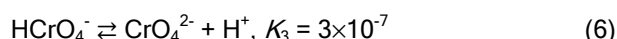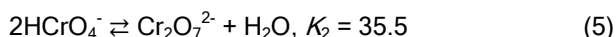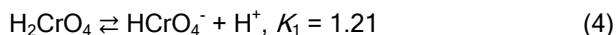| Operating variable	Solution pH	Amount of resin g/L	Concentration of Cr(VI) mg/L	Temperature °C	Phases contact time h
Effect of phases contact time	5.3	2	104	20	0.4-24
Effect of solution pH	2-6.5	2	104	20	24
Effect of resin dose	5.3	2-10	104	20	24
Effect of temperature	5.3	2	104	5-40	4
Effect of Cr(VI) concentration	5.3	2	41.6-208	20	24

Figure 1. Effect of the phases contact time on the Cr (VI) sorption by anionic resins: pH 5.3, 2 g resin/L, $C_0 = 104$ mg Cr/L, $T = 20$ °C.

The removal of Cr (VI) is quite rapid especially in the first two hours (about 50% of the chromium is sorbed within 30 min) and thereafter the rate of the sorption process gradually becomes slower. A further increase in phases contact time from 4 hours to 24 hours has a minor positive effect (an increase of the removal percentage values with 2.47% for A400 and 3.61% for A850, respectively). Both anionic resins have a gel structure with small and uniform pores that arise during the swelling of the resin particles in water and exhibit comparable kinetic properties in removal of Cr (VI) from aqueous solutions.

Effect of solution pH

In aqueous solutions Cr (VI) appears as different species: chromic acid (H_2CrO_4) and anionic species hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$), which distribution depends on pH and total chromium concentration [1,24]. Using published values of constants which characterize the following equilibriums for chromium anions [7,25]:

$$H_2CrO_4 \rightleftarrows HCrO_4^- + H^+, \; K_1 = 1.21 \tag{4}$$

$$2HCrO_4^- \rightleftarrows Cr_2O_7^{2-} + H_2O, \; K_2 = 35.5 \tag{5}$$

$$HCrO_4^- \rightleftarrows CrO_4^{2-} + H^+, \; K_3 = 3\times10^{-7} \tag{6}$$

A speciation diagram of Cr (VI) at a total concentration of 104 mg Cr(VI)/L (0.002M) was constructed (Figure 2).

Figure 3 shows the sorption of Cr (VI) from aqueous solutions at initial concentration 104 mg/L on anion exchange resins purolite A-400 and A-850 as a function of pH in the range 2-6.5, when $HCrO_4^-$ ions is the dominant species in solution.

Note that for both resins the values of Cr (VI) removal percentage are generally between 80 and 90% and vary insignificantly at pH increase in the range 2-6, in agreement with the behaviour of strong base anion exchange resins which are highly ionized and suitable for anions removal over the entire pH range:

$$R-N(CH_3)_3]^+Cl^- + HCrO_4^- \rightleftarrows$$
$$R-N(CH_3)_3]^+ HCrO_4^- + Cl^- \tag{7}$$
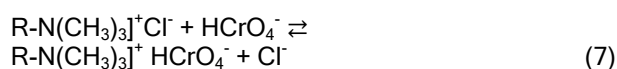
However, the maximum removal of Cr (VI) (92--90%) was achieved in the pH range 4-5.5. The observed decrease in the uptake value at pH 2-3 may be attributed to the higher concentration of chloride anions (HCl was used for pH adjustment) which com-
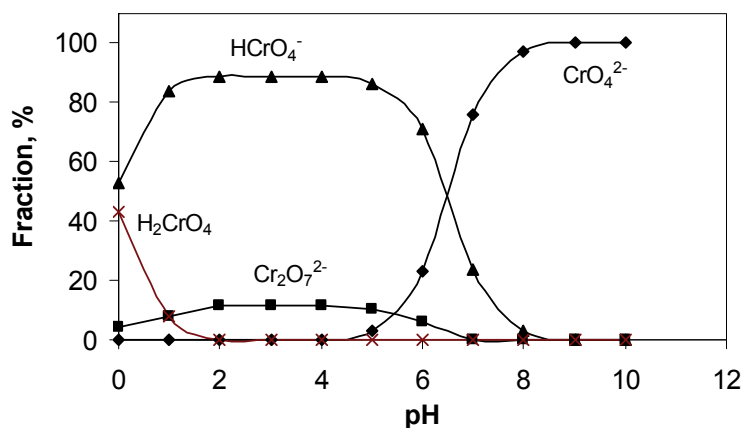

Figure 2. Relative distribution of Cr (VI) species as a function of pH for a total Cr (VI) concentration of 104 mg/L.
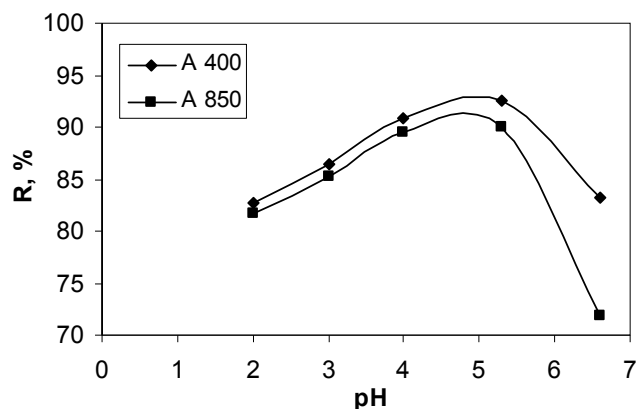
Figure 3. Effect of pH on the sorption of Cr (VI) by strongly base resins: 2 g resin/L, C_0 = 104 mg Cr/L, 24 h, T = 20 °C.

pete the $HCrO_4^-$ for interaction with amine active sites. When pH becomes 6-6.5 a decrease of percentage removal of Cr (VI) occurs, due to the increasing of CrO_4^{2-} concentration in solution (two ion exchange sites are needed to bind each Cr ion).

