Physicochem. Probl. Miner. Process., 55(6), 2019, 1382-1393

http://www.journalssystem.com/ppmp

Physicochemical Problems of Mineral Processing

ISSN 1643-1049

Received June 19, 2019; reviewed; accepted September 1, 2019

Sorption and reduction of chromium ions by the chelating ion exchanger Diaion CR20

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Abstract: The chelating ion exchanger Diaion CR20 was applied for removal of chromium(VI) ions in the pH range from 1.5 to 10 and in the presence of 1 M H_2SO_4. The speciation analysis was used to predict the reduction process. Reduction of chromium(VI) to chromium(III) was observed during the chromium(VI) ions sorption. The kinetic parameters for the pseudo-first-order and pseudo-second-order, Elovich and intraparticle diffusion models were calculated. The most common three isotherm models: Freundlich, Langmuir and Dubinin-Radushkevich were used to describe chromium(VI) uptake. It was proved that the polyamine groups present in selected ion exchanger are able to sorb both chromium(VI) and (III) ions. The maximal sorption capacity towards chromium(VI) ions was estimated at pH 1.5 – 169.49 mg Cr(VI)/g and 159.31 mg Cr(VI)/g in 1 M H_2SO_4. Both static and column methods were used in the investigations.

Keywords: chromium(III), chromium(VI), reduction, ion exchange, speciation, chelating resin

1. Introduction

The European Commission and World Health Organization qualified chromium(VI) and its compounds as a carcinogenic agents. It is well known that chromium(VI) is capable of damaging the DNA structure or cross-linking of protein. Chromium(VI) passes easily through the cell membrane and then can be reduced through the intermediate forms of chromium(V and IV) to trivalent chromium. Chromium(III) is believed to be non-toxic. However, the term less toxic is more suitable. Chromium(III) is not able to pass through the cells membrane, but is accumulated in them and finally can disrupt cellular functions and damage DNA (Wang et al., 2017). Chromium is used in many industries such as: electroplating, leather tanning, metal finishing, wood protection, stainless steel production, pigment manufacturing.

Besides well-known pollution sources new ones appear and the e-wastes are a current problem. Guiyu is one of the most heavily chromium-polluted areas in China. Children living in Guiyu had significantly higher chromium levels in blood as compared with those living in Chendian (Xu et al., 2015). Also improperly stored of e-wastes can release not only chromium ions but heavy metal ones too. Another problem is that a large amount will never be recycled, but it will pollute the environment.

Chromium(VI) compounds are well soluble in water and easily cover large areas of water or soil. The simplest method of their utilization is precipitation but it requires the use of a large amount of reagents. The extraction can be pointed out as another universal method. The new 1-methyl-1H-imidazole-substituted hexahomotrioxacalix[3] arene is an efficient extractant of $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ anions at low pH (Ni et al., 2013). Aliquat 336 and Alamine 336 were also tested for chromium(VI) ions extraction. The results showed that Aliquat 336 of quaternary ammonium group effectively extracted Cr(VI) ions and was more effective than Alamine 336. Both extractants removed chromium(VI) ions from the acidic media (Oh et al., 2000). The emulsion liquid membrane technique was also used for extraction of hexavalent chromium ions from the aqueous solution. Under the optimized conditions the maximum chromium(VI) extraction was found to be 89.20% and 96.15% using trioctylamine and

DOI: 10.5277/ppmp19056

Aliquat 336, respectively (Rajasimman and Sangeetha, 2009). As extraction requires toxic extractants and organic diluters, sorption on an ion exchangers or biosorbents seems to be more environmentally friendly. The biochar is a sorbent prepared from rice straw. The rice straw was pyrolyzed and chemically pretreated. The adsorption of Cr(VI) occurred partly through reduction of Cr(VI) to Cr(III) as well as via anionic adsorption. The best results of chromium(VI) ion sorption were obtained at pH 2 (Zhou et al., 2019). Addition of iron to biochar resulted in iron magnetic biochar preparation. At low pH values the redox mechanism took place but at higher solution pH, the redox reaction was inhibited and ion exchange dominated the adsorption process (Liu et al., 2019). Reduction of chromium(VI) was observed on the biomass of the algae species *Chlorella vulgaris*. It showed efficiency toward Cr(VI) reduction (Pradhan et al., 2017). The surface modified leaves were an effective sorbent for chromium(VI). The best results of chromium(VI) ions sorption were obtained at pH 2. Moreover, the chromium(VI) reduction was confirmed (Zhang et al., 2019). The polypyrrole/calcium rectorite composite adsorbent was tested for chromium(VI) ions sorption. The mechanism of sorption was described based on the electrostatic interactions, ion exchange process and chemical reduction (Xu et al., 2019).

