



## Sorption studies of chromium(VI) onto new ion exchanger with tertiary amine, quaternary ammonium and ketone groups

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### ABSTRACT

A new acrylic anion exchanger with both tertiary and quaternary ammonium as well as ketone groups in the structural unit has been prepared by the nucleophilic substitution reaction of aminolyzed vinylacetate:acrylonitrile:divinylbenzene copolymer of porosity structure in the swelling state with 2-chloroacetone as a halogenated compound. The new compound exhibits better qualities of strong base exchange capacity than the weak base anion exchangers. The obtained acrylic anion exchanger was used to remove Cr(VI) from the aqueous solution. Batch adsorption studies have been carried out to determine the effect of contact time, concentration of hexavalent chromium in the solution and pH on the sorption capacity. The kinetic parameters were determined on the basis of the static results. The thermodynamic parameters of Cr(VI) sorption process on the anion exchanger were calculated based on the Langmuir and Freundlich isotherms. Sorption was studied in the pH range of 1.5–7 and it was found that it depends on the solution acidity. At the pH values of 3.5 and 7 the anion exchanger exhibited large values of chromium sorption capacity. The speciation of chromium was investigated in the studied pH range by the Diffuse Reflectance Spectroscopy (DRS) method. Reduction of chromium(VI) to chromium(III) under acidic conditions was observed. The performed acrylic strong base anion exchanger is superior compared to the conventional one based on the styrene:divinylbenzene matrix due to its ability for reposition of the long spacer arm for providing exchange sites, hydrophilic character of matrix, and possible hydrogen bonds provided by carbonyl functional groups.

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### 1. Introduction

The waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units, and tanneries may contain heavy metals with the concentrations exceeding the local discharge limits. These waste streams contain toxic heavy metals such as chromium, cadmium, lead, mercury, nickel, and copper. They are not readily removed without specialized or advanced treatment. Chromium is a common pollutant occurs in the surface or groundwater due to the discharge of a variety of industrial wastewaters. On the other hand, chromium based catalysts are also employed in various chemical processes, including selective oxidation of hydrocarbons. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg L<sup>-1</sup>.

Like all transition metals, chromium can exist in several oxidation states ranging from Cr(0), the metallic form to the hexavalent

form, Cr(VI) [1]. While Cr(III) is generally non-toxic and is believed to be essential in glucose metabolism in mammals [2], Cr(VI) is toxic to animal and plant cells [3]. Furthermore, because of its mutagenic and carcinogenic properties, the hexavalent form has been included in the group "A" of human carcinogens [4,5]. At short-term exposure levels above the maximum contaminant level, Cr(VI) causes skin and stomach irritation or ulceration. Long-term exposure at the levels above maximum a contaminant can cause dermatitis, liver, kidney, nerve tissue damage, and even death in large doses [6].

On the other hand Cr(III), is less toxic than Cr(VI) and is almost insoluble at neutral pH. Cr(III) is listed as an essential element, as a micronutrient, to maintain good health and helps in maintaining the normal metabolism of glucose, cholesterol, and fat in human bodies [7]. It is poisonous only at high concentrations.

Therefore, reduction of Cr(VI) to Cr(III) or the removal of Cr(VI) from contaminated waters and wastewaters is a key process.

Several methods such as, adsorption, biosorption, reduction, and filtration reverse osmosis, ion exchange, foam flotation, electrolysis, and surface adsorption have been reported for chromium removal. In the past decades, adsorption techniques have been widely studied and seem to be a reasonable choice. Several mate-

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rials have been developed and tested, ranging from low cost waste material such as, moss peat [8], sawdust [9], zeolites, clay, hazelnut shell [10], to more sophisticated adsorbents such as, activated carbon, modified zeolite, modified clay [11,12], modified steel slag [13], nanoscale magnetic material [14], chitosan based composite [12,14–16], synthetic polymers [17–25].

Among the physicochemical methods developed for chromium removal from wastewaters, ion exchange is becoming a popular one receiving much attention in recent years. The main advantages of ion exchange are high degree of metal recovery, selectivity, lesser sludge volume produced and the ability to meet strict discharge specification and to reduce dissolved chromate concentration below the detectable levels in the water treatment plants. Ion exchange using synthetic resins is the method suitable for removing toxic contaminants from waters or wastewaters and anion exchange processes can be used for the removal of chromium from wastewaters at alkaline and acidic pH values in the presence of a high concentration of chloride, sulfate, bicarbonate and nitrate ions [26,27].

Strong base anion exchangers containing pyridine moieties have exhibited high selectivity for Cr(VI) and could represent a viable alternative for the selective retention of chromate ions. The previous work was focused on the thermodynamic and kinetic studies of Cr(VI) removal from aqueous solutions by the new adsorbents based on the pyridine resins with different types of substituents namely, methyl, ethyl, butyl, amide, benzyl or ketone functional groups at the quaternary nitrogen atom [28–31]. It has been shown that chromium retention capacity depends on the ionic form of the strong base anion exchangers and the substituent type at the quaternary ammonium atoms. In the competitive adsorption studies, chromate/sulfate revealed the selectivity of the pyridine adsorbents towards chromium ions due to the formation of a sandwich arrangement with the chromium anion and the functional groups attached to the quaternary nitrogen atom.

The literature related to the sorption of hexavalent chromium onto acrylic anion exchangers is rather poor. In fact, various studies presented in journals have used anion exchangers based on the styrene:divinylbenzene or pyridine:divinylbenzene copolymers.

In this paper the primary objective is to show our results about the synthesis of a new acrylic strong base anion exchanger with novel functional groups for selective retention of Cr(VI) as well as the study of chromium sorption and reduction process. Also, chromium sorption investigation in the solid phase was carried out by means of the Diffuse Reflectance Spectroscopy (DRS) method and has been reported for the first time using this acrylic anion exchanger.

The functional groups of the new anion exchanger have been attached to the quaternary nitrogen atoms by the nucleophilic substitution reactions of the acrylic weak base anion exchanger of porous structure in the swelling state with 2-chloroacetone (CIA) as a halogenated compound. The retention studies of the synthesized resin for Cr(VI) were performed under various conditions including phase contact time and pH. The DRS method was used also for tracing changes in time of chromium(VI) in the solid phase during the experiment. In addition, the equilibrium and kinetic parameters of Cr(VI) at pH 1.5 were analyzed at 20 °C.