The chromium removal percent of A400 resin is slightly higher than that of A850. This is because the binding of Cr (VI) by anion exchange resins involves a predominant electrostatic interaction and a secondary hydrophobic interaction. The low charge density of $HCrO_4^-$ (1 negative charge to 6 atoms) justifies its hydrophobic character and explains its affinity for hydrophobic polystyrene-DVB matrix (A400). Unlike resins with polystyrene-DVB matrix, the hydrophobic character of polyacrylic resins (A850) is weaker due to the presence of carbonyl groups (C=O), able to form hydrogen bridges with water molecules [26,27].

Another process that may contribute to the Cr (VI) removal in acidic media is the reduction of toxic Cr (VI) (E^0 = 1.33 V) to less toxic Cr (III) in presence of the electron donor groups from the resin structure [16,23]; this condition is fulfilled by the A850 acrylic resin containing the carbonyl groups.

Effect of strongly basic anion exchange resin dose

The effect of the resin dose on the removal efficiency of Cr (VI) is shown in Figure 4.

When the dose of anion exchange resin was increased from 2 to 10 g/L the percentage of Cr (VI) removed increase from 92.5 (for A400 resin) and 90.02% (for A850), respectively, to over 99.5% for both resins. This is because at higher amount of the resin more adsorption sites are available to retain the chromium anions. It is observed that the quantitative removal of 104 mg Cr (VI) in 1 L solution require a minimum resin amount of 6 g; however, for subsequent experiments the resin dose selected was 2 g/L.

Effect of temperature

The effect of temperature on the Cr (VI) removal by anion exchange resins Purolite A-400 and Purolite A-850 in solutions at pH = 5.3 and 104 mg Cr (VI)/L, with a resin dose of 2 g/L and a contact time of 4 hours was investigated. The results are presented in Table 4.

The obtained data shows an increase of Cr (VI) amount sorbed by anionic resins (A-400 > A-850) with increasing temperature in the range of 5-40 °C. In the mentioned experimental conditions the removal of Cr
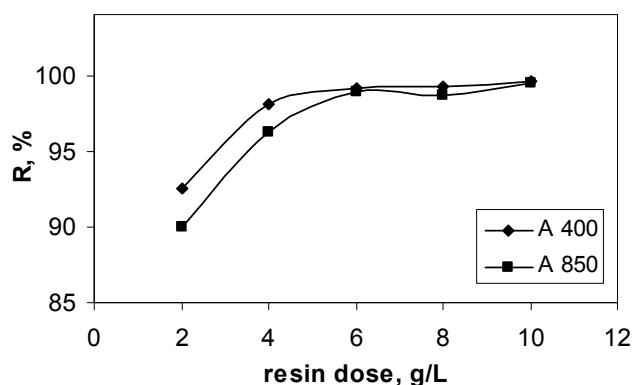

Figure 4. Effect of the resin dose on the removal of Cr (VI): pH 5.3, C_0 = 104 mg Cr/L, 24 h, T = 20 °C.

(VI) from aqueous solution is almost complete at 40 °C. This may indicate that the sorption of Cr (VI) by studied anion exchange resins is an endothermic process facilitated by the higher temperatures. In addition, the increase in Cr (VI) removal efficiency with rise in temperature might be due to the enhanced sorption rate.

Table 4. Effect of temperature on the Cr (VI) sorption by anion exchange resins

Temperature °C	Purolite A400		Purolite A850	
	q_e, mg Cr(VI)/g	R / %	q_e, mg Cr(VI)/g	R / %
5	37.54	72.2	33.18	63.8
20	48.10	92.5	46.81	90.02
40	51.64	99.3	51.32	98.70

Effect of initial Cr (VI) concentration

Cr (VI) removal by the two strong base anion exchange resins, purolite A400 and purolite A850, was studied in solutions with initial concentration between 41.6 and 208 mg/L and the results are presented in Figure 5.

The highest Cr (VI) removal percentages (93--94%) were obtained in solutions of initial concentration 40-80 mg Cr (VI)/L. The increase in chromium concentration over 80 mg/L decreases the percentage of Cr (VI) retained and thus in solutions with 208 mg Cr (VI)/L, the R values are 84.78 (for A400 resin) and 76.44% (for A850 resin). This is explained by that the occupation of available surface sorption sites (at the higher Cr (VI) concentrations) inhibits diffusion of hydrogen chromate anions to the sites from porous structure of the resins. The differences in the affinities of the two strong basic anionic resins result from their different hydrophobic character, as mentioned above.

