Hybrid polymer containing ferric oxides obtain using a redox polymer. Part II. Sorption properties towards chromate

Irena Jacukowicz-Sobala[1)], **Agnieszka Ciechanowska**[1)], **Elżbieta Kociołek-Balawejder**[1),*)]

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Abstract: In this work a hybrid material containing iron oxide was used as an effective sorbent for removal of Cr(VI) from water solutions. The hybrid sorbent was obtained by new method using redox S/DVB copolymer containing *N*-chlorosulfonamide functional groups in reduction/oxidation reaction with Fe(II) ions. The obtained product contained sulfonamide functional groups which are not charged in wide pH range (till pH = 11.0), what differs our product from other polymeric hybrid sorbents with iron oxide reported in the literature and obtained on the basis of ion exchangers. The sorption kinetic data were well described by pseudo-second order model indicating the chemisorption of chromate onto iron oxide surface. These data also correlated well with intraparticle diffusion model, what showed that diffusion within the polymer structure was the rate determining step of the chromate sorption process. The equilibrium studies showed that removal of Cr(VI) was pH dependent and was favored under acidic conditions (pH = 2.5—5.0). After adsorption process chromates were effectively desorbed from the adsorbent surface by NaOH solution.

Keywords: hybrid polymers, iron oxides, nanocomposites, chromate adsorption.

Polimer hybrydowy zawierający tlenki żelaza otrzymany z wykorzystaniem polimeru redoksowego. Cz. II. Badanie właściwości sorpcyjnych wobec chromianów

Streszczenie: W pracy przedstawiono wyniki badań sorpcji jonów Cr(VI) przy użyciu zsyntezowanego polimeru hybrydowego zawierającego tlenki żelaza. Hybrydowy sorbent otrzymano w wyniku reakcji utleniania jonów Fe(II) z wykorzystaniem makroporowatego, redoksowego polimeru S/DVB z *N*-chlorosulfonamidowymi grupami funkcyjnymi w formie Na^+. Uzyskany produkt zawiera sulfonamidowe grupy funkcyjne charakteryzujące się wysokim pK_a = 11, dzięki czemu nie wykazuje on właściwości jonowymiennych, a jedynie sorpcyjne (w odróżnieniu od opisanych w literaturze polimerów hybrydowych otrzymywanych z wykorzystaniem wymieniaczy jonowych). Badano sorpcję z roztworów Cr(VI), o stężeniach od 5 do 100 mg Cr(VI)/dm^3 i o różnym pH, od 2,5 do 11,0 a także w obecności innych jonów: Cl^- (500 mg/dm^3) i SO_4^{2-} (1000 mg/dm^3). Badania kinetyczne wykazały, że sorpcja chromianów przebiega zgodnie z modelem chemicznym (*pseudo-second order model*) (rys. 1), co dowodzi chemisorpcji chromianów na powierzchni tlenków żelaza. Z kolei, dobre dopasowanie danych eksperymentalnych do modelu dyfuzyjnego (*intraparticle diffusion model*) wskazuje, że czynnikiem determinującym szybkość procesu jest dyfuzja chromianów w głąb struktury ziarna polimeru (rys. 2). Wykazano również, że sorpcja chromianów jest zależna od pH roztworu i przebiega najbardziej efektywnie w środowisku kwasowym (pH = 2,5—5,0) (rys. 3). Przemywanie zużytego złoża hybrydowego polimeru roztworem 0,1 M NaOH, pozwoliło na zdesorbowanie 93 % jonów Cr(VI).

Słowa kluczowe: polimery hybrydowe, tlenki żelaza, nanokompozyty, adsorpcja chromianów.

Chromium(VI) compounds, according to the IARC (International Agency for Research on Cancer) classification, are 1 group carcinogens and exhibit mutagenic, teratogenic properties. The widespread use of chromium in metallurgy, leather tanning, electroplating and production of pigments and wood preservatives results in large quantities of waste and effluents containing its compounds. The Cr(VI) concentration in industrial effluents may vary from tens to hundreds mg/dm^3 [1], while its limit for discharge into surface waters is 0.1 mg/dm^3 [2]. Various methods are used for removal of chromate from wastewater, including chemical precipitation, electroche-

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1) Wrocław University of Economics, Department of Industrial Chemistry, ul. Komandorska 118/120, 53-345 Wrocław, Poland.

