



Chromium(VI) removal from aqueous solutions using a polyethylenimine–epichlorohydrin resin

SOFIA SARRI¹, PANAGIOTIS MISAILIDES^{1*}, DIMITRIOS ZAMBOULIS¹,
FOTINI NOLI¹, JOLANTA WARCHOŁ², FANI PINAKIDOU³ and MARIA KATSIKINI³

¹Department of Chemistry, Aristotle University, GR-54124 Thessaloniki, Greece, ²Department of Water Purification and Protection, Rzeszow University of Technology, Rzeszow, Poland and ³Department of Physics, Aristotle University, GR-54124 Thessaloniki, Greece

(Received 19 April, revised and accepted 9 June 2016)

Abstract: The ability of the synthesized polyethylenimine–epichlorohydrin resin to remove Cr(VI) from aqueous solutions was investigated in the absence (initial pH 2–7) and presence of background electrolytes (NaNO_3 and Na_2SO_4 solutions of initial pH 3 and 6). The determined Cr uptake was significantly higher than the one reported for the majority of other sorbents. The photometrically determined uptake data were modeled by the Langmuir, Redlich–Peterson, Langmuir–Freundlich and Toth equation. The modeling results did not indicate any preference to one specific model in terms of the goodness-of-fit and the prediction of maximum sorption capacity. The Cr-sorption kinetics were investigated at 15, 25, 35 and 45 °C using ^{51}Cr -labeled solutions and γ -ray spectroscopy. The Cr-sorption was very fast at all studied temperatures and well reproduced by the pseudo-second order kinetics equation. The rate constant and activation energy values were calculated using the experimental data. The Cr-loaded resin was also examined by XRD, XPS, XAFS and SEM/EDS. The XPS and XAFS investigations indicated a partial reduction of Cr(VI) to Cr(III). The environmental compatibility of the Cr-loaded resin was examined using the EPA-TCLP method. The Cr-binding by the resin was very stable and regeneration attempts with HCl solutions of pH 3 were rather unsuccessful.

Keywords: chromium; removal; polyethylenimine–epichlorohydrin resin; uptake isotherms; kinetics; modeling; XAFS.

INTRODUCTION

Chromium is a high priority environmental pollutant. Its toxicity strongly depends on its oxidation state.¹ Cr(III), which is an essential dietary nutrient, can only be toxic in cases of an enhanced dose, while Cr(VI) has been associated

* Corresponding author. E-mail: misailid@chem.auth.gr
doi: 10.2298/JSC160419061S

with increased incidences of cancers. The different bioavailability and bioactivity between Cr(III) and Cr(VI) could be reasons of their toxicity differences.²

Cr(VI) occurs naturally in the environment from the erosion of natural chromium deposits, but can also be produced in a number of industrial processes. There are demonstrated instances of chromium being released to the environment by leakage, poor storage, or inadequate industrial waste disposal practices.³

Cr(VI) predominantly exists in alkaline aqueous solutions as CrO_4^{2-} (chromate), whereas $\text{Cr}_2\text{O}_7^{2-}$ (bichromate) and HCrO_4^- (hydrogen chromate) are the main chromium forms in the pH region 2–6.

A number of conventional techniques (*e.g.*, adsorption onto a variety of natural and synthetic sorbents,^{4–15} biosorption,^{16–21} ultrafiltration,^{22,23} flotation²⁴ and membrane filtration²⁵) have been proposed and applied for the removal of Cr(VI) from waters and wastewaters. The reduction of Cr(VI) to Cr(III) by various reducing agents followed or not by removal using another technique has also been applied in various cases.^{26–32}

Among the sorbent materials studied in the literature, those possessing characteristic functional groups, such as –OH, –COOH and –NH₂, were found to be of enhanced interest.

Polyethylenimine is a polymer possessing a large number of amine groups in its molecule. These groups can both chelate cationic and adsorb anionic metal species, through electrostatic interactions or hydrogen bonding.^{33,34} The polymer has also found applications in Cr(VI)-removal functionalizing a number of magnetic sorbents, biosorbents, active coals and sludge.^{35–41}

The objective of this work was the investigation of the ability of a polyethylenimine–epichlorohydrin resin to remove Cr(VI) from aqueous media under various conditions. The experimental studies were supplemented by modeling of the sorption equilibrium as well as by an investigation of the separation kinetics. The obtained maximum chromium uptake was also compared with selected data presented in the literature for other sorbents.

EXPERIMENTAL

In the present study, a polyethylenimine–epichlorohydrin resin was prepared using high molecular weight (\bar{M}_w or $n \approx 25000 \text{ g mol}^{-1}$, *PDI*) polyethylenimine (Sigma–Aldrich) and studied as a Cr(VI) sorbent. The resin was prepared using a modification of a previously described synthesis method.⁴² The main modifications of the synthesis were the selection of a lower preparation temperature (60 °C) and the use of nonylphenol ethoxylate (IGEPAL BC/6) surfactant. Some physicochemical properties of the resin is given in the Supplementary material to this paper.