Chromium(VI) and (III) can be removed from water by means of the ion–exchange method. The weakly basic ion exchanger was used for chromium(VI) removal from wastewaters. The ion exchange capacity was 1.45 mol/L at pH 3 and it was regenerated by the sodium hydroxide solution (Xing et al., 2007). The strongly basic pyridine ion exchanger was synthesized and tested for chromium(VI) ion removal. The best results of chromium(VI) ions sorption were observed at pH 3–5 (Neagu, 2009). Two strongly basic pyridine resins with the benzyl and ketone groups were obtained and used for chromium(VI) ions sorption, and the sorption capacities of 113.63 mg/g and 142.85 mg/g were estimated, respectively (Neagu and Mikhalovsky, 2010). During chromium(VI) sorption on the ion exchangers the reduction may proceed. This requires the speciation analysis of both chromium(III) and (VI) simultaneously. The speciation analysis of Cr(VI) and Cr(III) using Ambersorb 563 carbonaceous resin was done to study sediment and tannery wastewaters. The level of Cr(III) was calculated by the difference of the total chromium and Cr(VI) concentrations (Narin et al., 2002). Recently, many types of nanomaterials such as carbon nanotubes, titanium dioxide nanoparticles, magnetic nanoparticles and others are used for chromium speciation from the environmental samples (Arain et al., 2018). The reduction process was confirmed using several sorbents and ion–exchangers: the acrylic anion exchanger with the tertiary amine, quaternary ammonium and ketone groups (Wójcik et al., 2011), Amberlite XAD16 impregnated by Aliquate 336 (Wójcik et al., 2009), strongly basic anion exchanger Dowex PSR-2 (Wójcik and Hubicki, 2018), weakly basic Purolite A830 (Wójcik and Hubicki, 2016), Varion AP (Wójcik et al., 2013) and strongly basic Amberlite IRA910 (Wójcik et al., 2011). The above examples show that reduction of chromium(VI) ions occurs not only on biosorbents but also on ion-exchangers of various type. In numerous literature reports reduction was not confirmed because the speciation analysis of chromium(III and VI) was not used during the sorption experiment.

The main goal of this paper was to examine the chelating ion exchanger Diaion CR20 for chromium(VI) removal from water and its reduction to chromium(III).

2. Materials and methods

2.1. Materials

The water for experiment was prepared in the demineralization system HLP 10 (Poland) for the HPLC quality. Standard solutions of chromium(III) and (VI) were prepared from the certified reference solution 1000 mg/L (ISO Guide 34), produced by Romil. The chromium(VI) solutions were prepared from the analytical grade potassium salt K_2CrO_4 – POCH Gliwice, Poland. The other reagents – NaOH, NaCl and H_2SO_4 of analytical grade were from POCH Gliwice, Poland.

Diaion CR20 was swollen in water and purified by rinsing in water. The chelating resin was dried at room temperature. The Diaion CR20 resin was produced by Mitsubishi Chemical Industries, Japan. The specification of Diaion CR20 is presented in Table 1.

Table 1. The specification of Diaion CR20 chelating ion exchanger

Shipping density	(g/L)	640
Effective size	(mm)	0.4
Uniformity coefficient		1.6
Total swelling	(%)	10
Particle density	(g/mL)	1.05
Mean particle size	(μm)	570
Maximum operating temperature	(°C)	100
Effective pH range		2-6

2.2. Adsorption experiments

2.2.1. Adsorption kinetic

0.25 g of chelating resin Diaion CR20 was swollen and equilibrated with the 25 mL chromium(VI) solution in the concentration of 100 mg/L, in the shaking bath at 293 K. The samples were shaken in the contact time range 1–360 min using the laboratory shaker Elpin+ type 358 (Poland), at amplitude 8 and speed 150 cpm. After the determined time the samples were filtered and the filtrates were analyzed. The speciation analysis was used for determination of Cr(VI) ions by the UV-VIS method (spectrophotometer Agilent Technologies Cary 60), with diphenylcarbazide for Cr(VI), Cr(VI)+Cr(III) by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES Varian 720 ES) and HPLC 1200 Infinity series (Agilent) coupled with the ICP-MS 7700 series (Agilent) for determination of Cr(III) and Cr(VI) in the samples at low concentrations of chromium ions in the solution.

2.2.2. Adsorption isotherms

To determine sorption capacity of the chelating resin Diaion CR20 for chromium ions, 0.25 g of the resin was equilibrated at room temperature with 25 mL of chromium(VI) solution in the concentration range 100–2000 mg/L, in the shaking bath for 1440 min. The filtrate was analyzed by the method described in section 2.2.1.

2.2.3. Temperature experiment

In the temperature experiment 0.25 g of Diaion CR20 was contacted with 25 mL of chromium(VI) solution at pH 1.5–10, at three different temperatures: 293, 303 and 313 K. The filtrate was analyzed by the method described in section 2.2.1.

2.2.4. Effect of Diaion CR20 dose on removal efficiency

Different mass (0.05–0.3 g) of Diaion CR20 was contacted with 25 mL of 100 mg/L chromium(VI) ions solution within 24 h.

2.3. Spectroscopic measurements

The UV-VIS Diffuse Reflectance Spectra were measured using the Jasco V-660 spectrometer equipped with a diffuse reflectance attachment PIV-756 produced by Jasco, Japan. The samples were measured in a dry form.

2.4. Reusability

0.25 g of Diaion CR20 was contacted with specific portions of 100 mg/L chromium(VI) solution at pH 1.5, in the shaking bath for 1440 min. The filtrate was analyzed by the method described in section 2.2.1.