## 2. Experiment

### 2.1. Materials

Vinylacetate (VAc) with a concentration of 99.50%, acrylonitrile with a concentration of 99.00% (AN) and dimethylaminopropylamine (DMAPA) with a concentration of 99% supplied from Fluka were purified by vacuum distillation immediately before to use.

Divinylbenzene (DVB) supplied from Fluka was a technical mixture of isomers ~80% (GC) with the residual mainly 3- and 4-ethylvinylbenzene.

The initiator (1 wt%), benzoyl peroxide and toluene as a diluent are of analytical grade and were used as received. In the polymerization process, the aqueous phase contains the polymeric stabilizer (0.5 wt%) prepared by hydrolysis with aqueous NH<sub>3</sub> solution of poly(styrene-co-maleic anhydride).

1 M HCl, 1 M NaOH, 5% NaCl and 5% Na<sub>2</sub>SO<sub>4</sub> solutions were used to determine the strong and weak base exchange capacities.

The solutions of 0.1 M NaOH and 0.1 M H<sub>2</sub>SO<sub>4</sub> were used for pH adjustment. Cr(VI) stock solution (from POCH Gliwice Poland) was prepared from potassium salt of chromate (K<sub>2</sub>CrO<sub>4</sub>) which was analytical grade.

### 2.2. Methods

#### 2.2.1. Synthesis of VAc/AN/DVB copolymer

VAc/AN/DVB copolymer with a morphology in the swelling state was obtained by free radical suspension polymerization in water of the corresponding monovinyllic monomer with 10% DVB as a crosslinking agent according to literature [32]. Toluene was used as a diluent throughout this study with a content of  $D=0.2$  calculated as follows:  $D = [\text{mL diluent}/(\text{mL diluent} + \text{mL monomers})]$ .

The polymerization reaction was left to proceed at 65 °C for 4 h, 75 °C for 6 h and then 8 h at 85 °C. Following polymerization, the copolymer beads were washed with warm water and then extracted with acetone in a Soxhlet apparatus to remove traces of residual monomers, linear oligomers, and diluent. Finally, they were vacuum dried at 50 °C for 48 h and sieved into fractions in the range of (0.3–0.8 mm diameter).

The content of DVB units in the copolymers was assumed to be the same as the monomer content in the feed.

#### 2.2.2. Aminolysis reaction of VAc/AN/DVB copolymers with DMAPA

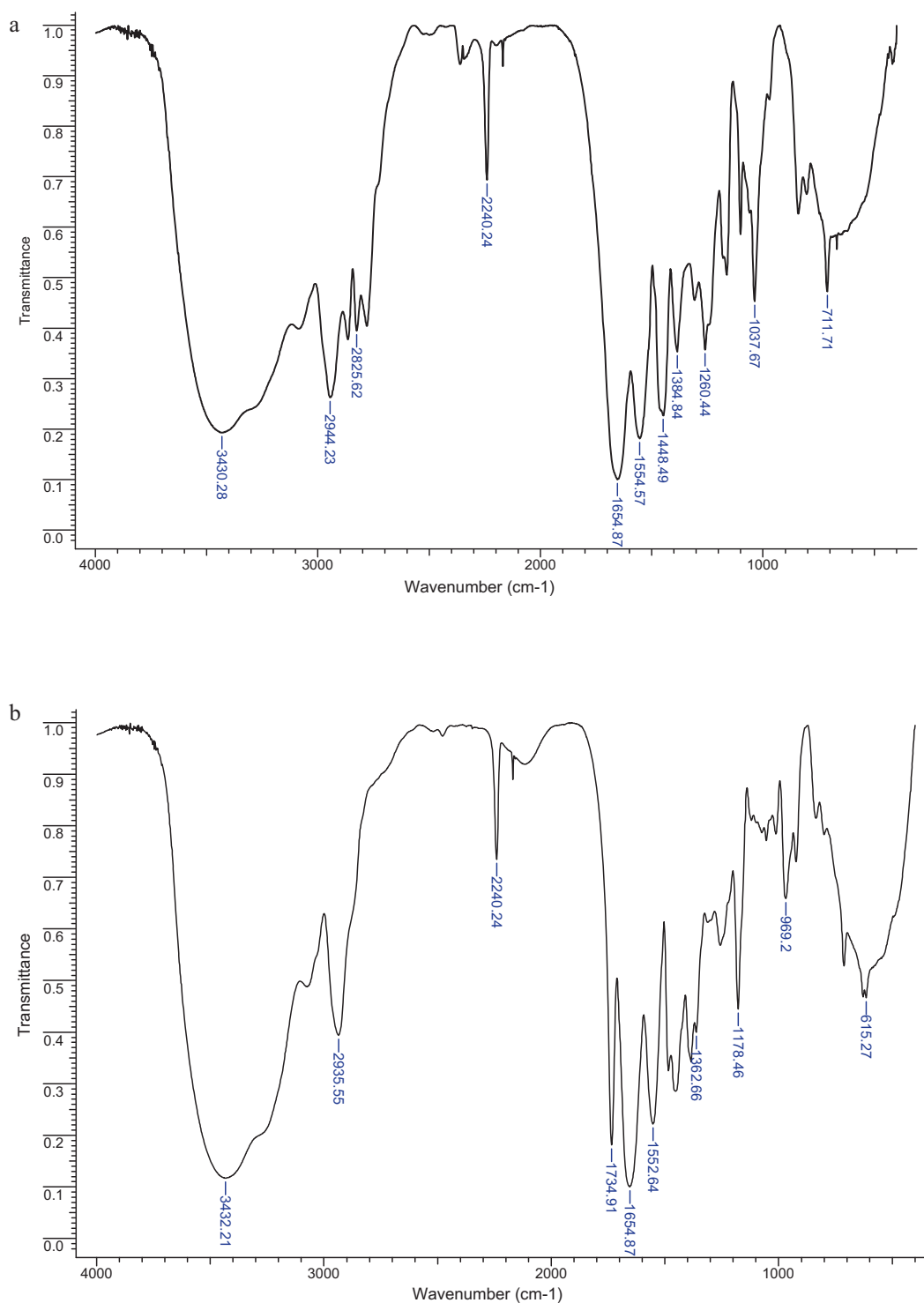
Aminolysis reactions were performed at 115–118 °C with DMAPA, under reflux for 14 h in a glass round-bottomed flask equipped with a stirrer, a reflux condenser and a thermometer. The copolymer:amine ratio was 1:2.5.