The Cr(VI)-solutions were prepared by dilution of a stock $\text{K}_2\text{Cr}_2\text{O}_7$ solution (Sigma–Aldrich, analytical grade reagent) with bi-distilled water. The pH of the solutions was adjusted using HCl and NaOH.

For the sorption experiments 50 mg of the resin were contacted in polypropylene tubes for 24 h with 10 mL of Cr(VI) solutions of the appropriate concentration (300 to 5000 mg Cr

L^{-1}) and pre-adjusted pH at room temperature. After separation of the solid and liquid phase by centrifugation, the equilibrium pH (pH_{equil}) of the solutions was measured and the chromium concentration photometrically determined at 540 nm using 1,5-diphenylcarbazide as the complex-forming agent.⁴³ The obtained data were used to calculate the corresponding chromium uptake (mg g^{-1}).

The Cr(VI) removal from aqueous solutions by the resin was investigated in both the absence and presence of background electrolytes (one component 0.1 M NaNO_3 and 0.033 M Na_2SO_4 solutions; ionic strength due to electrolyte: 0.1 M). The experiments in the absence of background electrolyte were performed using solutions of pH pre-adjusted to 2–7, whereas those in the presence were pre-adjusted to pH 3 and 6.

The kinetics of chromium sorption by the resin was investigated at four different temperatures (15, 25, 35 and 45 °C). For this purpose, 1.2 g of the resin were contacted with 240 mL of ^{51}Cr -labeled solution of $c_{\text{init}} = 3000 \text{ mg Cr L}^{-1}$ and pH 3. At pre-determined intervals (1–120 min), 1 mL samples were withdrawn and the amount of Cr was determined by gamma ray spectroscopy using a high-purity germanium detector (Canberra REGe, efficiency 23 %, resolution 2.1 keV for the 1332 keV ^{60}Co line) connected with a computer-based gammascintillation set-up.

The resin particles were examined after contacting the chromium solutions by X-ray photoelectron spectroscopy (XPS, SPECS LHS-10UHV, base pressure in both chambers 1×10^{-9} mbar, non-monochromatized MgK_α line at 1253.6 eV, analyzer pass energy 97 eV), X-ray diffraction (XRD, Philips PW 1710 diffractometer with Ni-filtered CuK_α radiation (scanning region 2θ 3–63° and speed $1.2^\circ \text{ min}^{-1}$) and scanning electron microscopy (JEOL 840A SEM equipped with an Oxford ISIS 300 SEM-EDS analyzer).

CrK-edge X-ray absorption fine structure (XAES) experiments were conducted at the beam-line C of the DESY electron storage ring (Hamburg, Germany). The spectra were recorded at room temperature in the fluorescence yield mode using a 7-pixel Si(Li) fluorescence detector cooled to 77 K and positioned on the horizontal plane, at right angles to the beam. The angle of incidence was 45°.

The environmental compatibility of the Cr-loaded resin was investigated using the toxicity characteristic leaching procedure (TCLP, U.S. EPA Method 1311).⁴⁴

Regeneration tests of the Cr-loaded material were also performed. For this purpose, 50 mg of the resin loaded with the maximum possible quantity of chromium were contacted with 10 mL of HCl solution of pH 3 for 24 h. After centrifugation, the amount of Cr extracted into the liquid phase was determined by photometry.

RESULTS AND DISCUSSION

Sorption isotherm studies

The determined isotherms for the Cr(VI)-sorption from solutions of pre-adjusted pH 2–7 by the resin under investigation in the absence of background electrolyte are given in Fig. 1. The pH of the solutions influences the chromium species present and consequently their uptake by the sorbents. According to the literature, Cr(VI) is present in the form of CrO_4^{2-} in solutions of $\text{pH} > 6$. At lower pH values, the Cr(VI) is present either as HCrO_4^- or as $\text{Cr}_2\text{O}_7^{2-}$ depending on its concentration (transition concentration $\approx 550 \text{ mg L}^{-1}$).⁴⁵ On the other hand, the addition of the resin into the chromates solutions considerably increased their pH (pH_{equil} , Fig. S-1 of the Supplementary material).

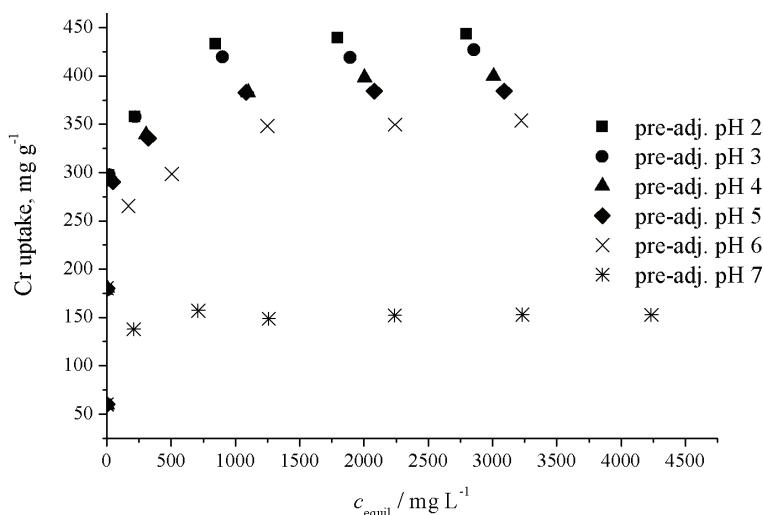
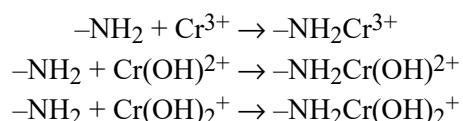


Fig. 1. Isotherms for the Cr(VI)-removal from aqueous solutions by the resin under investigation.