2.5. Column method

The glass columns with a diameter of 1.1 cm were used in the dynamic method. The columns were filled with 3 g of swollen Diaion CR20. The feed solutions 100 mg/L Cr(VI) in 1 M H_2SO_4 and at pH 1.5–10 were passed through the column with the speed of 0.5 mL/min. The fractions were collected and analyzed applying the method described in section 2.2.1.

3. Results and discussion

3.1. Effect of Diaion CR20 dose on removal efficiency

In order to determine the optimal mass of the ion exchanger, the study of Diaion CR20 mass effect on the removal efficiency ($R_{Cr(VI)}$) of chromium(VI) was carried out. That investigation was performed in the pH range 1.5–10 and in the presence of 1 M H_2SO_4.
The removal efficiency $R_{Cr(VI)}$ (%) was calculated from equation 1:

$$R_{Cr(VI)} = \frac{C_{Cr(VI)}}{C_i} \cdot 100\% \tag{1}$$

where: $C_{Cr(VI)}$ is the concentration of Cr(VI) in the Diaion CR20 (mg/L) (calculated as the difference of chromium(VI) ions concentrations in the solution before and after sorption); C_i is the initial concentration of Cr(VI) in the solution (mg/L).

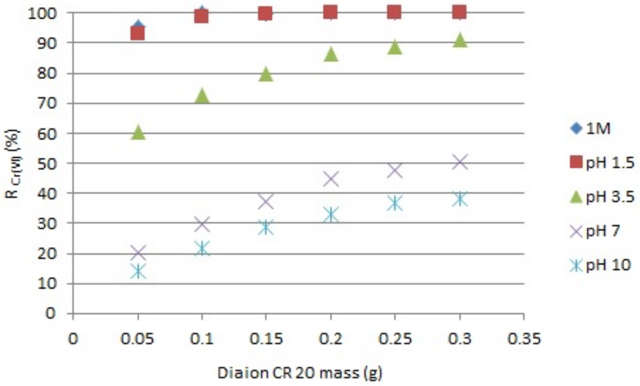


Fig. 1. Influence of Diaion CR20 mass on removal efficiency of chromium(VI) ions in the pH range of 1.5–10 and in the presence of 1 M H_2SO_4, C_i=100 mg/L

As it can be seen in Fig. 1, the removal efficiency depends on the sorbent mass and pH value. Both parameters have influence on removal efficiency of chromium(VI) ions. In the strong acidic solutions (at pH 1.5, 1 M H_2SO_4) the plateau of R(%) is for 0.1 g of Diaion CR20. In the pH range of 3.5–10 the removal efficiency increases together with increasing ion exchanger mass and for 0.25–0.3 g it changes slightly. For this reason 0.25 g of ion exchanger Diaion CR20 was used in further investigations.

3.2. Effect of contact time and pH

The kinetics of ions removal from water is a very usefully parameter. It should be taken into account during designing of the column for the dynamic sorption process. The influence of contact time on chromium(VI) ions removal is shown in Fig. 2.

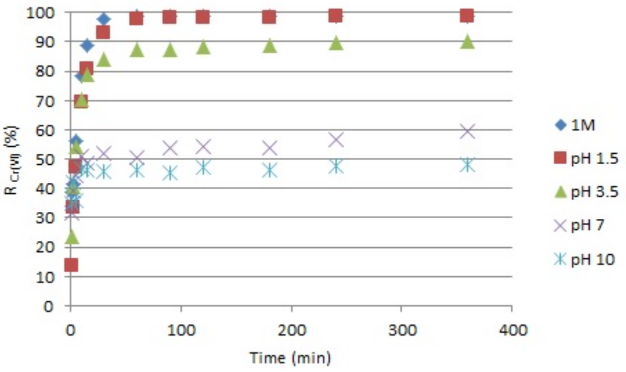
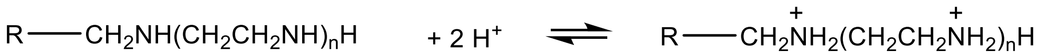


Fig. 2. Influence of contact time on chromium(VI) ions removal efficiency, C_i=100 mg/L

As can be seen in Fig. 2, the removal efficiency of chromium(VI) ions significantly depends on pH values. The increase of pH value results in decreasing removal efficiency of chromium(VI) ions. In the acidic media (at pH 1.5) and in the presence of 1 M H_2SO_4 the plateau is reached after 30–45 min and the removal efficiency is close to 99%. At pH 3.5–10 the equilibrium is reached rather slowly and the removal efficiency are pH 3.5 – 90%, pH 7 – 59% and pH 10 – 48%, respectively. This fact can be related with the chemical nature of polyamine groups. The polyamine groups are easily protonated in the acidic media. At pH 1.5 and in the presence of 1 M H_2SO_4 all amine groups are protonated and acquire a positive charge on nitrogen atoms:



$$R\text{---}CH_2NH(CH_2CH_2NH)_nH \quad + 2\,H^+ \rightleftharpoons R\text{---}CH_2\overset{+}{N}H_2(CH_2CH_2\overset{+}{N}H_2)_nH$$