At the end of the reaction the synthesized compound was separated by filtration, washed with water and then regenerated with 4% NaOH aqueous solution followed by washing with distilled water until complete removal of alkalinity. After this the ion exchanger was characterized by the following features: the volume weight (WV, g mL<sup>-1</sup>) which was determined by the measurement of the weight loss of a known volume of fully hydrated sample in the free base form, up to constant weight; the volume (CV, mequiv. mL<sup>-1</sup>) and weight (CWt, mequiv. g<sup>-1</sup>) weak base exchange capacities and transformation degree of the aminolysis reaction. The weak base exchange volume capacity (CV) was determined using the following method: a specific volume of the ion exchange resin was treated with a specific volume of 1 M HCl solution of known concentration and the excess of hydrochloric acid was removed by passing the solution of water:methanol 1:2 (v/v) through the resin. The eluent was measured by titration with the 1 M NaOH solution to the end point using the mixed indicator.

CV was calculated according to Eq. (1):

$$CV = \frac{(V_1 f_1 - V_2 f_2)}{V} \quad (1)$$

where  $V_1$  is the volume of 1 M HCl solution, mL;  $V_2$  is the volume of 1 M NaOH, mL;  $V$  is the volume of resin, mL;  $f_1$  is the factor of 1 M HCl solution;  $f_2$  is the factor of 1 M NaOH solution.



**Fig. 1.** FT-IR spectra of aminolyzed (a) VAc/AN/DVB copolymer and quaternized (b) compound.

Weak base anion exchange weight capacity (CWt) was determined by drying of the known volume of the weak base anion exchanger at 110 °C up to constant weight.

CWt was calculated according to Eq. (2):

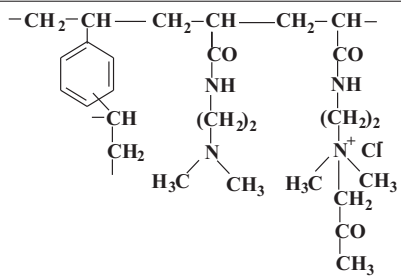
$$CWt = \frac{(V_1 f_1 - V_2 f_2)}{m} \quad (2)$$

where  $V_1$ ,  $V_2$ ,  $f_1$ ,  $f_2$  have the same meaning as in Eq. (1);  $m$  is the weight of the resin, g.

### 2.2.3. Quaternization reaction of the aminolyzed VAc/AN/DVB copolymer with 2-chloroacetone

The acrylic strong base anion exchange resin was obtained by the nucleophilic substitution reaction of EA/AN/DVB copolymer with 2-chloroacetone (CIA). The quaternization reaction was performed in dimethylformamide in the glass round bottomed flask equipped with a stirrer, a reflux condenser and a thermometer. The amount of CIA corresponded to the nitrogen:halogenated compounds molar ratio of 1:1.5. The reaction was carried out at 60 °C for 48 h. After this, the beads were isolated by filtration and washed

**Table 1**  
Characteristics of the preformed acrylic strong base anion exchanger.

Structural unit	WV		Weak base exchange capacity		Strong base exchange capacity	
	WBA (g mL <sup>-1</sup> )	SBA (g mL <sup>-1</sup> )	mequiv. g <sup>-1</sup>	mequiv. mL <sup>-1</sup>	mequiv. g <sup>-1</sup>	mequiv. mL <sup>-1</sup>
 <p style="text-align: center;">SBAE</p>	0.1818	0.1802	0.33	0.06	2.83	0.51

with methanol and finally with distilled water. The sample of anion exchanger was regenerated with 5% NaCl solution, followed by washing with distilled water until complete removal of chlorine ions. The yielded compound was characterized by strong base exchange capacity determined by the ion exchange of Cl<sup>-</sup> for SO<sub>4</sub><sup>2-</sup>.

The strong base exchange volume capacity was determined by the elution of Cl<sup>-</sup> anions with 5% Na<sub>2</sub>SO<sub>4</sub> aqueous solution, the chlorine ions being potentiometrically determined with 0.02 M AgNO<sub>3</sub> aqueous solutions. To calculate the gravimetric strong base anion exchange capacity, the resin was dried at 110 °C to constant weight.

The yielded beads were sieved at a particle size of 0.3–0.8 mm and stored after air drying for the chemical stability and sorption studies.

Chemical stability of the synthesized resin was studied by the batch method by contacting 15 mL of anion exchanger with 25 mL of various concentrations of HCl, NaOH and H<sub>2</sub>O<sub>2</sub> at room temperature for 24 h. After contact, the resin was separated by filtration, washed with distilled water in the glass columns up to the removal of acidity and basicity in the effluents. The resin was regenerated with 5% NaCl, followed by washing with distilled water to remove the excess of chloride ions and finally characterized by strong base exchange volume and weight capacities.

Immersing of a dry sample in distilled water for 24 h and then centrifuging it at 2000 rpm for 20 min determined the water retention capacity.

### 2.3. Sorption experiments

Prior to any experiments the resin was converted to the chloride form. The effect of the chromium concentration on the retention capacity was investigated using the Cr(VI) solutions in the concentration range of 500–2000 mg L<sup>-1</sup>. For the exchange equilibrium measurements, a series of swollen resin samples (0.1 g in the dry state) originally completely loaded with Cl<sup>-</sup> ions was equilibrated with the 25 mL chromate solution of different concentrations at 20 °C in a thermostatic shaker bath in the time range of 1–4320 min. The effect of pH on the removal of chromate ions was investigated by equilibrating 0.1 g resin with 25 mL of chromate solution. The solution pH values were controlled using 0.1 M NaOH and H<sub>2</sub>SO<sub>4</sub>. The solution pH value was controlled during the experiments in order to maintain the same ionic strength in the solution using 1 × 10<sup>-3</sup> M NaClO<sub>4</sub> solution.

In all experiments the samples were separated by filtration and the filtrate was analyzed by the colorimetric method with diphenylcarbazide for Cr(VI) and Arsenazo III for Cr(III) and AAS for Cr(VI) + Cr(III).

Additionally, the amount of chromium(VI) in the solid phase was investigated using the Diffuse Reflectance Spectroscopy (DRS) method.

Infrared spectra of the synthesized compounds were recorded as KBr pellets using a Bruker Vertex 70 FT-IR spectrometer collecting 124-scans with a resolution of 2 cm<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Synthesis of acrylic strong base anion exchanger

Physicochemical characteristics of the obtained compound are presented in Table 1.

In Table 1 it can be seen that the acrylic anion exchanger contains both weak and strong base anion capacities which indicates that the transformation degree of the nucleophilic substitution reaction is not complete. Some tertiary amine groups from the weak base anion exchanger did not transform into the quaternary ammonium ones during the quaternization reaction with 2-chloroacetone. It is obvious that this compound is an acrylic anion exchanger which contains tertiary, quaternary ammonium and ketone groups.