The highest chromium uptake by the sorbent under investigation was observed from solutions of pH 2. The uptake capacity decreased with increasing pH. This could be attributed to the increasing competition of the chromium anionic species by the hydroxyl ions present in the solutions but also to the reduction of hexavalent to trivalent chromium according to the reactions given by Eqs. (S-1)–(S-5) of the Supplementary material. The converted Cr(III) species may be chelated on the amine groups of the resin according to the following mechanism:



Cr^{3+} is the dominant chromium species in solutions of $\text{pH} < 3.5$, whereas Cr(OH)^{2+} mainly exists in the pH region between 3.5 and 6.5. Cr(OH)_2^+ could be present also in the pH region 5–8.5. The existence of Cr(III) on the sorbent surface (reduction of Cr(VI) to Cr(III)) was also verified by XPS measurements.

Assuming that Cr(VI) removal was also due to ion exchange, an additional reason for the uptake decrease in Cr(VI) solutions of pH 7 could be the presence at $\text{pH} > 6$ of CrO_4^{2-} that are less favorable for the sorption of Cr atoms because the charge ratio is 1:2 compared to 1:1 for HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$. The experimental Cr maximum sorption capacity values (q_{\max}) of the resin from solutions pre-adjusted to pH 2–7 are summarized in Fig. S-2 of the Supplementary material.

Effect of background electrolyte

The Cr(VI)-sorption by the investigated materials showed a dependence on the presence of competing anions. The experiments performed in the presence of background electrolytes indicated that sulfate ions reduced the Cr(VI) uptake to a higher extent than nitrates (Fig. S-3 of the Supplementary material). This could most probably be due to the larger charge density of the sulfates competing stronger than the nitrates. The experimental maximum sorption capacity (q_{\max}) values for the resin in the absence and presence of background electrolytes are given in Table I.

TABLE I. Experimental maximum sorption capacity q_{\max} / mg g⁻¹ values of the resin in the absence and presence of background electrolytes

Pre-adjusted pH	Maximum sorption capacity, mg g ⁻¹		
	No electrolyte	0.1 M NaNO ₃	0.033 M Na ₂ SO ₄
2	443		
3	427	356	342
4	399		
5	384		
6	354	325	291
7	153		

XPS, NEXAFS and EXAFS investigations of the Cr-loaded resin particles

An XPS examination of the Cr-loaded resin was performed in order to determine the form of chromium on the sorbent surface. The evaluation of the XPS data revealed a rather enhanced but not complete reduction of Cr(VI) to Cr(III). This conclusion was drawn by the deconvolution of Cr2p_{3/2} peak appearing on the binding energy spectrum into two components, one with maximum at 576.6 eV and another at 579.1 eV (Fig. 2). These two peaks can be assigned to Cr(III) and Cr(VI) oxides, respectively.⁴⁶ The partial reduction of Cr(VI) to Cr(III) was also observed by Sun *et al.* who removed chromium from aqueous solutions using aerobic granular sludge functionalized polyethylenimine.^{40,41} The use by the same group polyethylenimine functionalized by poly(glycidyl methacrylate) as the Cr sorbent did not indicate any Cr(VI) to Cr(III) reduction, supporting the assumption that the oxidation state modification was due to the micro-organisms present in the sludge.⁴⁷ In the present case the reduction of Cr(VI) is most probably connected with the presence of chlorine in the used sorbent.

The presence of Cr(III) on the resin particles was also proved by Cr-K-near edge X-ray absorption fine structure (Cr-K-NEXAFS) studies using K₂CrO₄ (Cr(VI)) and CrCl₃ (Cr(III)) as the reference materials (Fig. 3). The presence of considerable Cr(VI) concentration would induce a shift in the position of the absorption edge (E_{abs}) in the NEXAFS spectrum of the studied sample to higher

energies, compared to the E_{abs} of the Cr(III) reference, and would also yield an increase in the intensity of the pre-edge feature.