Sorption isotherms

Experimental isotherms are essential for the study of a sorption system, yielding data that faci-litates designing and optimizing the process. The equilibrium sorption experiments were carried out using initial concentration of Cr (VI) varying from 41.6 to 208 mg/L, at pH 5.3, a resin dose of 2 g/L, temperature of 20 °C and 24 h phases contact time. Figure 6 shows the distribution of solute (Cr (VI) as $HCrO_4^-$ anions) between the liquid phase (aqueous solution) and solid phase (anion exchange resins) at equilibrium state. The initial slope and curvature of the isotherms suggest a strong sorption of Cr (VI) by studied anionic resins.

The experimental isotherm data obtained on the sorption of Cr (VI) by anionic resins Purolite A400 and Purolite A850 were fitted by the well-known isotherm models given by Freundlich, Langmuir and Dubinin-Radushkevich.

The Freundlich isotherm model, which assumes a heterogeneous sorption surface and active sites with different energy, is expressed as [28]:

$$q_e = K_F C_e^{1/n} \tag{8}$$

where K_F (mg L$^{1/n}$/g mg$^{1/n}$) is a constant related to the sorption capacity and n is an empirical parameter that characterize the sorption intensity.

The Langmuir model assumes that sorption occurs in a monolayer onto a homogeneous surface containing a finite number of identical sites, without interactions between sorbed solutes. The Langmuir isotherm is given by the following equation [29]:

$$q_e = q_{max} \frac{C_e K_L}{1 + C_e K_L} \tag{9}$$

where q_{max} is the maximum monolayer sorption capacity of sorbent (mg/g) and K_L is the Langmuir constant related to energy of sorption (L/mg).

The Dubinin-Radushkevich (D-R) isotherm can be used to describe sorption on both homogeneous and heterogeneous surfaces and estimates the characteristics porosity of the sorbent and the mean free
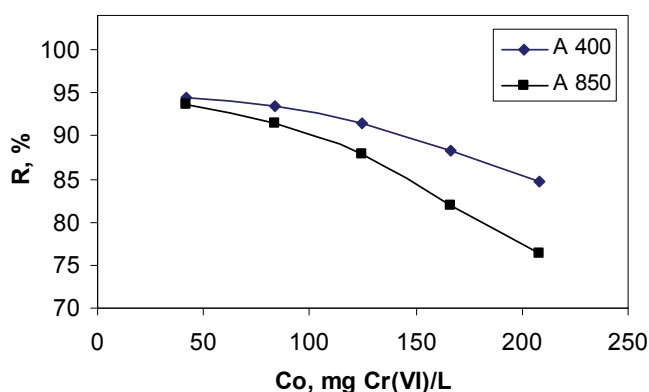
Figure 5. Effect of initial Cr (VI) concentration on the removal by anion exchange resins: pH 5.3; 2 g resin/L, 24 h, T = 20 °C.

energy of sorption [30]. The isotherm equation is given as follows:

$$\ln q_e = \ln q_D - B\varepsilon^2 \tag{10}$$

where q_D is the maximum amount sorbed (mg/g), and the Polany potential (ε) is equal to:

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \tag{11}$$

Using the value of coefficient B (mol^2/kJ^2), the mean free energy of sorption, E (kJ/mol), can be calculated using the relationship:

$$E = \frac{1}{\sqrt{-2B}} \tag{12}$$

The isotherm models were fitted to experimental data for Cr (VI) sorption onto the strongly basic anion exchange resins purolite A-400 and purolite A-850, using both linear and nonlinear regression methods. In the linear regression the constants of the isotherms were determined by means of "Regression" function in the Excel Analysis Tools, using the linear forms of isotherm models (log q_e vs. log C_e, C_e/q_q vs. C_e and ε^2 vs. ln q_e, respectively). Nonlinear regression analysis was performed using the Solver add-in functions of Microsoft Excel software, to minimize the sum of the squared errors. In order to evaluate whether the model was adequate to describe the experimental equilibrium data, along with the values of correlation coefficients (R^2), two error functions were used for error analysis, namely the residual root mean square error (RMSE) and chi-square test, expressed by equations [31,32]:

$$RMSE = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}(q_{e,exp} - q_{e,calc})^2} \tag{13}$$

$$\chi^2 = \sum_{i=1}^{n}\frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,calc}} \tag{14}$$

where subscripts "exp" and "calc" indicate the experimental and calculated values for the each isotherm model, respectively, and n is the number of measurements. The higher R^2 values and smaller RMSE and chi-square are better for data fitness.

The comparison of the experimental data with the Freundlich, Langmuir and Dubinin-Radushkevich isotherms obtained by non-linear method (more appropriate to obtain the isotherms parameters due to the uniform error distribution) showed in Figure 6 suggests that the Langmuir model is the best one in simulating the sorption isotherms of Cr (VI) on both anion exchange resins. The isotherm parameters obtained using linear and nonlinear regression, the correlation coefficients R^2 and the error functions associated at each model are summarized in Table 5.

As can be seen from Table 5, for both anionic resins and all studied isotherm models, the values of R^2, RMSE and chi-square are smaller for the non-linear regression confirms that this is a better way to predict the isotherm parameters; evaluating the degree of fitness to the isotherm models leads to the following order: Langmuir > Dubinin-Radushkevich > > Freundlich.