The synthesized acrylic anion exchanger was characterized by FT-IR spectroscopy. For illustration Fig. 1 shows the FT-IR spectra of the aminolyzed VAc/AN/DVB copolymer and the product prepared by its quaternization with 2-chloroacetone.

Spectrum (2) shows the additional band at 1734 cm<sup>-1</sup>, which is characteristic of ketone groups. The bands of 1550 and 1650 cm<sup>-1</sup> belonging to the amide and amine groups, respectively are presented in both spectra. The broad bands at 3432 cm<sup>-1</sup> in spectrum (2) and 3430 cm<sup>-1</sup> in spectrum (1) are attributed to the physically adsorbed water by the aminolyzed acrylic copolymer and anion exchanger, respectively.

Chemical stability and water retention capacity values of the strong base acrylic anion exchanger are presented in Table 2 by comparison with a commercial one based on the styrene:divinylbenzene matrix namely, Amberlite IRA-400.

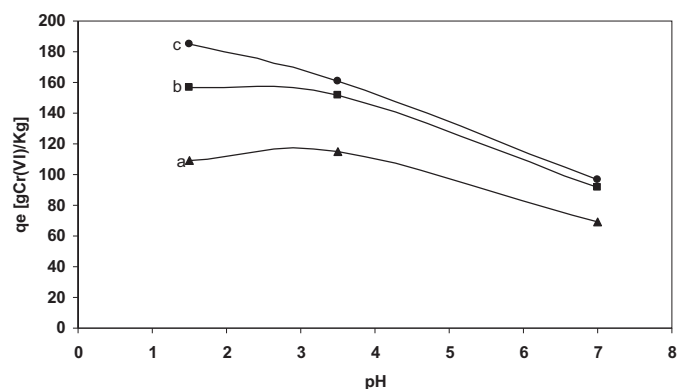
From the data presented in Table 2 it can be seen that the acrylic anion exchanger is more hydrophilic than the styrene anion exchanger and exhibited a very good chemical stability in all used media, except the cases when the concentrations of 5% and 10% H<sub>2</sub>O<sub>2</sub> were used.

### 3.2. Kinetics study

The chromate can be represented in various forms such as, HCrO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, H<sub>2</sub>CrO<sub>4</sub>, CrO<sub>4</sub><sup>2-</sup> as a function of pH and concentration of the solution. In the pH range from 1.5 to 3.5 the

**Table 2**  
Chemical stability of acrylic strong base anion exchanger in various media.

Sample	Code sample	Degradation agent	Concentration	Strong base exchange capacity		Loss of the weak base exchange capacity (%)	
				mequiv. mL <sup>-1</sup>	mequiv. g <sup>-1</sup>	mequiv. mL <sup>-1</sup>	mequiv. g <sup>-1</sup>
SBAE	B	–	–	0.51	2.93	–	–
	B <sub>1</sub>	NaOH	1 M	0.51	2.93	0	0
	B <sub>2</sub>	NaOH	5 M	0.51	2.93	0	0
	B <sub>3</sub>	HCl	1 M	0.51	2.93	0	0
	B <sub>4</sub>	HCl	5 M	0.51	2.93	0	0
	B <sub>5</sub>	H <sub>2</sub> O <sub>2</sub>	5%	0.20	2.60	8.40	5.37
	B <sub>6</sub>	H <sub>2</sub> O <sub>2</sub>	10%	0.04	2.40	20.61	10.48
Amberlite IRA-400	C	–	–	1.25	4.60	–	–
	C <sub>1</sub>	NaOH	1 M	1.25	4.60	0	0
	C <sub>2</sub>	NaOH	5 M	1.20	3.84	4.00	15.98
	C <sub>3</sub>	HCl	1 M	1.25	4.60	0	0
	C <sub>4</sub>	HCl	5 M	1.25	4.60	0	0
	C <sub>5</sub>	H <sub>2</sub> O <sub>2</sub>	5%	1.22	4.00	2.40	13.04
	C <sub>6</sub>	H <sub>2</sub> O <sub>2</sub>	10%	1.20	3.84	4.00	16.52

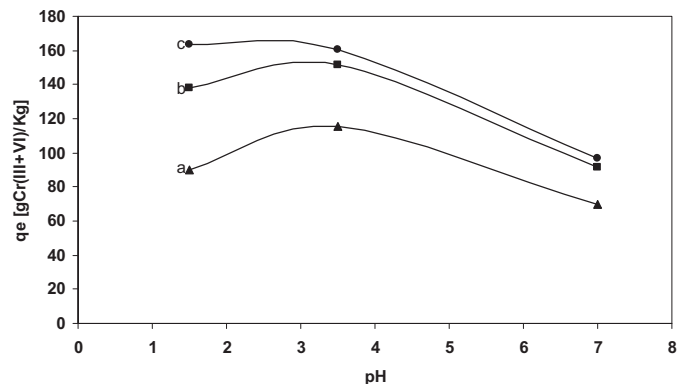


**Fig. 2.** Effect of pH on the sorption of Cr(VI) at 72 h contact time (a –  $C_{Cr} = 500 \text{ mg L}^{-1}$ , b –  $C_{Cr} = 1000 \text{ mg L}^{-1}$ , c –  $C_{Cr} = 2000 \text{ mg L}^{-1}$ ).

predominant form is  $\text{HCrO}_4^-$  at the concentration of  $100 \text{ mg L}^{-1}$  or  $\text{Cr}_2\text{O}_7^{2-}$  at the concentration of  $2000 \text{ mg L}^{-1}$ .  $\text{CrO}_4^{2-}$  ions exist in the experimental chromium concentration range of  $100\text{--}2000 \text{ mg L}^{-1}$  at pH 7.

The interaction between hexavalent chromium and acrylic anion exchanger was investigated with different values of pH and concentrations of chromium ions. Effect of pH on the sorption capacity of chromium by the anion exchanger is shown in Figs. 2 and 3.

Figs. 2 and 3 clearly show that the removal of chromium ions from aqueous solution on the resin is favourable at the pH values of 3 and 4.