*) Corresponding author; e-mail: elzbieta.kociolek-balawejder@ue.wroc.pl

mical reduction, ion exchange and membrane processes [3, 4]. These methods have been designed for purification of effluents containing high concentrations of Cr(VI) but are not useful for its removal at low concentrations. For this purpose the most promising are adsorption methods, which in the past decade have been widely studied. The most commonly used sorbents are activated carbons and biosorbents, often produced from waste biomass [5, 6]. The disadvantage of these materials is their low selectivity towards metal ions. In contrast to activated carbons and biosorbents, iron oxides show selective sorption capacity for removal of heavy metals. Several authors have examined the adsorption of chromate by iron oxide, reporting high selectivity and efficiency of this process [7—10]. To overcome the difficulties caused by agglomeration of iron oxide nanoparticles, diminishing their surface and causing the drop of hydraulic pressure in the fixed-bed unit flow systems, the iron oxides are dispersed within the matrix of the polymeric ion exchangers. The obtained products are called hybrid polymers. The authors of articles concerning hybrid polymers focus on their applications in sorption processes such as removal of trace copper(II), cadmium(II), lead(II) arsenite, arsenate, phosphate, perchlorate and 2,6-dichlorophenol from waters [11—19]. There is relatively little information on application of this type of material for chromate removal [20, 21].

In this study we used hybrid polymer obtained as a result of the Fe(II) oxidation reaction using the *N*-chlorosulfonamide reactive polymer as an oxidant and matrix for iron oxide deposition. The obtained hybrid polymer was highly porous, mechanically durable and easily separable material which synthesis and characteristics was described in previous study [22]. This material contained primarily sulfonamide groups (with pK_a over 11.0) which are charged only in a very narrow pH range, characteristic for strongly basic solutions, in contrast to other hybrid polymers described in the literature, containing cationic or anionic functional groups active over the whole pH range. The absence of ion-exchange groups in the polymer matrix enables one to eliminate the Donnan exclusion effect during the adsorption processes [12]. In regard to practically nonionic structure of the host polymer it is interesting to investigate the sorptive properties of the obtained product towards chromate. In this work the hybrid S/DVB sulfonamide polymer containing iron oxide was tested for Cr(VI) adsorption from water solutions.

EXPERIMENTAL PART

Reagents and materials

All reagents used in this study were of analytical grade. The chromate stock solution [1 mg Cr(VI)/cm^3] was prepared from $K_2Cr_2O_7$ (Chempur, ≥ 99,5 % purity). As the sorbent for chromate removal was used the hybrid S/DVB sulfonamide polymer containing iron oxide which method of synthesis and characteristic was described earlier [22].

Adsorption experiments

The adsorption kinetic experiment was carried out in the batch regime by mixing 1.0 g of dried hybrid polymer sample (non-neutralized) with 100 cm^3 of K_2CrO_4 solution at 50 mg Cr(VI)/dm^3 concentration and pH = 7.7. Adsorption isotherm studies were conducted by mixing 0.5 g of the dried hybrid polymer with 25 cm^3 of K_2CrO_4 and varying Cr(VI) concentrations from 5 to 100 mg Cr(VI)/dm^3 of solution. The experiments were carried out in four series at various pH levels: 2.5, 5.5, 7.5 and 11.0. Since the obtained hybrid polymer caused the acidification of the solutions during the adsorption process, the samples of sorbent were previously neutralized with Na_2CO_3 solution in order to transform the residual sulfonic groups from hydrogen form into the sodium form. This procedure allowed maintaining constant pH of the solutions (5.5, 7.5 and 11.0). The samples were shaken on a shaker for 48 h at 330 rpm. After the sorption process the solutions were analyzed for chromate and total chromium concentration. Fixed-bed column adsorption experiments were performed using a glass column (11 mm in diameter, 300 mm in length) and a constant-flow stainless steel pump. Samples of hybrid polymer 8.0 g in the dry state after swelling in water were packed into the column (BV— bed volume = 15.5 cm^3). Then K_2CrO_4 solutions (10 mg Cr(VI)/dm^3 and 10 mg Cr(VI)/dm^3 with competing anions 500 mg Cl^-/dm^3, 1000 mg SO_4^{2-}/dm^3) were passed through the hybrid polymer beds at the flow rate of 3.5 BV/h. Fractions (100, 250 cm^3) were collected and analyzed for pH, total chromium, chromate, chloride, sulfate, ferrous and ferric ion concentrations. After the sorption process, in order to recover adsorbed Cr(VI) anions 0.1 M of NaOH solution was passed through the bed of hybrid polymer. Fractions (50 cm^3) were collected to estimate chromate concentration. All the adsorption experiments were carried out at 22.0 °C.