Based on a comparison of the mentioned values, it is obvious that the Langmuir isotherm model verifies the experimental sorption data better than
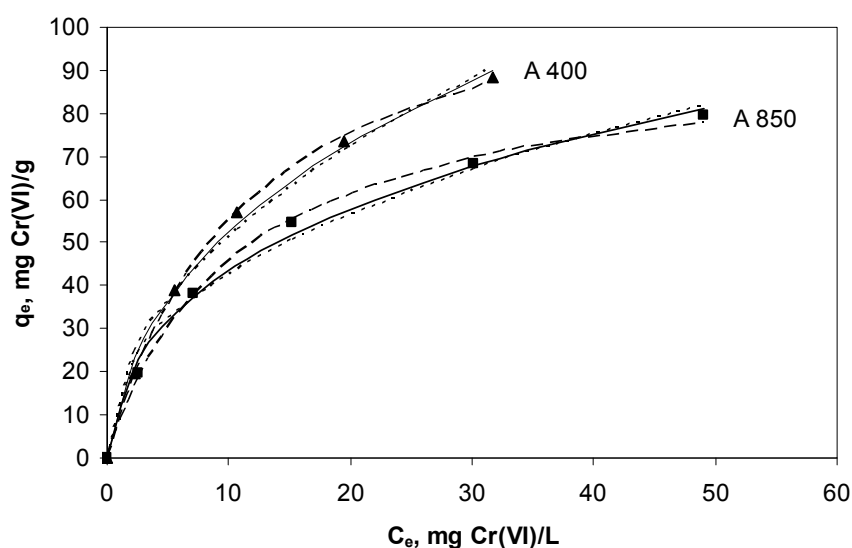

Figure 6. Sorption isotherms of Cr (VI) on strong base anionic resins: pH 5.3; 2 g resin/L, 24 h, T = 20 °C., ▲, ■ experimental points; - - - Freundlich isotherm; · · · Langmuir isotherm; —— Dubinin-Radushkevich isotherm.

Table 5. Isotherm constants for Freundlich, Langmuir and Dubinin-Radushkevich isotherm models for Cr (VI) sorption on purolite A400 and purolite A850 anionic resins

Isotherm parameter	Linear regression analysis		Nonlinear regression analysis	
	A-400	A-850	A-400	A-850
Freundlich				
$1/n$	0.5712	0.4737	0.4961	0.4123
K_F, mg L$^{1/n}$/g mg$^{1/n}$	13.397	13.670	16.378	16.462
R^2	0.9749	0.9724	0.9857	0.9832
RMSE	6.0607	5.4496	4.3115	4.0777
Chi-test	1.7400	1.5883	1.5720	1.4551
Langmuir				
q_{max}, mg/g	120.55	95.822	120.04	95.206
K_L, L/mg	0.0840	0.0913	0.0846	0.0916
R^2	**0.9970**	**0.9976**	**0.9979**	**0.9972**
RMSE	0.9537	1.6702	0.9452	1.6238
Chi-test	0.0438	0.1709	0.0423	0.1687
R_L	0.054 ÷ 0.222	0.050 ÷ 0.208	0.054÷ 0.221	
Dubinin-Radushkevich				
q_D, mg/g	573.56	331.49	457.43	280.03
B, mol^2/kJ^2	0.00556	0.00476	0.00499	0.00430
E, kJ/mol	9.483	10.249	10.010	10.782
R^2	0.9869	0.9870	0.9963	0.9978
RMSE	4.3956	3.8263	3.1051	2.8708
Chi-test	0.9216	0.7889	0.8589	0.7474

other the models, which suggests that sorption of chromium ions by the resin particles occurs in homogeneous sites and generates monolayer patterns. The purolite A400 resin with polystyrene-DVB matrix exhibits higher sorption capacity than polyacrylic A850; the maximum sorption capacity of Cr (VI) corresponds to 62.62 (for A400) and 43.7% (for A850), respectively, from total exchange capacity of the dry anionic resins. Besides electrostatic interactions, hydrophobic interactions also contribute to the affinity of hydrophobic hydrogen chromate anion for non-polar polystyrene-DVB matrix.

The maximum sorption capacity of Cr (VI) by the anion exchange resins Purolite A-400 and A-850 was comparable with of other anionic resins reported in literature and much higher than of natural sorbents (Table 6).

The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor, R_L, expressed as [38]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{15}$$

The value of R_L indicated the shape of the

Table 6. Comparison of Cr (VI) sorption capacity by different sorbents

Sorbent	Sorption capacity, [a]mg/g ; [b]mmol/g	Experimental conditions	Ref.
Lewatit M 62; Lewatit MP 610	0.40[b]; 0.41[b]	pH 5; 1.7 g resin /L; 25 °C; 2h	[12]
Amberlite IRA-96; Dowex 1x8	0.46[b] ; 0.54[b]	pH=5; 1.6 g resin/L; 25 °C; 50 min	[17]
D301; D314; D353	151.52[a]; 120.48[a]; 156.25[a]	pH = 4-5; 27 °C ; 2h	[19]
SBAB	161.2[a]	pH 3.5; 4 g/L; 20 ºC; 72h	[23]
Natural sorbents (rice straw, rice bran, rice husk, hyacinth roots, neem leaves, coconut shell)	12.17[a]; 12.34[a]; 8.5[a]; 15.28[a]; 15.95[a] ;18.69[a]	pH 1.5-2; 10 g sorbent/ L; 30 °C; 3-6 h	[33]
PGME1-deta; PGME2-deta; PGME3-deta	132[a]; 143[a]; 25.6[a]	pH 1.8; 25 °C; 10 g resin/L; 3h	[34]
Magnetic m-poly[DVB-VIM] microbeads	108.7[a]	pH 2; 1 g resin/L; 25 °C	[35]
PGMA; PGMA Fe	132.5[a]; 162.9[a]	pH 4; 25 °C	[36]
Amberlite IRA 743	29.35[a]	pH 4; 1 g resin/L; 30 °C; 30 min	[37]
Purolite A-400; purolite A-850	120.55[a] ; 95.82[a]	pH 5.3; 2 g resin/L; 20 ºC; 24h	This study