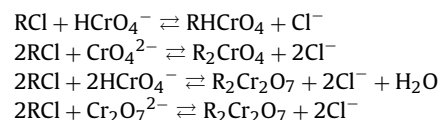


**Fig. 3.** Effect of pH on the sorption of Cr(VI)+Cr(III) at 72 h contact time (a –  $C_{Cr} = 500 \text{ mg L}^{-1}$ , b –  $C_{Cr} = 1000 \text{ mg L}^{-1}$ , c –  $C_{Cr} = 2000 \text{ mg L}^{-1}$ ).

It is obvious that the sorption capacity depends on the chromium concentration. As it can be seen from both figures, the highest sorption capacity values were found with the high concentration of chromium. Sorption capacity of chromium is higher at pH 1.5 than 3.5. This result could be explained by the presence of larger amount of  $\text{Cr}_2\text{O}_7^{2-}$  than  $\text{HCrO}_4^-$  with the concentration of  $2000 \text{ mg L}^{-1}$ .

At pH 1.5 the sorption of chromate in the solution is lower for Cr(VI+III) than for Cr(VI).

The pH dependence of ion exchange indicates that the sorption of Cr(VI) proceeds by the ion exchange mechanism. An anion exchange resin will adsorb chromates from aqueous solution according to the reactions [26]:



The recovery factor of Cr(VI) was calculated from Eq. (3):

$$\%R_{\text{Cr(VI)}} = \frac{g_0}{g_w} \times 100\% \quad (3)$$

where  $g_0$  is the concentration of Cr(VI) in the anion exchanger (calculated as the difference of concentrations in the solution before and after sorption);  $g_w$  is the initial concentration of Cr(VI) in the solution.

From these experiments the dependence of %R of Cr(VI) on time was investigated.

In order to optimize the recovery factor the experiments were conducted with  $100 \text{ mg L}^{-1}$  of Cr(VI) solution containing  $0.1 \text{ g}$  amount of the anion exchange resin in the pH range of 1.5 and 7.

As follows from Fig. 4, the recovery factors of chromium(VI) exhibited high values at pH 3.5 and 7 and phase contact time of 100 min ( $R = 99\%$ ) and  $R \cong 95\%$  at pH 1.5 for the phase contact time of 60 min.

Reduction of chromium(VI) to chromium(III) was also observed during the experiments.

The recovery factors of Cr(VI)+Cr(III) at pH 1.5 were calculated using Eq. (4):

$$\%R_{\text{Cr(III+VI)}} = \frac{g_0}{g_w} \times 100\% \quad (4)$$

where  $g_0$  is the concentration of Cr(VI)+Cr(III) in the anion exchanger (calculated as the difference of concentrations in the solution before and after sorption);  $g_w$  is the initial concentration of Cr(IV) in solution.

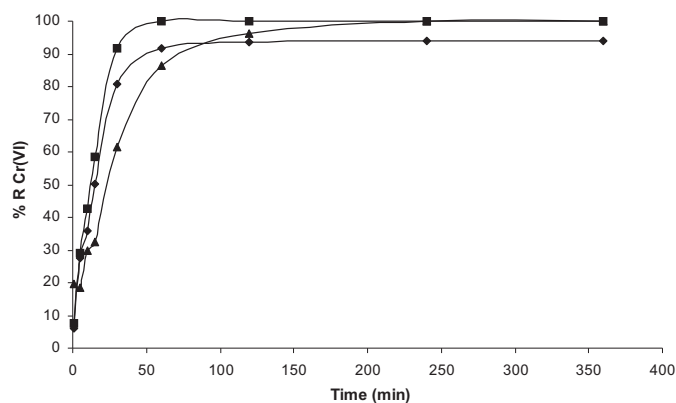


Fig. 4. Effect of the contact time and pH on the recovery factor of the Cr(VI) sorption at  $C_0 = 100 \text{ mg L}^{-1}$  (♦ pH 1.5; ■ pH 3.5; ▲ pH 7).

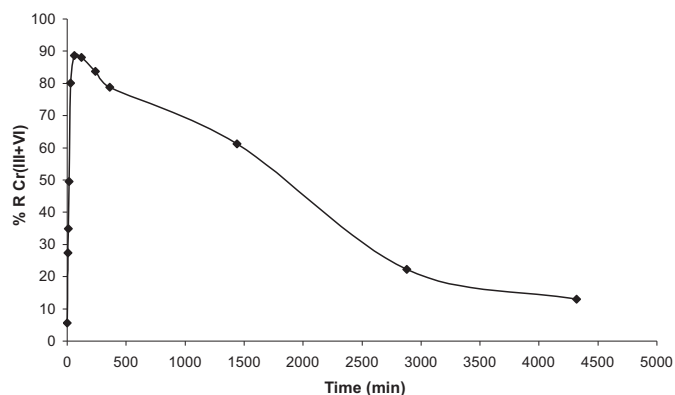


Fig. 5. Dependence of the recovery factor of Cr(III) + Cr(VI) on the phase contact time at pH 1.5 ( $C_0 \text{ Cr(VI)} = 100 \text{ mg L}^{-1}$ ).

As it was shown in Fig. 5 at the beginning of the sorption process of chromium ions the recovery factors increase to about 95% due to very fast sorption of chromium(VI). When chromium(VI) is present in the solid phase of the resin, then the reduction process starts and the values of recovery factors decrease.

A pH 1.5 the occurrence of the reduction of chromium(VI) was observed as shown in Fig. 6. After the sorption process of chromium(VI) onto the anion exchanger the reduction of hexavalent chromium to chromium(III) started. Chromium(III) occurs at pH 1.5 as the aqueous complexes  $\text{Cr(H}_2\text{O)}_6^{3+}$  and they are not able to be sorbed by the ion exchange groups. Therefore, chromium(III) passes to the external solution and it is determined.

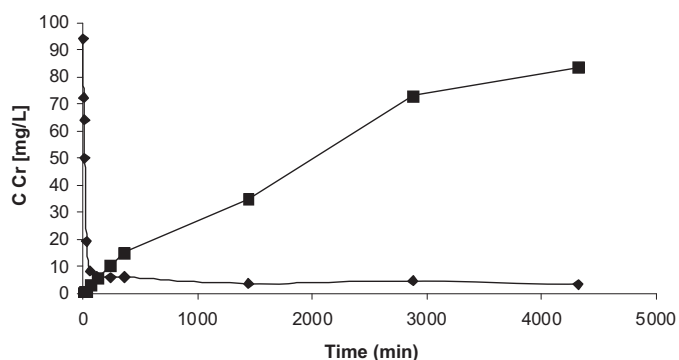


Fig. 6. Effect of the contact time on the concentration of (♦) Cr(VI) and (■) Cr(III) at pH 1.5 ( $C_0 \text{ Cr(VI)} = 100 \text{ mg L}^{-1}$ ).