Methods of testing

The concentrations of Cr(VI), Fe(II) and Fe(III) were measured by spectrophotometric methods using a Spekol 1200 spectrophotometer (Analytik Jena, Germany). Concentrations of Cr(VI), Fe(II) and Fe(III) were determined with respectively 1,5-diphenylcarbazide, 1,10-phenanthroline and potassium thiocyanate. Absorbance measurements were taken at 540 nm, 510 nm and 480 nm, respectively. The detection limits of spectrophotometric methods were as follows: Cr(VI) 0.0125 mg/dm^3, Fe(II) 0.002 mg/dm^3 and Fe(III) 0.2 mg/dm^3 [23]. In order to determine total chromium concentration, the samples of effluent were oxidized with $KMnO_4$ the excess of which after 5 min was reduced with sodium azide (the reactions were conducted at 100 °C). The concentrations of chloride and sulfate were determined with the ion chromatography method using a Merck-Hitachi liquid chromatograph equipped with a conductometric detector, Knauer SmartLine 1000 gradient pump and Hamilton PRP-X100 column. The analysis was performed at the temperature of 35 °C using 4 mM *p*-hydroxybenzoic acid aqueous solution with 2.5 % methanol and pH 8.9 as a mobile phase. The flow rate of the eluent was 2.0 cm^3/min.

RESULTS AND DISCUSSION

Fig. 1 shows the kinetic study of the chromate sorption process on the hybrid polymer which proceeded with high efficiency. After 24 hours the uptake of Cr(VI) was about 75 %. During the following 48 hours of contact, additional adsorption of chromate occurred and reached 85 % of its removal. One should note the pH changes of chromate solution during the adsorption process. After 30 minutes, pH decreased from 7.7 to 2.7 and remained at that level until the end of the experiment. The acidification of the solution may be a result of the protons release from residual sulfonic groups (0.3 mmol/g) due to ion exchange reaction, which occurred between sulfonic groups and potassium ions. Since the precipitation of inorganic deposit occurred under acidic conditions and the by-product of reaction (1, Part I) is sulfuric acid, a part of residual sulfonic groups is probably in the hydrogen form (the kinetic study was carried out using non-neutralized hybrid polymer). Another explanation of the acidification is the desorption of protons from the surface hydroxyl groups of iron oxide, which was also highly protonated after synthesis.

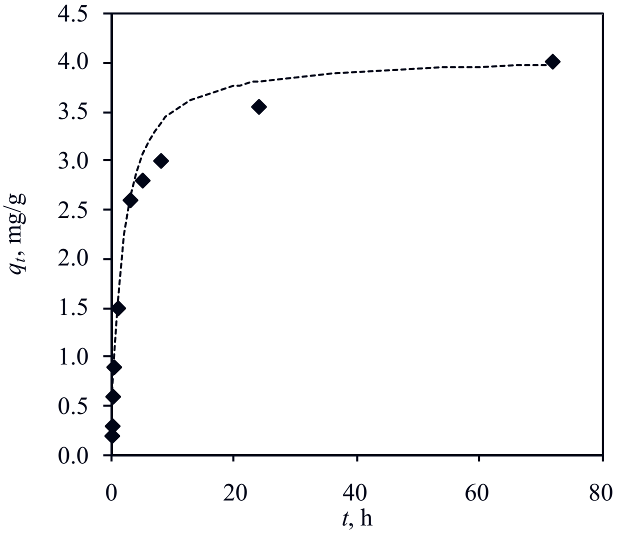

Fig. 1. Effect of time on Cr(VI) removal by hybrid polymer (1.0 g of R/S/Fe sample + 100 cm^3 K_2CrO_4 solution [50 mg Cr(VI)/dm^3]). Experimental data and pseudo-second order model calculations are represented by symbols and lines, respectively

The mechanism of the adsorption process is generally described by a combination of three major steps: (a) transport of adsorbate molecules from bulk solution to the adsorbent surface, (b) transport of adsorbate molecules within the porous structure of the adsorbent particle and (c) adsorption at a site on the surface. The adsorption models, both kinetic and isothermal, provide more details about the performance and the mechanism of this process.