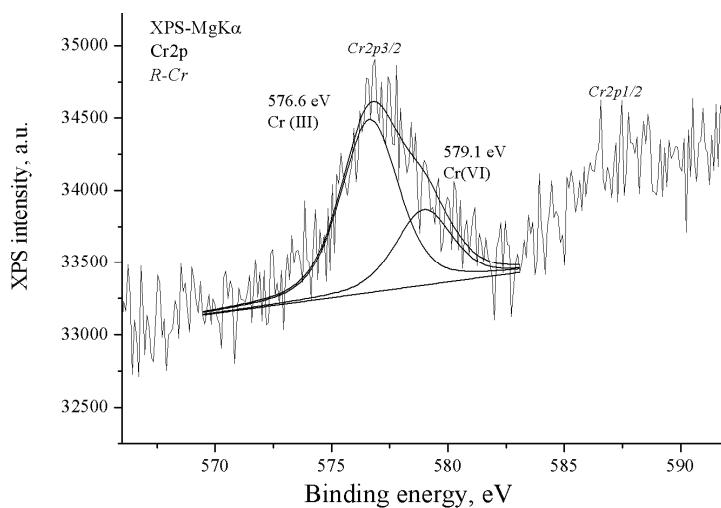


Fig. 2. XPS spectrum of the Cr-loaded resin.

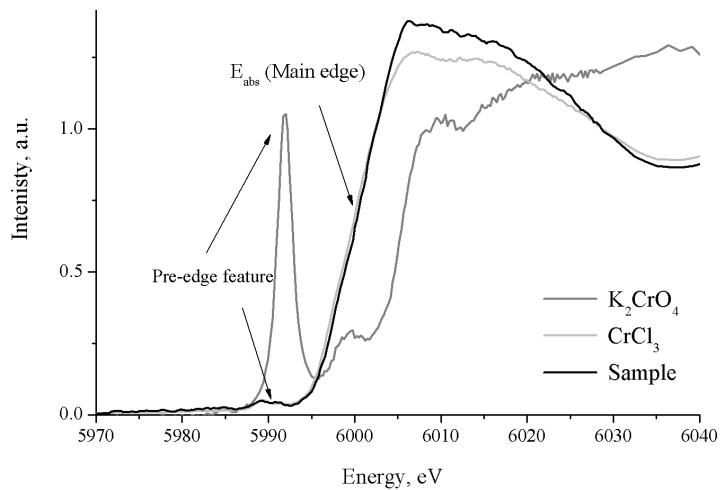


Fig. 3. Cr-K-NEXAFS spectra of the Cr-loaded resin and the reference samples.

The E_{abs} (main edge in Fig. 3) corresponds to transitions in the continuum ($1s \rightarrow 4p$), whereas the region below (pre-edge peak) to the electron transitions $1s \rightarrow 3t_2$ that are dipole forbidden. However, these transitions gain intensity due to reasons determined by the geometry around the absorbing metal. In this way, the pre-edge region of the spectrum provides information about the coordination of the chromium and consequently its oxidation state. Thus, when Cr is octahed-

rically coordinated (Cr(III)), the pre-edge peak is characterized by low intensity and large FWHM, whereas when Cr is tetrahedrally coordinated (Cr(VI)), the transition gains intensity due to the mixing of the Cr 3d orbitals with the 4p orbitals of the ligand atoms, *i.e.*, the pre-edge feature is sharp and intense.⁴⁸

The Fourier Transform (FT) of the extended X-ray absorption fine structure (EXAFS) spectra of the studied sample showed only one resolved peak corresponding to the first nearest neighboring shell and no further structure after this peak. This finding was an indication that the compound under investigation was characterized by short-range order, *i.e.*, it was amorphous or nanocrystalline. The amorphous character of the resin and its Cr-loaded form was also proven by their XRD patterns indicating no crystalline phases.

SEM/EDS examination of the resin particles

The SEM/EDS examination of cross sections of the Cr-loaded resin particles revealed that chromium was evenly distributed throughout the bulk of the resins and not bound only to their surface (Fig. 4).

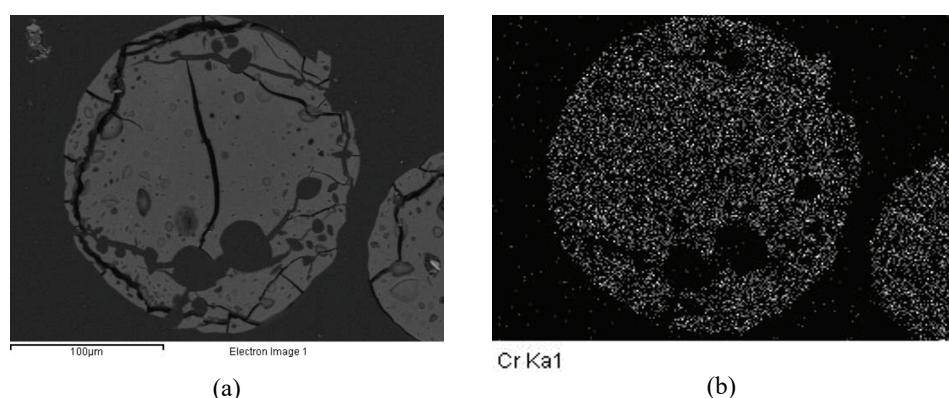


Fig. 4. SEM image of a section of resin grains after Cr-sorption (a) and the corresponding Cr mapping by EDS using the Ka_1 X-ray line of Cr (b).