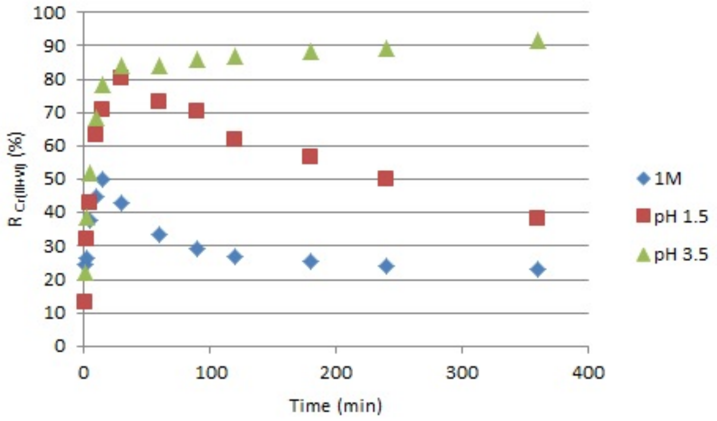


Fig. 3. Influence of contact time on chromium(III and VI) removal efficiency, C_i=100 mg/L

In the acidic media (1 M H_2SO_4 and at pH 1.5) the reduction process of chromium(VI) to chromium(III) was detected. During the sorption process the reduction occurs in the phase of Diaion CR20. The reduced chromium(III) ions are released to the solution and detected using the speciation analysis. The removal coefficient was recalculated according to equation 2:

$$R_{Cr(III+VI))} = \frac{C_{Cr(III+VI)}}{C_i} \cdot 100\% \tag{2}$$

where: $C_{Cr(III+VI)}$ is the concentration of Cr(VI) and Cr(III) in the ion exchanger (calculated as the difference between chromium(VI) concentration in the solution before sorption as well as chromium(III) and chromium(VI) concentrations after sorption); C_i is the initial concentration of Cr(VI) in the solution.

The removal coefficients $R_{Cr(III+VI)}$ are presented in Fig. 3. They increase up to 50% during 15 min of the process in the 1 M H_2SO_4 medium, and after that time they decrease. At pH 1.5 the $R_{Cr(III+VI)}$ increase up to 80% during 30 min and then rapid decrease is observed. Such a course of curves indicates reduction and is more effective in the 1 M H_2SO_4 medium than at pH 1.5. It is known that hydrogen cations take part and are responsible for the reduction of chromium(VI) to (III).

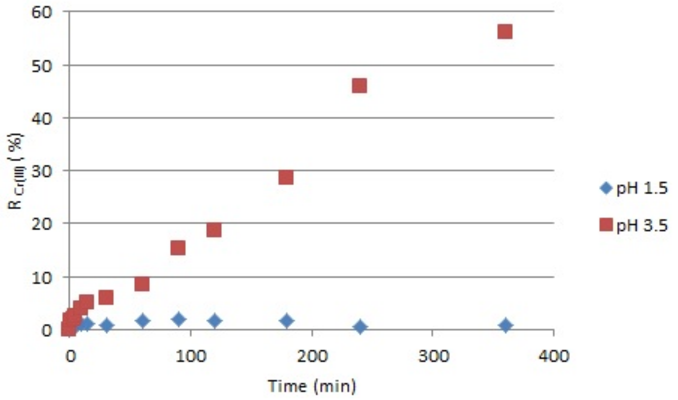


Fig. 4. The influence of contact time on the chromium(III) ions sorption at pH 1.5-3.5, $C_{iCr(III)}$ – 100 mg/L

The effect of contact time on the sorption of chromium(III) at pH 1.5–3.5 is presented in Fig. 4. Sorption of chromium(III) ions depends on the pH values. At pH 1.5 chromium(III) ions are not sorbed on Diaion CR20, because the polyaminie groups are protonated and their positive charge repulse the positively charged chromium cations. At pH 3.5 the chromium(III) ions are sorbed and the removal coefficient is 56% after 360 min. The chromium(III) ions can be desorbed quantitatively by 1 M HCl. Acids protonate the Diaion CR20 polyamine groups and chromium(III) ions can be released.

3.3. Kinetic models

Commonly known kinetic models were used to describe sorption of chromium(VI) ions on Diaion CR20. The most common are: the pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich and intraparticle kinetic models. The linear forms of kinetic models are presented in Table 2 (Ghasemi et al., 2013; Ho and McKay, 1998; Ho and McKay, 2002).