To determine the adsorption rate and equilibrium sorption capacity, we examined the pseudo-first order and pseudo-second order kinetic models. The pseudo-first order model equation is the most widely used to describe the kinetic evaluation of the liquid-solid phase adsorption processes [24]. This model is expressed with the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

where: k_1 — the equilibrium rate constant of the pseudo-first order adsorption [g/(mg·min)]; q_e — the amount adsorbed at equilibrium (mg/g); q_t — the amount adsorbed at time t (mg/g).

The integrated form of equation (1) is written as:

$$\ln(q_e - q_t) = \ln q_e - kt \tag{2}$$

According to the literature data, the pseudo-second order model much better represents sorption of divalent metal ions processes than other kinetic models [25—27]. This model relies on the assumption that the rate-determining step of the adsorption process is the chemical reaction between adsorbate molecules and the adsorbent surface. The pseudo-second order model can be presented as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

where: k_2 — the equilibrium rate constant of the pseudo-second order adsorption [g/(mg·min)]; t, q_e, q_t have the same meaning as mentioned above.

The linear form of the integrated pseudo-second order equation is written as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

From the equation:

$$h = k_2 q_e^2 \tag{5}$$

the initial sorption rate expressed in mg/(g·min) can be calculated.

The correlation coefficients for the linear plots of the pseudo-first order and pseudo-second order kinetic equations showed that the process of chromate adsorption followed the pseudo-second order model. From Table 1 the equilibrium sorption capacity was 4.057 mg/g, and the initial sorption rate and rate constant were 0.0416 mg/(g·min) and $2.53 \cdot 10^{-3}$ g/(mg·min), respectively. This fact suggests that Cr(VI) anions interacted with the iron oxide surface by chemical bonding, presumably by forming inner-sphere complexes [7, 28].

T a b l e 1. Kinetic parameters for Cr(VI) adsorption onto hybrid polymer

Parameter	Value
	Pseudo-first order model
k_1	1.40×10^{-3} min^{-1}
q_e	2.787 mg/g
r^2	0.8211
	Pseudo-second order model
k_2	2.53×10^{-3} g·mg^{-1}·min^{-1}
q_e	4.057 mg/g
h_0	0.0416 mg·g^{-1}·min^{-1}
r^2	0.9982
	Intraparticle diffusion model
k_{id1}	0.1974 mg·g^{-1}·min$^{-0.5}$
r^2_1	0.9962
k_{id2}	0.0264 mg·g^{-1}·min$^{-0.5}$
r^2_2	0.9555

The pseudo-first order and pseudo-second order models are classified as adsorption reaction models and describe the whole process of adsorption without considering its diffusion steps. To determine the effects of diffusion of chromate in porous structure of hybrid polymer particles the kinetic data were also analyzed by the intraparticle diffusion model equation (6) [27, 29]

$$q_t = k_{id} t^{0.5} + c \tag{6}$$

where: k_{id} — the intraparticle diffusion rate constant [mg/(g·min)], the value of intercept c is related to the thickness of the boundary layer.

If the extrapolation of the plot of adsorbate mass adsorbed per unit mass of the adsorbent against the square root of the contact time gives a straight line passing through the origin, the intraparticle diffusion is the sole rate-limiting step; if the intercept c is a positive value, the adsorption kinetics is controlled by both intraparticle diffusion and boundary layer diffusion.

As can be seen, the data points in Fig. 2 could be connected with two straight lines whose correlation coefficients showed that this model described the kinetic data very well. From the slopes of the two linear portions, k_{id1} and k_{id2} were calculated (Table 1). The first, sharper line represented macropore diffusion and the second line depicted mesopore diffusion. The extrapolation of the first linear portion showed that the plot almost passes through the origin (intercept $c = -0.0374$), indicating that the macropore diffusion was the sole controlling-step in the early stage of adsorption. The second line was attributed to the slow transport of Cr(VI) ions into the mesoporous hybrid polymer structure. These findings suggest that the intraparticle diffusion was the important rate-determining step for Cr(VI) adsorption.