Modeling of the sorption isotherms

The obtained experimental Cr uptake data were used for modeling calculations using four isotherm equations (Table S-I of the Supplementary material). The non-linear curve fitting was performed using the Levenberg–Marquardt algorithm. The isotherm parameters were determined by minimizing the sum of the error squares (objective function) across the concentration range studied:

$$\sum_{i=1}^N (q_{e,\text{exp}} - q_{e,\text{calc}})_i^2 \quad (1)$$

where N is the number of experimental data points, $q_{e,\text{exp}}$ and $q_{e,\text{calc}}$ are the experimental and calculated equilibrium concentrations in the solid phase, respectively. The relationship between two variables (experimental and theoretically predicted) was assessed by the coefficient of determination (correlation coefficient squared, R^2), an approximation of the standard deviation (S), the Fisher test (F) and the mean error (ME , %).⁴⁹

It is well known that the quality of the fit is usually connected with the number of the parameters involved in the model. On the other hand, when the number of parameters involved increases, several local minima of the objective function can occur during the process of curve fitting.^{50,51} Thus, similar to a previous study, in order to find the global minimum of the objective function, the experimentally obtained value of the maximum adsorption capacity ($q_{e,\text{max}}$) was used as an initial guess of the q_{max} parameter, while the value of K_{init} was changed by one order of magnitude at a time (0.0001, 0.001, 0.01, 0.1, 1.0, *etc.*). The border range of optimization was from 1×10^{-10} to 1×10^{10} .⁵²

This procedure was repeated until the objective function achieved the lowest value. Such an approach made the iteration procedure well-posed and independent of the rest parameters guess, in case of three-parameter models containing the formulae reducible to the Langmuir one.⁵³ However, the results of the present study (representative sorption equilibrium data are given in Table II) indicated that even in the case of the two-parameter Langmuir model there are many sets of optimum parameters (K and q_{max}) depending on the initial value of K_{init} . Based on the statistical tests, the best set of parameters was achieved for $K_{\text{init}} = 0.4$, although visual comparison of fitting curves obtained for different initial K guesses (Fig. S-4 of the Supplementary material) confirmed the unacceptable match of the equilibrium data. Such a situation could be due to the scattering points or to the incomplete isotherm curve.⁵⁴ As it was already pointed out, there is a minor difference between the number of experimental data obtained in this study (7 points) and those presented in previous works (12 and 21 points^{55,56}). Thus, a lower number of experimental points can provide a higher robustness of the model (problem with global minimum localization).

The same iterative procedure was applied in order to find the best set of parameters for the three-parameter models. As shown in Fig. S-4b, the three-parameter models closely overlap each other. The best value of the statistical test was obtained for the Redlich–Peterson model (Table III).

On the other hand, the Langmuir–Freundlich as well as the Toth models served to estimate the maximum chromium uptake values (q_{max}) that were obtained during the experiment ($q_{e,\text{max}}$).

All three-parameter models applied were narrowed to the Langmuir one when the exponential parameter n was equal to unity. In the case of the Langmuir–Freundlich and Toth models, the value of the exponential parameter n con-

siderably deviated from unity indicating a strong degree of heterogeneity of the system. In contrast, the value of $n = 0.961$ for the Redlich–Peterson model incorporates features of the Langmuir form.

TABLE II. The Langmuir (L) model sensitivity to the initial guess of estimated parameter (K) for sorption of Cr(VI) by the resin from aqueous solutions at pH_{init} 3; $q_{\text{init,max}}$ was set equal to $q_{\text{e,max}}$ (427.05 mg g⁻¹)

Initial K_{init}	Calculated parameters			Statistical tests		
	$q_{\text{max}}/\text{mg g}^{-1}$	K	S	F	R^2	$ME / \%$
0.1	394.9	0.869	61.06	5.358	0.844	17.87
0.2	395.0	0.869	61.07	5.357	0.844	17.87
0.3	394.8	0.869	61.06	5.359	0.844	17.88
0.4	391.6	0.878	60.99	5.370	0.845	17.95
0.5	406.1	0.842	62.53	5.110	0.837	17.63
0.8	425.9	0.798	69.32	4.157	0.800	18.03

TABLE III. Isotherm parameters of the RP, LF and T models (see Table S-I) for Cr(VI) sorption by the resin from aqueous solutions of pre-adjusted pH 3; $q_{\text{e,max}}$ (427.05 mg g⁻¹)

Model	Calculated parameters				Statistical tests			
	$q_{\text{max}}/\text{mg g}^{-1}$	K	n	m	S	F	R^2	$ME / \%$
RP	309.4	1.172	0.961	—	54.77	6.661	0.900	13.57
LF	427.1	0.206	0.599	—	58.75	5.789	0.885	13.61
T	418.9	1.306	0.577	—	58.13	5.912	0.887	14.47

The kinetics of Cr sorption

The kinetics of the Cr-sorption by the investigated resins was fast ($t_{1/2} \leq 2$ min). The maximum removal occurred within 10–15 min of contact time. Moreover, no significant influence of the temperature was observed (Fig. S-5 of the Supplementary material).