Table 2. The linear forms of kinetic models

Name	Linear form
Pseudo-first-order	$\ln(q_1 - q_t) = ln q_1 - k_1 \cdot t$
Pseudo-second-order 1	$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{1}{q_e} \cdot t$
Pseudo-second-order 2	$\frac{1}{q_t} = \left(\frac{1}{k_2 . q_e^2}\right) \cdot \frac{1}{t} + \frac{1}{q_e}$
Pseudo-second-order 3	$q_t = q_e - \left(\frac{1}{k_2 . q_e}\right) \cdot \frac{q_t}{t}$
Pseudo-second-order 4	$\frac{q_t}{t} = k_2 \cdot q_e^2 - k_2 \cdot q_e \cdot q_t$
Elovich	$q_t = \frac{1}{\beta} \cdot ln(\alpha \cdot \beta) + \frac{1}{\beta} \cdot lnt$
Intra-particle diffusion	$q_t = k_{ip} \cdot t^{0.5} + C$

where: q_1 is the amount of chromium ions sorbed at equilibrium (mg/g) for the PFO model, q_t is the amount of chromium ions sorbed (mg/g) at the time t (min), q_e is the amount of chromium ions sorbed at equilibrium (mg/g) for the PSO model, k_1 is the equilibrium state constant (1/min) for the PFO, k_2 is the equilibrium state constant (g/mg·min) for the PSO model, α is the Elovich sorption rate (g/mg·min), β is the Elovich sorption constant (mg/g), k_{ip} is the intraparticle diffusion rate constant (mg/g·min$^{0.5}$), C is the intercept (mg/g).

From the equations presented in Table 2, the kinetic parameters were calculated and the results are given in Table 3. The pseudo-first-order, pseudo-second-order, Elovich and intraparticle kinetic models describe chromium(VI) ions sorption with different accuracy. The coefficients values change in a wide range depending on the chosen model. For the intraparticle diffusion model, the coefficients values are in the range of 0.5056 for adsorption process performed at pH 10 up to 0.8331 for pH 1.5. This indicates that intraparticle diffusion is a not limiting stage during the sorption process. The Elovich model describes sorption better than the intraparticle diffusion one. The R^2 values are in the range of 0.6564–0.9741 and are higher in the acidic media than at pH 7–10. This may indicate that sorption is more physical in neutral and alkaline media than in the acidic one. Among proposed kinetic models the best fit of experimental data was obtained for the pseudo-second-order model PSO type 1. The values of R^2 are close to 0.999 and the sorption capacities q_e are similar to those from experiments.

3.4. Sorption isotherms

Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models were used for the calculation of adsorption parameters. The Langmuir isotherm model is expressed by equation 3:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot Q_0} + \frac{C_e}{Q_0} \tag{3}$$

where: q_e is the amount of adsorbed metal ions per unit mass of the adsorbent (mg/g); C_e is the equilibrium concentration (mg/L); b is the Langmuir isotherm constant (L/mg); Q_0 is the maximum

Table 3. Kinetic parameters for chromium(VI) ions sorption

	pH	k_1 (1/min)	q_1 (mg/g)	R^2
PFO	1 M	0.0721	4.10	0.9083
	1.5	0.0567	5.75	0.9431
	3.5	0.0341	3.52	0.8014
	7	0.0117	1.66	0.5601
	10	0.0094	1.78	0.1507
PSO 1	**pH**	**k_2 (g/mg·min)**	**q_e (mg/g)**	**R^2**
	1 M	0.0332	10.29	0.9988
	1.5	0.0168	10.58	0.9989
	3.5	0.0373	9.10	0.9997
	7	0.1716	5.34	0.9990
	10	0.3300	5.15	0.9995
PSO 2	**pH**	**k_2 (g/mg·min)**	**q_e (mg/g)**	**R^2**
	1 M	0.1643	8.39	0.7353
	1.5	0.6548	12.07	0.9854
	3.5	0.3183	8.76	0.9879
	7	0.1248	5.11	0.9514
	10	0.0710	4.53	0.6149
PSO 3	**pH**	**k_2 (g/mg·min)**	**q_e (mg/g)**	**R^2**
	1 M	0.0668	9.08	0.6435
	1.5	0.0119	11.57	0.9849
	3.5	0.0355	9.13	0.9617
	7	0.2937	5.14	0.9168
	10	0.6724	4.56	0.5836
PSO 4	**pH**	**k_2 (g/mg·min)**	**q_e (mg/g)**	**R^2**
	1 M	0.0385	10.16	0.6435
	1.5	0.0116	11.65	0.9849
	3.5	0.0337	9.24	0.9617
	7	0.2664	5.20	0.9168
	10	0.3744	4.78	0.5836
Elovich	**pH**	**α (g/mg·min)**	**β (mg/g)**	**R^2**
	1	7.59	0.56	0.9164
	1.5	3.24	0.45	0.9741
	3.5	5.65	0.59	0.9527
	7	24.82	1.31	0.8374
	10	563.97	2.45	0.6564
Intra-particle diffusion	**pH**	**k (mg/g·min$^{0.5}$)**	**C (mg/g)**	**R^2**
	1	0.9867	3.59	0.8041
	1.5	1.2334	1.78	0.8331
	3.5	0.9006	3.03	0.7719
	7	2.4440	3.65	0.5887
	10	0.1557	3.69	0.5056

monolayer coverage capacity (mg/g).

The values of R^2 for the Langmuir isotherm are close to 0.99 and show that this model describes the experimental data better than the Freundlich one. The calculated sorption capacities are 159.3 mg/g in 1 M H_2SO_4 and 169.4 mg/g at pH 1.5.

The Langmuir isotherm allows to estimate the R_L parameter. It can be calculated using equation 4.

$$R = \frac{1}{1+b\cdot C_0} \tag{4}$$

where: C_0 is the initial concentration of metal ions in the solution (mg/L).