To establish the sorption capacity of the obtained hybrid polymer towards Cr(VI) ions, the adsorption isotherms in different environmental pH conditions were plotted and the results are illustrated in Fig. 3. The experimental data obtained at pH 2.5 and 7.5 correlated well with the Freundlich equation (Table 2):

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m \cdot b} \tag{7}$$

and the adsorption of Cr(VI) determined at pH 5.5 was better described by the Langmuir equation (Table 2):

$$\log Q_e = \log K_F + \frac{1}{n} \cdot \log C_e \tag{8}$$

where: Q_e, C_e — the equilibrium adsorption capacity in mg/g and the equilibrium chromate concentration in mg/dm^3, respectively; K_F expressed in mg$^{1-(1/n)}$ (dm^3)$^{1/n}$/g, n — Freundlich experimental constants; Q_m, b — Langmuir experimental constants, where Q_m — the maximum

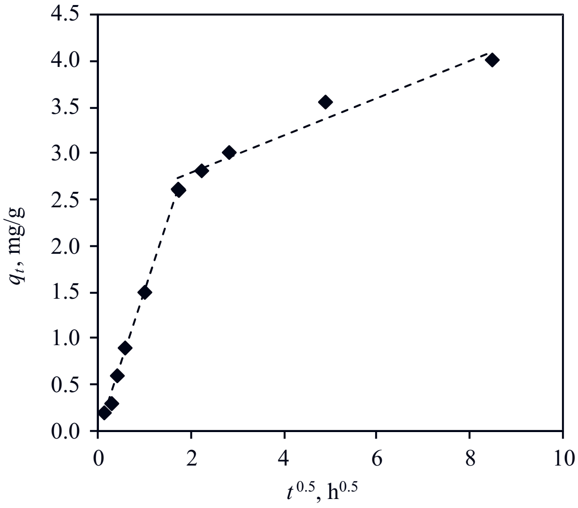

Fig. 2. Intraparticle diffusion plot for the removal of Cr(VI) by hybrid polymer [1.0 g of R/S/Fe sample + 100 cm^3 K_2CrO_4 solution (50 mg Cr(VI)/dm^3)]

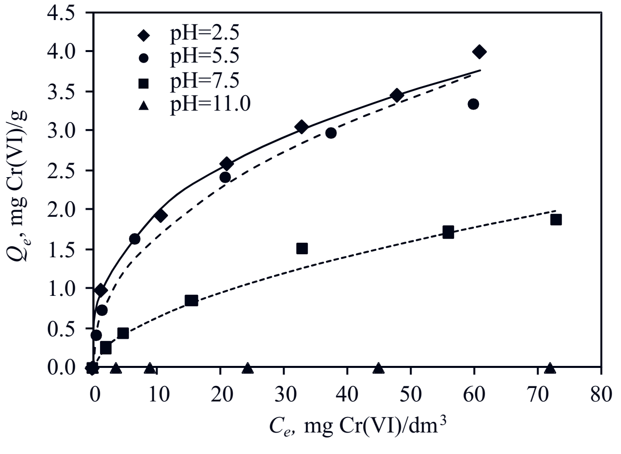

Fig. 3. The equilibrium chromate concentration (C_e) versus the equilibrium adsorption capacity (Q_e) for Cr(VI) adsorption by hybrid polymer R/S/Fe at varying pH of 2.5—11.0. Experimental data and Freundlich model calculations are represented by symbols and lines, respectively

sorption capacity given in units of mg/g, *b* — given in dm^3/mg.