Two equations were used to reproduce the kinetics of the sorption data: the pseudo-first and the pseudo-second order.⁵⁵

The Lagergren equation for pseudo-first order rate, in linear form, is given by:

$$\log(q_{\text{equil}} - q_t) = \log q_{\text{equil}} - \frac{k_1}{2.303}t \quad (2)$$

where k_1 / min^{-1} is the rate constant of pseudo-first-order sorption and q_{equil} and $q_t / \text{mg g}^{-1}$ respectively denote the amounts of sorbed metal ions at equilibrium and at time t . A plot of $\log(q_{\text{equil}} - q_t)$ versus t should give a straight line confirming the applicability of the kinetic model.

The pseudo-second-order equation is given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\text{equil}}^2} + \frac{t}{q_{\text{equil}}} \quad (3)$$



where $k_2 / \text{g mg}^{-1} \text{ min}^{-1}$ is the rate constant of pseudo-second order sorption. A plot of t/q_t versus t should give a linear relationship for second-order kinetics.

The kinetics of the Cr sorption by the resin under investigation seems to obey the pseudo-second order model giving a straight line in the plot t/q_t vs. t for all investigated temperatures (15, 25, 35 and 45 °C, Fig. S-6 of the Supplementary material).

The determination of the rate constant k for the metal sorption at different temperatures enables the calculation of the activation energy of the reaction, $E_a / \text{kJ mol}^{-1}$ using the Arrhenius equation. As seen in Fig. S-7, the typical Arrhenius plot of $\ln k$ versus $1/T$ was found to give a straight line. The obtained E_a value was 21.42 kJ mol⁻¹. This value is marginally above the characteristic range for physisorption (5–20 kJ mol⁻¹),⁵⁶ a fact that could be taken as an indication of the complex nature of the sorption process (chemi- and physisorption).

Study of the environmental compatibility and regeneration of the Cr-loaded resin

The results of the study of the environmental compatibility (TCLP method) of the Cr-loaded resin showed that the amount of Cr extracted from the resin was 3.35 mg L⁻¹. The discharge threshold for chromium is, according to the law, 5.0 mg L⁻¹ and therefore the quantity of Cr extracted from the resin was lower than the legal limits.⁵⁷

The regeneration of the sorbent loaded with the maximum possible quantity of chromium (427 mg g⁻¹ for pH 3) using HCl solution of pH 3 was not especially successful. Only 63 ng L⁻¹ of chromium were extracted from the resin. These results indicated that it is not possible to regenerate the resin, while implying a high stability of chromium binding.

Comparison of the experimental results with literature data

A number of publications in the literature deal with the separation of Cr(VI) from aqueous solutions. A comparison between the results obtained during this work and some characteristic data for other sorbents found in the literature is presented in Table S-II of the Supplementary material. The values of Cr(VI) uptake determined in this work were significantly higher than those of most of the sorbents reported by other authors.

CONCLUSIONS

This study indicated that the investigated resin could very effectively remove Cr(VI) from aqueous solutions. The Cr(VI)-separation depended on the pH of the solutions and on the presence of competing anions. XPS and XAFS investigations of the Cr-loaded resin particles indicated a considerable reduction of Cr(VI) to Cr(III). The binding of chromium appeared to be very stable. Regeneration attempts of the Cr-loaded resins using HCl solutions of pH 3 were not especially successful.

The modeling of the sorption equilibrium was highly sensitive to the initial parameter guess. The three-parameter models were found to provide a better fit to the experimental equilibrium data than the Langmuir one. However, the results of modeling calculations did not indicate any preference for one over the other models in terms of the goodness-of-fit, as well as the prediction of maximum sorption capacity.

The Cr-sorption onto the resin very rapid at all studied temperatures and well reproduced by the pseudo-second order kinetics equation.

The experimental results indicated that the investigated resin shows application potential for the removal of Cr(VI) from waters and wastewaters.

SUPPLEMENTARY MATERIAL

The additional data related to the resin, adsorption efficiency kinetics and modelling are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД
УКЛАЊАЊЕ ХРОМА(VI) ИЗ ВОДЕНИХ РАСТВОРА ПОМОЋУ
ПОЛИЕТИЛЕНИМИН-ЕПИХЛОРИДИН СМОЛЕ

SOFIA SARRI¹, PANAGIOTIS MISAEELIDES¹, DIMITRIOS ZAMBOULIS¹, FOTINI NOLI¹, JOLANTA WARCHOŁ²,
FANI PINAKIDOU³ и MARIA KATSIKINI³

¹*Department of Chemistry, Aristotle University, GR-54124 Thessaloniki, Greece*, ²*Department of Water Purification and Protection, Rzeszow University of Technology, Rzeszow, Poland* и ³*Department of Physics, Aristotle University, GR-54124 Thessaloniki, Greece*