The R_L parameters calculated from the Langmuir isotherm for chromium(VI) ions adsorption are presented in Table 4. The values of R_L are in the range of 0.0189–0.3266. The lower values of R_L parameter were obtained in the acidic solution than in the basic one. This indicates that the sorption is more favorable in the acidic media.

The Freundlich isotherm model is expressed by the equation (5):

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

where: q_e is the amount of adsorbed metal ions per unit mass of the adsorbent (mg/g); K_F is the characteristic constant related to the adsorption capacity (L/g); n is the adsorption intensity; C_e is the equilibrium concentration (mg/L).

The values of R^2 coefficient for the Freundlich isotherm are lower than those for the Langmuir and D-R models. This indicates that Freundlich isotherm model does not describe sorption of chromium(VI) ions enough, the same as the Langmuir and D-R ones.

The linear form of the Dubinin-Radushkevich (D-R) model is presented in equation (6):

$$\ln q_e = \ln q_m - \beta \cdot \varepsilon^2 \tag{6}$$

where: q_m is the maximum of chromium(VI) ions in Diaion CR20 (mol/g); β is related to the adsorption energy (mol^2/kJ^2), ε is the Polanyi potential which can be calculated from equation (7):

$$\varepsilon = RT\ln\left[1 + \frac{1}{C_e}\right]. \tag{7}$$

On the basis of the β parameter the D-R model allows to calculate the adsorption free energy E (kJ/mol):

$$E = \frac{1}{\sqrt{2\beta}}. \tag{8}$$

The D-R model describes the sorption of chromium(VI) ions at pH 3.5–10 better than the Langmuir and Freundlich ones. The D-R model enables also determination of a free energy. When the free energy is higher than 8 kJ/mol, the process is of chemisorption nature. However, for the values lower than 8 kJ/mol physisorption takes place. The obtained values of a free energy of 9.86 kJ/mol in 1 M H_2SO_4, 10.24 kJ/mol at pH 1.5 and 8.11 kJ/mol at pH 3.5 indicate chemisorption. The values of free energy are lower than 8 for adsorption process performed at pH 7 and 10, and thus are responsible for the physisorption process.

In the 1 M H_2SO_4 solutions and at pH 1.5 the reduction of chromium(VI) ions is observed. Figure 5 presents the adsorption isotherms, taking into account the concentration of chromium(III) in the solution after reduction.

The speciation analysis enabled determination of sorption isotherms taking into account the concentrations of chromium(III) in the solution. The isotherms are S shaped. Adsorption process performed using low-concentrated solutions, up to around 400 mg/L, caused that the concentration of chromium(VI) in Diaion CR20 is low because chromium(III) ions pass to the solution. This (S) shape of the isotherm is described better by the Freundlich model than by the Langmuir and D-R ones. The values of free energy calculated from the D-R isotherm are: 4.016 kJ/mol and 4.28 kJ/mol when adsorption was realized in 1 M H_2SO_4 and at pH 1.5, respectively. The low values of free energy are related with the fact that sorption and reduction proceed simultaneously. The sorption capacity of Diaion CR20 towards chromium(VI) ions reached value of 169.49 mg Cr(VI)/g during adsorption tests at pH 1.5. This value is higher than for the strongly basic ion exchanger Dowex PSR-2 – 121.95 mg Cr(VI)/g (Wójcik and Hubicki, 2018). In the literature, various types of ion exchangers which have higher sorption capacity towards chromium(VI) ions than Diaion CR20 at pH 1.5, such as ion exchanger with the tertiary amine, quaternary ammonium and ketone groups – 188.6 mg Cr(VI)/g (Wójcik et al., 2011), Varion AP – 188.67 mg Cr(VI)/g (Wójcik et al., 2013), Purolite A830 – 196 mg Cr(VI)/g (Wójcik and Hubicki, 2016) and Amberlite IRA 910 – 197.06 mg Cr(VI)/g (Wójcik et al., 2011), can be found.

3.5. Thermodynamic parameters

The thermodynamic parameters like: ΔG^0 Gibbs free energy (kJ/mol), ΔH^0 enthalpy (kJ/mol) and ΔS^0 entropy (kJ/K·mol) were calculated for chromium(VI) ions adsorption using the equations 9 and 10:

Table 4. The Langmuir, Freundlich and D–R isotherm model constants for Cr(VI) ions sorption on the chelating Diaion CR20 resin

pH	**Langmuir**				**Freundlich**			**Dubinin-Radushkevich**			
	Q_0	b	R_L	R^2	K_f	n	R^2	β	q_m	E	R^2
1 M	159.32	0.0369	0.0263	0.9972	2.78	2.24	0.8702	$5.13 \cdot 10^{-9}$	0.0162	9.86	0.9231
1.5	169.49	0.0537	0.0183	0.9970	17.42	2.33	0.8287	$4.77 \cdot 10^{-9}$	0.0175	10.24	0.8787
3.5	97.09	0.0041	0.1944	0.9901	1.50	1.66	0.9813	$7.59 \cdot 10^{-9}$	0.0081	8.11	0.9957
7	46.30	0.0021	0.3266	0.9920	0.58	1.74	0.9841	$9.41 \cdot 10^{-9}$	0.0042	7.29	0.9972
10	33.22	0.0023	0.3046	0.9925	0.60	1.90	0.9850	$8.71 \cdot 10^{-9}$	0.0031	7.58	0.9952