isotherm: unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$). The values of R_L were found to be between 0 and 1 for all the Cr (VI) concentrations in this study and both A-400 and A-850 resins, indicating favourable sorption of Cr (VI) by anionic resins.

The magnitude of R^2, RMSE and chi-square test indicated a good fit of experimental data to the Dubinin-Radushkevich equation (Table 5). The values of the maximum sorption capacity, q_D (mg/g) as a measure of the porosity characteristics of the sorbent, are much higher than those obtained from Langmuir equation (monolayer sorption capacity), probably because the Dubinin-Radushkevich isotherm follows a pore filling mechanism.

The parameter B (mol^2/kJ^2) gives the mean free energy of sorption, E (kJ/mol), per molecule of the sorbate when is transferred from solution infinity to the surface of the sorbent. Magnitude of E values provides information about sorption mechanism: less than 8 kJ/mol indicate a physisorption process and between 8 and 16 kJ/mol a chemisorption process (ion exchange). The calculated values of E for the Cr (VI) sorption by strongly basic anion exchange resins A-400 and A-850 (Table 4) show, as expected, that the sorption process is chemical in nature.

The values of $1/n$ parameter obtained from Freundlich model (Table 5) are between 0.0 and 1.0 indicating favourable sorption of Cr (VI) onto both resins.

Thermodynamic parameters

The temperature effect on the Cr (VI) sorption by strongly basic anionic resins was used to determine thermodynamic parameters, such as Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0), according to the following equations [19,33]:

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{16}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{17}$$

$$K_d = \frac{C_s}{C_e} \tag{18}$$

where K_d is the sorption equilibrium constant, C_e is the equilibrium concentration of Cr(VI) (mg/L) in aqueous phase, C_s is the amount of Cr (VI) at equilibrium (mg/L) sorbed in the solid resin, R is the ideal gas constant (8.314 J/mol K) and T is the Kelvin temperature.

The values of enthalpy and entropy changes calculated from the slope and the intercept of the plots ln K_d vs. $1/T$ (R^2 values: 0.9750 for A-400 and 0.9848 and for A-850) are given in Table 7.

The negative values of ΔG^0 indicate the spontaneous nature of the sorption. The positive values ΔH^0 revealed that the sorption process is endothermic, favoured by higher temperatures. The ΔS^0 values are positive, suggesting increasing randomness at the solid/liquid interface during the sorption process.

Kinetic study of Cr (VI) removal by anionic resins

The sorption kinetics is an important parameter defining the efficiency of the pollutant removal process because the rate of the sorption controls the residence time of sorbate species at the solid-liquid interface.

The sorption process by ion exchange resins can be described by the three main consecutive steps: *i*) transport of exchangeable ions from the bulk solution to the external surface of the sorbent through the liquid film surrounding resin particles, *ii*) transport of ions in the liquid contained in the pores of resin particles and *iii*) sorption and desorption of ions on/from the active sites of the exchanger. The overall sorption rate may be controlled by any of these steps; a combined effect of few steps is also possible [39]. In order to establish the mechanism of the sorption process and the potential rate controlling step, the experimental data were tested using two types of kinetic models, namely reaction-based and diffusion-based models.

The widely used kinetic models employed to explain solid/liquid sorption as a chemical reaction are pseudo-first order kinetic model (Lagergreen

Table 7. Thermodynamic parameters for the sorption of Cr (VI) by anionic purolite resins

Resin	T/ K	K_d	ΔG / kJ mol^{-1}	ΔH / kJ mol^{-1}	ΔS / kJ mol^{-1} K^{-1}
A-400	278	2.597	-1.680	83.398	0.306
	293	9.256	-6.269		
	313	141.868	-12.389		
A-850	278	1.762	-0.931	78.299	0.285
	293	6.558	-5.206		
	313	75.916	-10.906		

model) and pseudo-second order kinetic model (Ho model), expressed by following simplified linear equations [40-42]:

pseudo-first order kinetic model:

$$\log\left(q_e - q_t\right) = -\frac{k_1}{2.303}t + \log q_e \qquad (19)$$

pseudo-second order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \qquad (20)$$

where q_t and q_e are amount of Cr(VI) sorbed at any time t and at equilibrium (mg/g), respectively, k_1 is the rate constant of pseudo-first order model (min^{-1}), k_2 is the rate constant of pseudo-second order model (mg/g min^{-1}) and $h = k_2 q_e^2$ is the initial sorption rate (mg/g min^{-1}).