Испитивана је способност синтетисане полиетиленамин-епихлорохидрин смоле за уклањање Cr(VI) из водених растворова у одсуству (почетна pH вредност 2–7) и у присуству носећих електролита (раствори NaNO₃ и Na₂SO₄, почетне pH вредности 3 и 6). Утврђено преузимање хрома је значајно више него оно које је публиковано за већину других сорбената. Фотометријски одређени подаци су анализирани Langmuir, Redlich–Peterson, Langmuir–Freundlich и Toth моделима. Резултати моделовања нису дали било какву предност неком од модела у смислу слагања са резултатима и предикције максималног сорпционог капацитета. Кинетика сорпције испитана је на температурима од 15, 25, 35 и 45 °C коришћењем раствора обележених помоћу ⁵¹Cr и спектрометријом ўзрацима. Сорпција хрома је врло брза на свим испитиваним температурима и одговара закону брзине псевдо-првог реда. Вредности константе брзине и енергије активације израчунате су из експерименталних података. Смола засићена хромом је испитана методом EPA-TCLP. Везивање хрома за смолу је врло стабилно, а регенерација смоле помоћу раствора HCl (pH 3) је углавном неуспешна.

(Примљено 19. априла, ревидирано и прихваћено 9. јуна 2016)

REFERENCES

- U.S. Environmental Protection Agency, *Toxicological Review of Hexavalent Chromium*, National Center for Environmental Assessment, Office of Research and Development, Washington DC, 1998, <http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1006B2Z.txt> (accessed 11.4.16)

2. U.S. Department of Health and Human Services, *Toxicological Profile for Chromium*, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), Atlanta, GA, 2012, <http://www.atsdr.cdc.gov/toxprofiles/tp7.pdf> (accessed 11.4.16)
3. D. E. Kimbrough, Y. Cohen, A. M. Winer, L. Creelman, C. Mabuni, *Crit. Rev. Env. Sci. Tech.* **29** (1999) 1
4. M. C. Brum, J. L. Capitaneo, J. F. Oliveira, *Miner. Eng.* **23** (2010) 270
5. N. K. Lazaridis, D. N. Bakoyannakis, E. A. Deliyanni, *Chemosphere* **58** (2005) 65
6. G. M. Haggerty, R. S. Bowman, *Environ. Sci. Technol.* **28** (1994) 452
7. P. Misaelides, D. Zamboulis, Pr. Sarrisdis, J. Warchol, A. Godelitsas, *Micropor. Mesopor. Mater.* **108** (2008) 162
8. E. Pehlivan, S. Cetin, *J. Hazard. Mater.* **163** (2009) 448
9. S. Edebali, E. Pehlivan, *Chem. Eng. J.* **161** (2010) 161
10. M. Ghiaci, R. Kia, A. Abbaspur, F. Seyedeyn-Azad, *Sep. Purif. Technol.* **40** (2004) 285
11. T. Shi, Z. Wang, Y. Liu, S. Jia, D. Changming, *J. Hazard. Mater.* **161** (2009) 900
12. S. X. Liu, X. Chen, X. Y. Chen, Z. F. Liu, H. L. Wang, *J. Hazard. Mater.* **141** (2007) 315
13. F. Di Natale, A. Lancia, A. Molino, D. Musmarra, *J. Hazard. Mater.* **145** (2007) 381
14. S. Mor, K. Ravindra, N. R. Bishnoi, *Bioresour. Technol.* **98** (2007) 954
15. N. Zhao, N. Wei, J. Li, Z. Qiao, J. Cui, F. He, *Chem. Eng. J.* **115** (2005) 133
16. L. Yang, J. P. Chen, *Bioresour. Technol.* **99** (2008) 297
17. Z. Aksu, E. Balibek, *J. Hazard. Mater.* **145** (2007) 210
18. M. Ziagova, G. Dimitriadis, D. Aslanidou, X. Papaioannou, E. Litopoulou Tzannetaki, M. Liakopoulou-Kyriakides, *Bioresour. Technol.* **98** (2007) 2859
19. J. Anandkumar, B. Mandal, *J. Hazard. Mater.* **186** (2011) 1088
20. G. Z. Kyzas, M. Kostoglou, N. K. Lazaridis, *Chem. Eng. J.* **152** (2009) 440
21. A. C. Zimmermann, A. Mocabô, T. Fagundes, C. A. Rodrigues, *J. Hazard. Mater.* **179** (2010) 192
22. M. K. Aroua, F. M. Zuki, N. M. Sulaiman, *J. Hazard. Mater.* **147** (2007) 752
23. G. Arthanareeswaran, P. Thanikaivelan, N. Jaya, D. Mohan, M. Raajenthiren, *J. Hazard. Mater.* **139** (2007) 44
24. S. E. Ghazy, G. A. Moustafa, *Bull. Chem. Soc. Jpn.* **74** (2001) 1273
25. F. J. Alguacil, C. Caravaca, M. I. Martin, *J. Chem. Technol. Biotech.* **78** (2003) 1048
26. C. E. Barrera-Díaz, V. Lugo-Lugo, B. Bilyeu, *J. Hazard. Mater.* **223–224** (2012) 1
27. H. Cui, M. Fu, S. Yu, M. K. Wang, *J. Hazard. Mater.* **186** (2011) 1625
28. G. Qin, M. J. McGuire, N. K. Blute, C. Seidel, L. Fong, *Environ. Sci. Technol.* **39** (2005) 6321
29. A. H. Caravelli, L. Giannuzzi, N. E. Zaritzky, *J. Hazard. Mater.* **156** (2008) 214
30. A. Bampaiti, F. Noli, P. Misaelides, *J. Radioanal. Nucl. Chem.* **298** (2013) 909
31. S. E. Lee, J. U. Lee, H. T. Chon, J. S. Lee, *J. Geochem. Explor.* **96** (2008) 144
32. N. Zaitseva, V. Zaitsev, A. Walcarius, *J. Hazard. Mater.* **250–251** (2013) 454
33. L. Wang, W. Liu, T. Wang, J. Ni, *Chem. Eng. J.* **225** (2013) 153
34. Y. G. Zhao, H. Y. Shen, S. D. Pan, M. Q. Hu, *J. Hazard. Mater.* **182** (2010) 295
35. I. Larraza, M. López-Gómez, T. Corrales, G. Marcelo, *J. Colloid Interface Sci.* **385** (2012) 24
36. L. Xu, L. Yang, M. Luo, X. Liang, X. Wei, J. Zhao, H. Liu, *J. Hazard. Mater.* **189** (2011) 787
37. S. Deng, Y. P. Ting, *Environ. Sci. Technol.* **39** (2005) 8490
38. M. Owlad, M. K. Aroua, W. M. Wan Daud, *Bioresource Technol.* **101** (2010) 5098
39. R. A. Khaydarov, R. R. Khaydarov, O. Gapurova, *Water Res.* **44** (2010) 1927