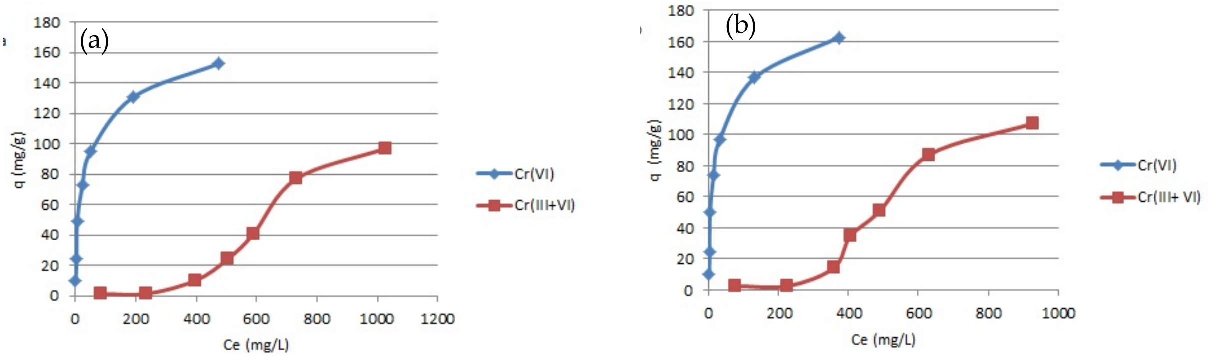


Fig. 5. Isotherms concerning adsorption of chromium ions in: a) 1 M H_2SO_4 and at b) pH 1.5

$$\Delta G^0 = -RT\ln(K_D) \tag{9}$$

$$\ln(K_D) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{T} \tag{10}$$

The values of ΔH^0 (kJ/mol) and ΔS^0 (kJ/K·mol) were obtained from the slope and intercept in the plot $ln(K_D)$ vs. $1/T$. K_D parameter is the distribution coefficient (L/g), R is the universal gas constant ($8.314 \cdot 10^{-3}$ kJ/K·mol). The values of the thermodynamic parameters are presented in Table 5.

For the chromium(VI) ions sorption on the chelating ion exchanger Diaion CR20 the negative value for ΔH^0 suggested exothermic interactions at temperatures 293–313 K. The slight negative ΔS^0 values indicate decreasing randomness at the solid-solution interface during the chromium(VI) ions sorption.

The positive ΔG^0 values show the existence of an energy barrier and that the reaction has a non-spontaneous nature for pH higher than 3.5. The free enthalpy increases with the increasing pH values. The negative values of free enthalpy obtained during chromium(VI) ions sorption at pH 1.5 are related with the protonation of polyamine groups and the spontaneous sorption process. The values of free enthalpy are consistent with the sorption capacity of Diaion CR20 towards chromium(VI) ions. Summing up, the sorption of chromium(VI) ions proceeds more efficiently with the decreasing temperature of solution.

Table 5. The values of thermodynamic parameters for Cr(VI) ions removal

pH	**ΔH^0 (kJ/mol)**	**ΔS^0 (kJ/K·mol)**	**ΔG^0 (kJ/mol)**		
			293 K	**303 K**	**313 K**
1.5	-4.6965	-0.0094	-1.9418	-1.8836	-1.7529
3.5	-4.4902	-0.0232	2.3016	2.5580	2.7646
7	-10.9099	-0.0591	6.4523	6.9281	7.6401
10	-11.4407	-0.0614	6.5483	7.1621	7.7764

3.6. Reusability

In order to better understand the sorption and reduction processes, five cycles of tests were performed. Diaion CR20 was contacted with other portions of solution. The results of this analysis are shown in Fig. 6.

As can be seen in Fig. 6 chromium(III) ions were determined in the solution after 1–5 cycles. The concentration of chromium(III) slightly increased reaching 85 mg/L and 90 mg/L when adsorption was realized at pH 1.5 and in 1 M H_2SO_4 in the 5th cycle, respectively. In 1–4 cycles sorption of chromium(VI) ions was effective but in the 5th the estimated concentration of chromium(VI) in the solution was 4.6–4.7 mg/L. This experiment confirmed effective sorption and reduction of chromium(VI) ions in the presence of Diaion CR20.