The kinetic experiments were carried out using initial concentration of Cr (VI) = 104 mg/L, at pH 5.3, a resin dose of 2 g/L and temperature of 20 °C, and the phases contact time varying between 15 and 240 min. The experimental data of Cr (VI) sorption by studied resins were fitted to the mentioned kinetic models using linear regression. The linear plots log (q_e - q_t) vs. t and t/q_t vs. t, respectively, are presented in Figure 7 and the values of kinetic parameters are systematized in Table 8. The validity of either kinetic model was assessed by means of R^2, RMSE and chi-square test values, calculated using the "Regression" function in the Excel Analysis Tools.

The values of the regression correlation coefficient and especially of error functions (Table 8) show a poor correlation of the pseudo-first order kinetic model with the experimental data of Cr (VI) sorption by both studied anionic resins. The experimental q_e

values are not in good agreement with the theoretical values calculated with the pseudo-first order kinetic model. It is obvious that the pseudo-first order kinetic model shows a much better correlation with experimental data ($R^2 > 0.99$ and error functions values are much lower). In addition to this, theoretical q_e values calculated from pseudo-second order kinetic model are very close to experimental values. Based on these data, it can be concluded that sorption of Cr (VI) by strong base anion exchange resins purolite A-400 and purolite A-850 follows the pseudo-second order kinetic model and sorption is a chemical nature. According to this model derived on the basis of the sorption capacity of the solid phase, the overall sorption rate is proportional with the square of driving force, represented by available fraction of active sites from the sorbent. The initial sorption rates (h) are relatively high, however, small values of k_2 constant rate may be connected with the longer time required to reach the equilibrium state. Similar results were reported by several authors, however a good fitting did not illustrate the real nature of rate-limiting step [22,35,36].

It is well known that the rate of ion exchange is controlled by diffusion, either through the hydrostatic boundary layer (film-diffusion control) either through the pores of the resin matrix (particle-diffusion control) [38]. To highlight the influence of diffusion on the sorption mechanism of Cr (VI) by studied strong base anionic resins, the intraparticle diffusion model (Weber-Morris model) was used. This kinetic model is commonly used to identify the steps involved during sorption with pseudo-second order rate equation and is expressed by equation [43]:
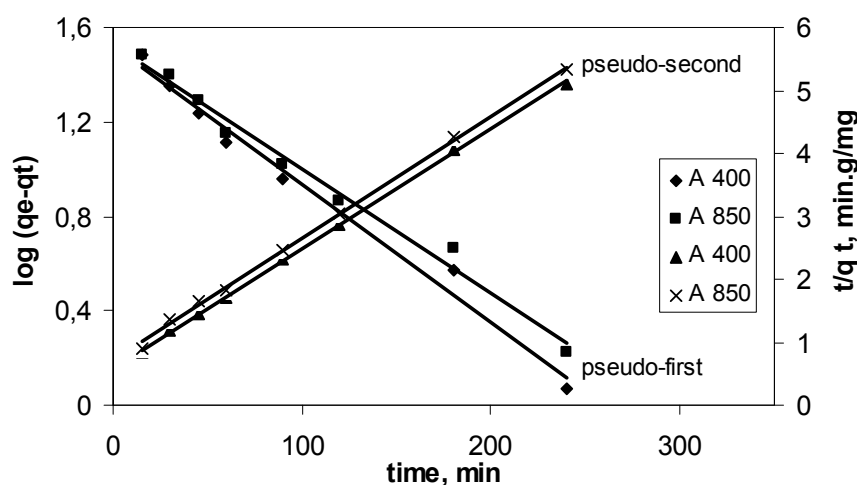
$$q_t = k_d t^{0.5} + C \qquad (21)$$

Figure 7. Pseudo-first order kinetic model and pseudo-second order kinetic model plots for Cr (VI) sorption by anion exchange resins: pH 5.3, C_0 = 104 mg Cr/L, 2 g resin/L, T = 20 °C.

Table 8. Kinetic parameters for the sorption of Cr (VI) by strong base anionic Purolite resins

Kinetic parameter		Purolite A400	Purolite A850
		$q_{e\,exp} = 52.16$ mg/g	$q_{e\,exp} = 51.02$ mg/g
Pseudo-first order model	q_e, mg/g	32.96	33.76
	k_1, 1/min	0.0136	0.0122
	R^2	0.9858	0.9863
	RMSE	10.4445	13.0967
	Chi-test	0.8687	1.0125
Pseudo-second order model	q_e, mg/g	52.63	51.54
	h, mg/g min	1.6955	1.3976
	k_2, g/mg min	0.00061	0.00053
	R^2	0.9997	0.9982
	RMSE	0.4659	2.6690
	Chi test	0.04056	0.3220
Intraparticle diffusion model	k_{d1}, mg/g min$^{1/2}$	4.5753	4.1268
	R^2	0.9997	0.9978
	k_{d2}, mg/g min$^{1/2}$	1.2727	1.3998
	R^2	0.9845	0.9830
Boyd-Reichenberg	R^2	0.9872	0.9845

where k_d is the intraparticle diffusion rate constant (mg/g min$^{0.5}$) and C is the intercept indicating the boundary-layer surface sorption.

The k_d values can be evaluated from the slope of the linear plot q_t *vs.* $t^{0.5}$ (Figure 8a; Table 8).