40. X. F. Sun, Y. Ma, X. W. Liu, S. G. Wang, B. Y. Gao, X. M. Li, *Water Res.* **44** (2010) 2517
41. X. F. Sun, C. Liu, Y. Ma, S. G. Wang, B. Y. Gao, X. M. Li, *Colloids Surfaces, B* **82** (2011) 456
42. A. D. Ebner, J. A. Ritter, H. J. Ploehn, R. L. Kochen, J. D. Navratil, *Sep. Sci. Technol.* **34** (1999) 1277
43. A. D. Eaton, L. S. Clesceri, A. E. Greenberg, *Standard Methods for the Examination of Water and Wastewater*, 19th ed., APHA, Washington DC, 1995, pp. 3–59
44. EPA, Method 1311, *Toxicity Characteristic Leaching Procedure*, <https://www.epa.gov/sites/production/files/2015-12/documents/1311.pdf> (accessed 11.4.16)
45. C. F. Baes Jr., R. E. Mesmer, *The Hydrolysis of Cations*, Krieger Publishing Company, Malabar FL, 1986, pp. 211–220
46. A. V. Naumkin, A. Kraut-Vass, S. W. Gaarenstroom, C. J. Powell, *NIST X-ray Photo-electron Spectroscopy Database*, NIST Standard Reference Database 20, Version 4.1, 2012, http://srdata.nist.gov/xps/EngElmSrchQuery.aspx?EType=PE&CSOpt=Retri_ex_dat&Elm=Cr (accessed 11.4.16)
47. X. Sun, L. Yang, H. Xing, J. Zhao, X. Li, Y. Huang, H. Liu, *Colloids Surfaces, A* **457** (2014) 160
48. M. Tromp, J. Moulin, G. Reid, J. Evans, *Cr K-edge XANES spectroscopy: ligand and oxidation state dependence - what is oxidation state?* Proceedings of the 13th Int. Conference on X-Ray Absorption Fine Structure - XAFS13, AIP, 2007, Stanford, CA, USA, AIP Publishing, Melville NY, 2007, pp. 699,882
49. S. C. Chapra, R. P. Canale, *Numerical methods for engineers*, 2nd ed., McGraw Hill International, USA, 1990
50. D. I. Song, W. S. Shin, *Environ. Sci. Technol.* **39** (2005) 1138
51. M. Cernik, M. Borkovec, J. C. Westall, *Environ. Sci. Technol.* **29** (1995) 413
52. E. Repo, R. Petrus, M. Sillanpää, J. K. Warchał, *Chem. Eng. J.* **172** (2011) 376
53. J. Warchał, M. Matłok, P. Misaelides, F. Noli, D. Zamboulis, A. Godelitsas, *Micropor. Mesopor. Mater.* **153** (2012) 63
54. K. V. Kumar, S. Sivanesan, *J. Hazard. Mater.* **134** (2006) 237
55. Y. S. Ho, G. McKay, *Process. Biochem.* **34** (1999) 451
56. Y. S. Ho, J. C. Y. Ng, G. McKay, *Sep. Sci. Technol.* **36** (2001) 241
57. U.S. Environmental Protection Agency, *Introduction to Hazardous Waste Identification* (40 CFR Parts 261) EPA530-K-05-012, 2005, <http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=P1009II8.txt> (accessed 11.4.16).