Table 3

Values of kinetic parameters calculated by using the pseudo-first and pseudo-second order models of sorption.

pH	$k_1$	$R^2$	SD	$k_2$	$q_2$	$R^2$	SD	$h$
1.5	8.98	0.630	0.425	0.0036	24.49	0.998	0.216	2.17
3.5	4.34	0.636	1.030	0.0042	25.85	0.998	0.190	2.83
7	17.45	0.931	1.241	0.0018	26.66	0.995	0.353	1.34

Moreover, as shown in Fig. 6 the concentration of Cr(III) increased linearly in time with the correlation coefficient of 0.9732. The linear increase of chromium(III) concentration versus time is compatible to the zero order mechanism.

The kinetic analysis is required to obtain an insight into the rate of adsorption and the rate limiting step of the transport mechanism, which are primarily used in the modelling.

In order to analyze the sorption rate, the kinetic data were modelled using the pseudo-first-order and pseudo-second order equations.

To determine the kinetics of adsorption the pseudo-first order chemical sorption (Eq. (5)) and the pseudo-second order chemical sorption (Eq. (6)) were used:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \quad (5)$$

where  $k_1$  is the equilibrium rate constant of the pseudo-first order ( $\text{L min}^{-1}$ ),  $q_1$  is the amount of Cr(VI) sorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_t$  is the amount of Cr(VI) sorbed at time  $t$  ( $\text{mg g}^{-1}$ ).

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \quad (6)$$

where  $k_2$  is the equilibrium rate constant of pseudo-second order ( $\text{g (mg min)}^{-1}$ ),  $q_2$  is the amount of Cr(VI) sorbed at equilibrium ( $\text{mg g}^{-1}$ ),  $q_t$  is the amount of Cr(VI) sorbed at time  $t$  ( $\text{mg g}^{-1}$ ).

The initial sorption rate was calculated by Eq. (7):

$$h = kqe^2 \quad (7)$$

where  $h$  is the initial sorption rate ( $\text{mg (g min)}^{-1}$ ).

The values of the kinetic parameter calculated by using the pseudo-first and pseudo-second order models of sorption are presented in Table 3.

From the calculations, it was stated that the sorption kinetics is better described by the pseudo-second order mechanism than that of the pseudo-first order (Table 3). The values of kinetic parameters indicate high sorption capacity ( $q_2$ ) of chromium(VI) ions in the pH range from 1.5 to 7.

Moreover, the highest value of the sorption rate is attained at pH 3.5 while at pH 7 the rate is vary fast. The differences in the sorption rate are related with formation of bivalent  $\text{CrO}_4^{2-}$  ions at pH 7. Similar observations are reported in literature [18,19,34,37].

The validity of the obtained anion exchanger for Cr(VI) adsorption was justified by comparing its adsorption data with those presented in the literature [33–37]. It has been found that the maximum adsorption capacity value for Cr(VI) adsorption onto the compound performed in this study was equal or higher than those obtained for commercial or other synthesized anion exchangers. This comparison shows that this anion exchanger is more effective for this purpose.

### 3.3. Adsorption isotherms

The relationship between the adsorbed chromium concentration and that of the solution at equilibrium is described by the isotherm models, of which Langmuir and Freundlich are the most widely used. Langmuir model assumes that all adsorption sites are equivalents, there are no interactions between the adsorbed

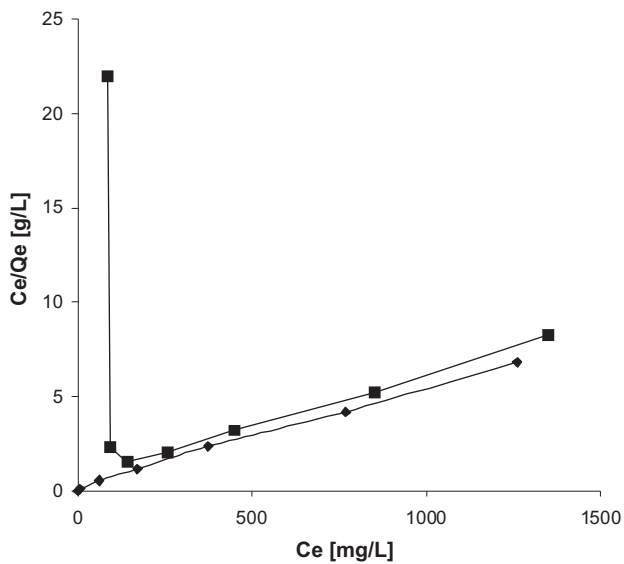


Fig. 7. Freundlich isotherms for (◆) Cr(VI) and (■) Cr(III)+Cr(VI) at pH 1.5.

molecules and adjacent sites, and adsorption is of the monolayer type. Langmuir isotherm is type I, occurring generally in the case of micro-porous adsorbents, with progressive saturation of adsorption sites. By comparison, Freundlich equation is valid for heterogeneous sorption on a surface of sludge containing several sites. These isotherms show the rate of Cr(VI) uptake per unit weight of sorbent ( $q_e$ ) to the equilibrium sorbate concentration in the bulk fluid phase ( $C_e$ ).

Adsorption isotherms were applied for two contact times after 2 and 72 h and are illustrated in Fig. 6.

As follows from Fig. 6 after 2 h the reduction of chromium(VI) to (III) is minimal but after 72 h it is very effective.

The Freundlich isotherm was calculated according to equation (7) and is presented in Fig. 7:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7')$$

where  $q_e$  is the amount of adsorbate in the adsorbent ( $\text{mg g}^{-1}$ );  $K_F$  is the characteristic constant related to the adsorption capacity ( $\text{L g}^{-1}$ );  $n$  is the adsorption intensity;  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ ).

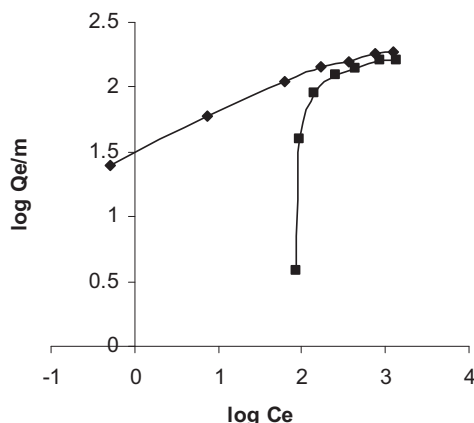


Fig. 8. Langmuir isotherms for (◆) Cr(VI) and (■) Cr(III)+Cr(VI) at pH 1.5.