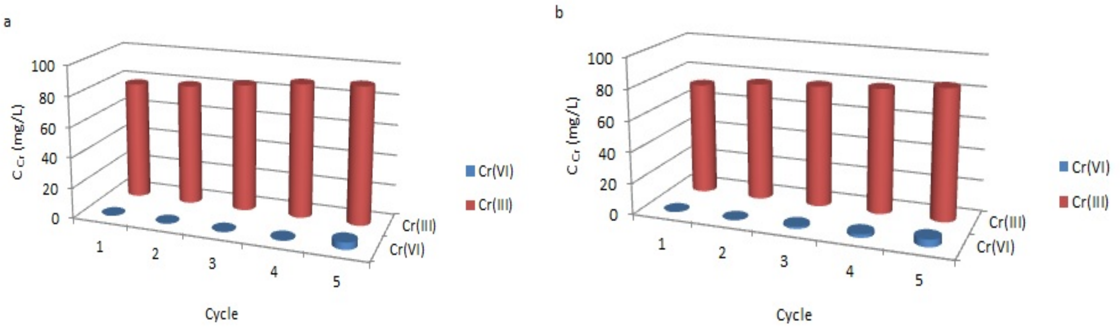


Fig. 6. Reusability of Diaion CR20 for chromium(VI) ions sorption performed in a) 1 M H_2SO_4 and at b) pH 1.5

3.7. DRS spectra

The UV-VIS DRS method was used to analyze the solid phase of Diaion CR20 after chromium(VI) ions sorption. The spectra were recorded for the samples after sorption of ions at the concentration of 2000 mg/L in 1 M H_2SO_4 and at pH 1.5–10. The DRS method is very useful enabling observation of the reduction process in the solid phase of the chelating ion exchanger Diaion CR20. A band at 610 nm confirms the presence of chromium(III) specie. In this region chromium(VI) ions are not visible. Chromium(VI) ions can be assigned to the bands at the values lower than 500 nm. Moreover, the intensity of a band at 394 nm decreases with the increasing pH values of adsorption process. This fact is related with decreasing sorption capacity of Diaion CR20 towards Cr(VI). Analysis of the presented spectra is in an agreement with the kinetic and isotherms studied results.

3.8. The column method

Due to toxic nature of chromium(VI), its concentration in water should not exceed 0.05 mg/L. The breakthrough capacities of chromium(VI) ions were estimated: in 1 M H_2SO_4 – 68.8 mg/g, at pH 1.5 – 80 mg/g, at pH 3.5 – 6.6 mg/g, at pH 7.0 – 2.5 mg/g, at pH 10 – 1.66 mg/g.

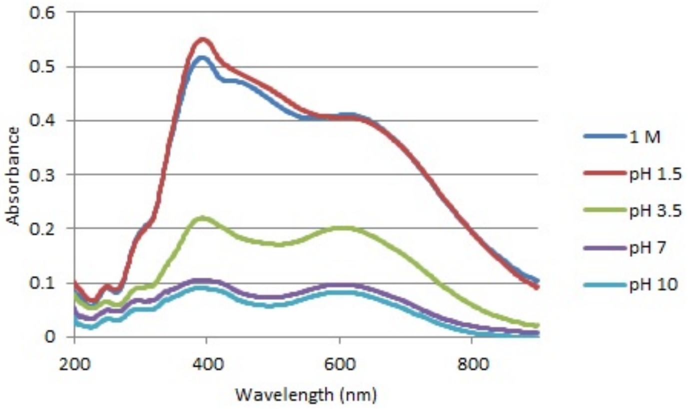


Fig. 7. The DRS spectra of Diaion CR20 after chromium(VI) ions sorption in 1 M H_2SO_4 and at pH 1.5–10, ($C_{iCr(VI)}$ – 2000 mg/L)

As it can be seen from the results obtained during the batch experiments the reduction process of chromium(VI) to chromium(III) was observed when adsorption was realized in 1 M H_2SO_4 and at pH

1.5, respectively. Therefore, the chromium(III) presence was determined during chromium(VI) ion sorption. The chromium(III) ions were detected in the solution before and after the breakthrough points measured in 1 M H_2SO_4 and at pH 1.5 – the concentrations of Cr(III) were 40 mg/L and 30 mg/L, respectively. The higher concentration of chromium(III) in 1 M H_2SO_4 than at pH 1.5 indicates a stronger process of reduction that occurs in 1 M H_2SO_4. It is related with higher concentration of H^+ ions in 1 M H_2SO_4 than at pH 1.5. Because chromium(III) ions can be sorbed by Diaion CR20, the column test was performed in the pH range of 1.5–3.5. For chromium(III), the breakthrough capacities were 0 mg/g at pH 1.5 and 15 mg/g at pH 3.5. The results of breakthrough capacity from the column experiment confirmed the influence of pH on chromium(III) ions sorption and are consistent with those obtained by the batch method.

4. Conclusions

On the basis of the research, there following conclusions were drawn:

- the chelating ion exchanger Diaion CR20 is able to sorb chromium(VI) ions,
- the sorption of chromium(VI) ion is efficient in 1 M H_2SO_4 and at pH 1.5,
- in analyzed system, the reduction of chromium(VI) to chromium(III) ions occurs,
- the sorption of chromium(III) cations proceeds at pH 3.5,
- the chromium(VI+III) ions were detected in the solid phase of Diaion CR20 by the DRS method.
- in the acidic solution the sorption mechanism is ion-exchange supported by reduction phenomena.

The investigated chelating ion exchanger Diaion CR20 has a rare property because it is able to sorb chromium(VI) anions and chromium(III) cations. This property is related with ion exchange and chelating mechanisms of sorption. Moreover, during sorption of chromium(VI) ions in the acidic media, the reduction process responsible for an increase in the concentration of chromium(III) cations in the solution, should be taken into consideration.

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