If the plot q_t *versus* $t^{0.5}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step; if the plot presents multi-linearity, the sorption proceeds by two or more steps. As can be seen from Figure 8, two steps occur at sorption of Cr (VI) by strong base resins A-400 and A850. The first linear portion is attributed to the external mass transfer (boundary layer surface sorption) and the second to the intraparticle (pore) diffusion [44].

An additional confirmation of these results is obtained using the Boyd-Reichenberg kinetic model described by the following equation [45, 46]:

$$F = 1 - \frac{6}{\pi^2} \sum_1^\infty \frac{1}{n^2} \exp\left(-n^2 Bt\right) \tag{22}$$

where F is the fractional attainment of equilibrium at time t and n is a constant and Bt is a mathematical function of F:

$$Bt = -0.4977 - \ln(1 - F) \tag{23}$$

For F values less than 0.85, using Eq. (23), Bt values were calculated at different times, t, and plotted against time, t (Figure 8b). It was observed

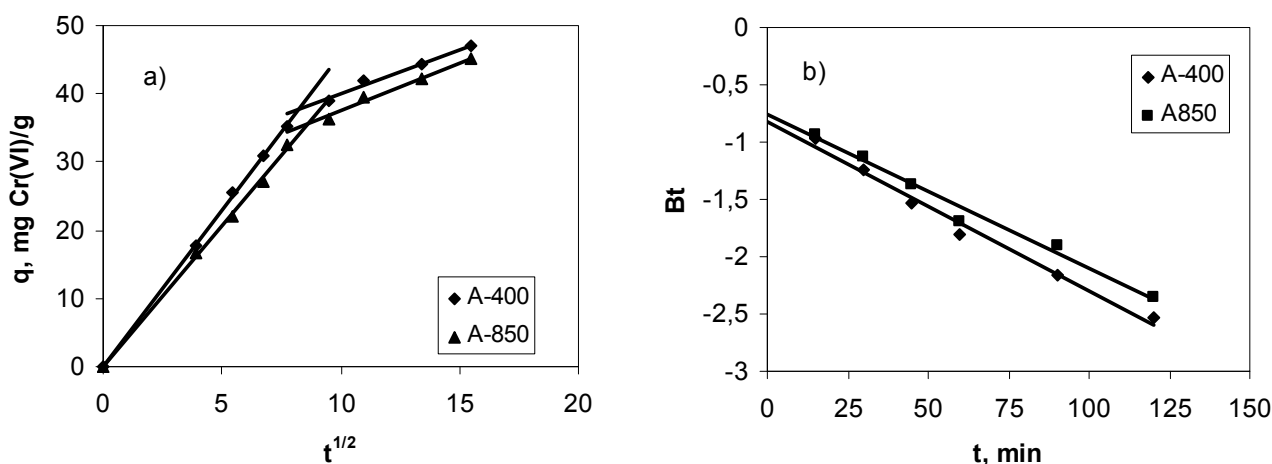*Figure 8. Weber-Morris plots and Boyd-Reichenberg plots for Cr (VI) sorption by anion exchange resins: pH 5.3 C_0 = 104 mg Cr/L, 2 g resin/L, T = 20 °C.*

that the relation Bt-t is linear for both studied resins but does not pass through origin, confirming that the in the initial stages of sorption surface diffusion is the rate-limiting step.

This information, as well as the comparison of the regression correlation coefficients R^2 of the applied diffusion-based kinetic models, shows that under the investigated conditions, for both resins, in the early stage of sorption the film diffusion process is the slowest step, while in the later stage, intraparticle diffusion becomes the limiting mechanism.

It can also be observed that the values of kinetic parameters of all used kinetic models are slightly higher for styrene-divinylbenzene resin than polyacrylic resin, in agreement with the influence of matrix type on Cr (VI) sorption (stronger hydrophobic interactions in the first case).

FT-IR analysis

Additional information about Cr (VI) sorption mechanism by studied anion exchange resins can be obtained using FT-IR analysis. Figure 9 shows FT-IR spectra of the A-850 resin before and after Cr (VI).

Comparing the two FT-IR spectra reveals that after the sorption of Cr (VI) onto the A-850 resin the position and intensity of peaks assigned to the -$N^+(CH_3)_3$ groups were affected. Thus, the peaks corresponding to C-H symmetric bending of the methyl groups of the quaternary ammonium and the C-N stretching vibration were minimized and shifted from 1489.04 and 1456.25 cm^{-1} to 1473.61 and 1458.18 cm^{-1}, respectively [47,48]. These observations show that the sorption of Cr (VI) implies an ion exchange reaction with a quaternary ammonium functionalized polymer.

In addition, in the resin spectrum after Cr (VI) sorption two new significant peaks are evidenced at 948.96 and 777.31 cm^{-1}, assigned to the Cr=O and Cr-O bonds, respectively.