Table 4

Values of Langmuir and Freundlich constants for the adsorption of Cr(VI) at 2 h phase contact time.

pH	Langmuir constants				Freundlich constants		
	$Q_0$	$b$	$R^2$	$R_L$	$n$	$K_F$	$R^2$
1.5	161.2	0.0258	0.9998	0.087	3.02	18.57	0.8658
3.5	144.9	0.0866	0.9997	0.030	5.11	41.56	0.9311
7	88.4	0.0270	0.9978	0.084	7.01	31.92	0.9797

Table 5

Values of Langmuir and Freundlich constants for the adsorption of Cr(VI) at 72 h phase contact time.

pH	Langmuir constants				Freundlich constants		
	$Q_0$	$b$	$R^2$	$R_L$	$n$	$K_F$	$R^2$
1.5	188.6	0.0287	0.9973	0.080	3.83	33.37	0.9784
1.5 <sup>a</sup>	-2000	-7.5E-05	0.0011	1.078	1.09	0.38	0.5385
3.5	161.2	0.0853	0.9997	0.046	5.425	50.06	0.9276
7	99.1	0.0213	0.9964	0.102	6.82	33.69	0.9911

<sup>a</sup> The values were calculated as a sum of Cr(VI)+Cr(III).

The Langmuir isotherm was calculated according to Eq. (8) and is presented in Fig. 8:

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (8)$$

where  $q_e$  is the amount of adsorbate in the adsorbent ( $\text{mg g}^{-1}$ );  $C_e$  is the equilibrium concentration ( $\text{mg L}^{-1}$ );  $b$  is the Langmuir isotherm constant ( $\text{L g}^{-1}$ );  $Q_0$  is the maximum monolayer coverage capacity ( $\text{mg g}^{-1}$ ).

Tables 4 and 5 include the values of the Langmuir and Freundlich constants calculated for the sorption experiments performed after 2 and 72 h of the phase contact time. The  $Q_0$  values after 2 h are lower than that after 72 h, which means that the time of 2 h is not sufficient to reach equilibrium.  $Q_0$  calculated using the Langmuir isotherm indicates increased sorption with the decrease of pH. This result could be explained by the presence of  $\text{CrO}_4^{2-}$  anions, which have a large diameter of the hydrated form, and therefore, their access to the ionic sites of resin is limited.

As can be seen in Figs. 7 and 8 in the low equilibrium concentration range, curves of different shapes are obtained. This is caused by the fact that the significant parts of Cr(VI) are reduced to Cr(III) which passes to the external solution.

In Table 5 the row at 1.5R presents the results calculated as a sum of Cr(VI)+Cr(III) which are different from that those calculated only for Cr(VI). In this case the Freundlich model describes better the sorption of Cr(VI) which is reduced in the anion exchanger and then desorbed to the external solution as Cr(III).

The essential feature of the Langmuir adsorption can be expressed by means of  $R_L$ , a dimensionless constant reported as a separation factor of equilibrium parameter for the prediction if the adsorption system is favourable or not.  $R_L$  can be calculated using Eq. (9).

$$R_L = \frac{1}{1 + bC_0} \quad (9)$$

where  $C_0$  is the initial concentration of the chromate solution ( $\text{mg L}^{-1}$ ).

The  $R_L$  values obtained in the presented case are smaller than 1 and lower than 0.1 and, therefore they also indicate a favourable adsorption. In the case when  $R_L$  values are calculated for Cr(III)+Cr(VI) (1.5R) the values are very close to 1 and suggest unfavourable adsorption or reduction and desorption process.

The mechanism of chromium sorption onto the acrylic strong base anion exchanger is ion exchange. This is supported by the

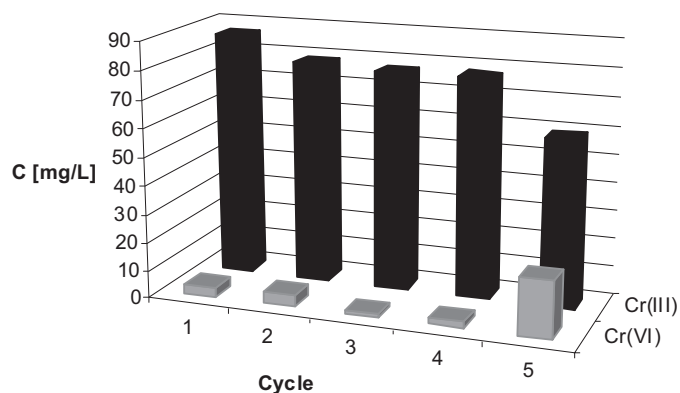


Fig. 9. Effect of cycles on sorption and reduction of Cr(VI) to Cr(III) ( $C_0$  Cr(VI) = 100 mg L<sup>-1</sup>).

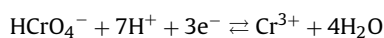
fact that the tertiary amine groups are less protonated than the quaternary ammonium groups at pH 3.5 and 7 [18].

The superiority of the synthesized anion exchanger over the conventional one based on the styrene:divinylbenzene matrix is attributed to several factors including (a) its ability for reposition the long spacer arm to provide exchange sites, (b) hydrophilic character of acrylic matrix, and (c) possible hydrogen bonds provided by the carbonyl functional groups [35].

#### 3.4. Cyclic sorption and reduction of chromium(VI)

Cr(VI) is a strong oxidizing agent and its oxidation power is influenced by the structure of the reagent, nature of the reaction medium and pH. As well known strong acids enhance the oxidizing power of Cr(VI) [19].

The slight increase of pH was observed during the ion exchange process of chromium ions onto the yielded acrylic strong base anion exchanger. The reduction of Cr(VI) to Cr(III) leads to the increase of pH and hydrogen ions are consumed according to the following reaction:



Therefore, adsorption and reduction of chromate ions determine the consumption of protons, which results in the increase of pH [36].

The cyclic experiments of sorption–reduction of Cr(VI) were carried out to measure the stability of the resin in the acidic media. The 0.1 g ion-exchanger was put into a small flask and contacted with 25 mL of Cr(VI) solution at pH 1.5. The total amount was shaken for 4320 min and then the anion exchanger was filtered to determine the content of Cr(VI) and Cr(III) in the solution. After that the resin was contacted with a new volume of Cr(VI) solution. The procedure was repeated five times and the results are shown in Fig. 9.