CONCLUSIONS

Two commercially strong base anionic resins, purolite A400 (styrene-divinylbenzene) and purolite A850 (acrylic), were used in batch conditions to remove Cr (VI) from aqueous solutions. The effect of
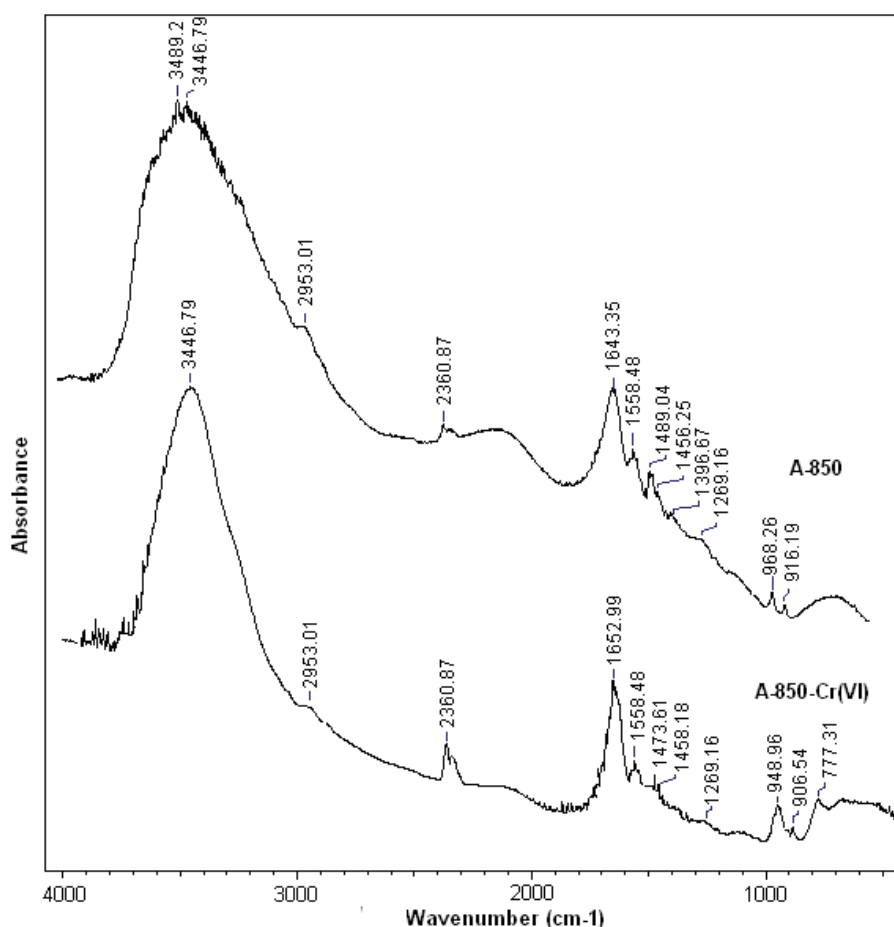

Figure 9. FT-IR spectra of anion exchange resin A-850 before and after sorption of Cr (VI).

process variables, such as pH, resin amount, concentration of Cr (VI), temperature and phases contact time, on the sorption of Cr (VI) was investigated. The Cr (VI) removal efficiency is highest in solutions of initial pH between 4 and 5.5 and a chromium concentration up to 80 mg/L and increases with the rise of resin dose, solution temperature and phases contact time. The equilibrium data were better correlated with the Langmuir isotherm, which indicates a chemosorption process in a monolayer on homogeneous active sites of the resin particles (ionic exchange). The values of mean free energy and of thermodynamic parameters confirm an endothermic chemisorption process. Kinetic analysis of the experimental data shows that sorption of Cr (VI) on the studied resins follows well the pseudo-second order equation and is controlled by film diffusion in the initial stage of the sorption and by intraparticle diffusion in the later stage. Due to the differences in hydrophobic/hydophilic character of the resin matrix, the removal efficiency of Cr (VI) is slightly higher on styrene-divinylbenzene resin purolite A400 compared with polyacrylic resin purolite A850.

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NAUČNI RAD

UKLANJANJE HROMA (VI) IZ VODENIH RASTVORA POMOĆU PUROLITA - BAZNE ANJONSKE SMOLE SA GEL STRUKTUROM

Ispitivano je uklanjanje Cr(VI) iz vodenog rastvora korišćenjem dve bazne anjonske smole sa gel strukturom: purolit-400 (stiren-divinilbenzen matriks) i purolit-850 (akrilni matriks), korišćenjem šaržnom tehnikom. Efikasnost sorpcije je određena kao funkcija vremena faznog kontakta, pH rastvora, količine smole, temperature i početne koncentracije Cr (VI). Procenat uklonjenog Cr(VI) dostiže maksimalnu vrednost (do 99%) u opsegu pH 4 ,0-5,3 pri količini smole od 6 g/l i koncentraciji Cr(VI) do 100 mg/l. Povećanje temperature pozitivno utiče na sorpciju Cr(VI). Podaci ravnotežne sorpcije su fitovani pomoću Freundlich-ovog, Langmuir-ovog i Dubinin-Radushkevich-ovog modela, korišćenjem linearnog i nelinearnog metoda regresije. Langmuir-ov model veoma dobro fituje eksperimentalne podatke i daje maksimalni kapacitet sorpcije od 120,55 mg Cr (VI)/g i 95,82 mg Cr (VI)/g za A-400 i A-850 smole, resdom. Termodinamičko ispitivanje i vrednost slobodne energije sorpcije izračunate pomoću Dubinin-Radushkevich-eve jednačine pokazuje da je sorpcija endotermni proces. Kinetika je u skladu sa jednačinom pseudo-drugog reda i proces sorpcije je kontrolisan pomoću eksterne i intrapartikularne difuzije.

Ključne reči: anjonske smole, hrom(VI), izoterme, kinetika, odstranjivanje.