Throughout the first four cycles the acrylic anion exchanger worked very well and the sorption and reduction of chromium ions was almost identical. After the fifth cycle of sorption, the concentration of 19 mg L<sup>-1</sup> Cr(VI) was found in the solution and the concentration of Cr(III) was lower than that determined in the first four cycles. These results indicate that the functional groups are slightly oxidised.

#### 3.5. DRS measurements

The DRS spectra were measured at pH 1.5, 3.5 and 7 in the time range from 1 to 72 h and are shown in Figs. 10–12.

The spectra include characteristic signals below 500 nm after 1 h sorption of Cr(VI). The signals are related to the interaction of anion exchanger groups with Cr(VI). After 6 h these signals

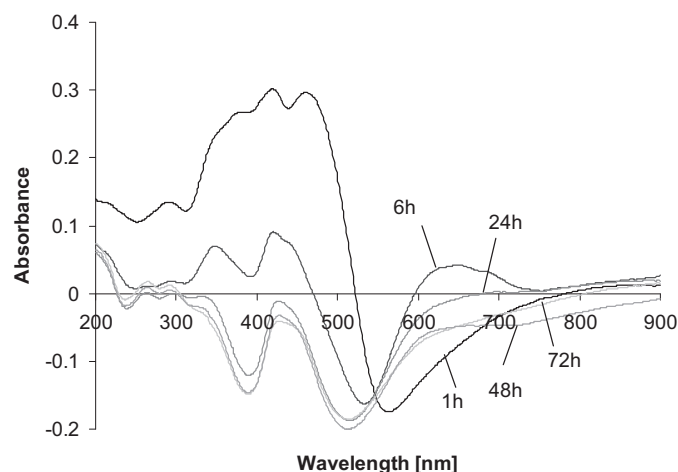


Fig. 10. The DRS spectra of the ion-exchanger with the sorbed Cr(VI) after a time range from 1 to 72 h at pH 1.5.

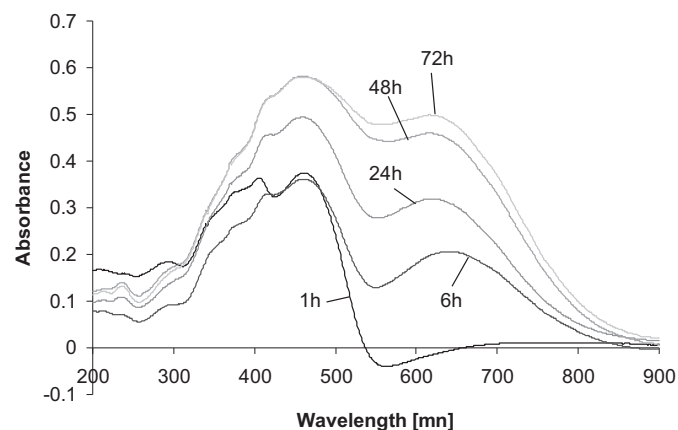


Fig. 11. The DRS spectra of the ion-exchanger with the sorbed Cr(VI) ions after a time range from 1 to 72 h at pH 3.5.

decreased and the signal at 620 nm related to chromium in the III oxidation form appeared, then the concentration of Cr(III) in the solid phase decreased and the signal at 620 nm disappeared. This phenomenon is in agreement with the results obtained from the measurements in solution at pH 1.5 (Figs. 5 and 6).

The DRS spectra at pH 3.5 and 7 after 72 h show the signal at 620 nm which demonstrates that the reduction occurred at pH 3.5 and 7. The product of reduction exists only in the solid phase as

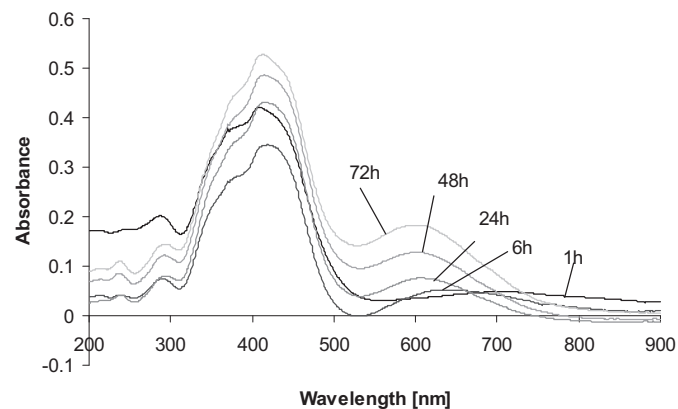


Fig. 12. The DRS spectra of the ion-exchanger with the sorbed Cr(VI) ions after a time range from 1 to 72 h at pH 7.



chromium hydroxide. However, the equilibrium in the solid phase between Cr(VI) and Cr(III) exists at pH 3.5 and 7.

#### 4. Conclusions

The crosslinked copolymer based on the VAc, AN and DVB monomers in the presence of toluene as a diluent was prepared by the polymerization process as precursors for the anion exchangers.

The acrylic copolymer was aminolyzed with dimethylamino-propylamine in order to obtain an acrylic weak base anion exchanger with the tertiary amine groups.

The reaction of the yielded compound with 2-chloroacetone led to the formation of a new structure of acrylic strong base anion exchanger with the tertiary amine, quaternary ammonium and ketone groups.

The obtained compound exhibited good values of strong base exchange capacity, higher value of water retention capacity compared to the traditional anion exchangers and chemical stability in HCl and NaOH of high concentrations.

The acrylic anion exchanger under investigation is characterized by high sorption capacity for hexavalent chromium by comparison with the data presented in the literature. The Langmuir isotherm data indicate the increase of sorption capacity with the decreasing pH values.

The mechanism of chromium sorption onto the studied acrylic strong base anion exchanger is ion exchange. The behaviour of this acrylic strong base anion exchanger for Cr(VI) is superior over the conventional one based on the styrene:divinylbenzene matrix due to its ability for reposition of the long spacer arm for providing exchange sites, hydrophilic character of matrix, and possible hydrogen bonds provided by the carbonyl functional groups.

According to the results obtained by the DRS method, the reduction of hexavalent chromium occurred at pH 3.5 and 7. The yielded product is presented in the solid phase as chromium hydroxide.

In the sorption–desorption experiments the acrylic anion exchanger exhibited very good results during the first four cycles while in the fifth, the chromium sorption capacity is not completely achieved, low amounts being found in the solution.

Cr(VI) can be reduced to Cr(III) in a simple way and this reduction could help in the process of Cr(VI) removal from contaminated waters and wastewaters.

#### Acknowledgment

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