T a b l e 2. Langmuir and Freundlich model parameters at different pH for Cr(VI) adsorption onto hybrid polymer

Langmuir isotherm model			
pH	Q_m, mg/g	*b*, dm^3/mg	r^2
2.5	3.87	0.116	0.960
5.5	3.62	0.145	0.990
7.5	2.39	0.042	0.985
Freundlich isotherm model			
pH	K_F, $mg^{1-(1/n)}$ $(dm^3)^{1/n}$/g	$1/n$	r^2
2.5	0.849	0.362	0.990
5.5	0.598	0.447	0.987
7.5	0.168	0.575	0.985

The test showed that the sorption capacity strongly depended on environmental pH conditions. The highest sorption capacity 3.87 mg/g was determined at pH = 2.5. A noteworthy observation is the slightly smaller value of maximum sorption capacity at pH 5.5. In basic solution (pH = 11.0) the adsorption of chromate failed to occur. Considering the strong influence of environmental pH conditions on chromate adsorption, it can be stated that electrostatic effects played a critical role. In an acid environment the surface hydroxyl groups occurred in the protonated form ($=FeOH_2^+$), which resulted in higher sorption capacity of Cr(VI) anions. Under alkaline conditions with pH higher than pH_{PZC} (PZC — point of zero charge) the surface of iron oxide was negatively charged ($=FeO^-$) and sorption capacity diminished due to electrostatic repulsion of Cr(VI) anions. The obtained results agreed with literature data according to which the optimal pH for chromate adsorption is between pK_{a1} of chromic acid ($pK_{a1} = 0.81$) and pH_{PZC} of the sorbent [9, 10, 27]. The spectroscopic results indicated that iron oxide deposited in the polymer matrix was in the form of ferrihydrite whose determined value of pH_{PZC} is about 8.0. The high sorption capacity under weak acidic conditions was presumably due to the relatively high value of the point of zero charge (PZC), which for different forms of iron oxide ranges from 6.3 to 9.5 [28].

Fig. 4 presents the results of chromate sorption tested by the column method. From the breakthrough curve it can be stated that the obtained hybrid polymer was an effective sorbent for Cr(VI) anions. The breakthrough point was achieved at 64 BV (defined as exceedance of the Cr(VI) detection limit, 0.0125 mg/dm^3). The concentration allowable in sewage discharged in surface waters (0.1 mg Cr(VI)/dm^3) in the effluent was exceeded after 86 BV treatment volume (1330 cm^3 of purified water). Noteworthy is the fact that $C/C_0 = 0.5$ on the breakthrough curve was obtained at 435 BV and the calculated total sorption capacity reached the value of 9.3 mg/g of hybrid polymer (in dry state). Accordingly it can be stated that by reducing the flow rate of the influent and extending the contact time of reagents it is possible to achieve higher sorption capacity of Cr(VI) anions. This supposition can be confirmed by kinetic data which showed that the adsorption equilibrium took a long time to establish.

A notable observation during treatment of the hybrid polymer column bed with chromate solution was the acidification of the effluent from 7.7 in the influent to pH = 2.6 in the first fraction. During the process pH increased insignificantly and subsequently reached the value of 3.5 in the last fraction. The acidification of the solution during the process allowed us to obtain a pH of the environment which according to results from adsorption isotherms favored removal of Cr(VI) anions.

The analysis of Fe(II) and Fe(III) concentration in the effluent showed that its content was remarkably high only in the first fraction 1.8 mg and 3.5 mg, respectively, which gave 0.55 % of the total iron load in the hybrid polymer bed (960 mg Fe). In the next fractions of the effluent, Fe(II) and Fe(III) ion content was under 0.01 mg Fe(II) and 0.1 mg Fe(III). Since the total iron loss in the whole

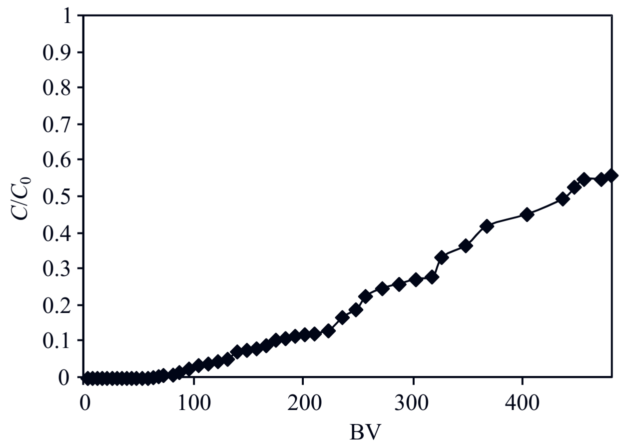

Fig. 4. Breakthrough curve for hybrid polymer R/S/Fe bed at 10 mg Cr(VI)/dm^3 (BV = 15.5 cm^3, flow rate 3.5 BV/h)

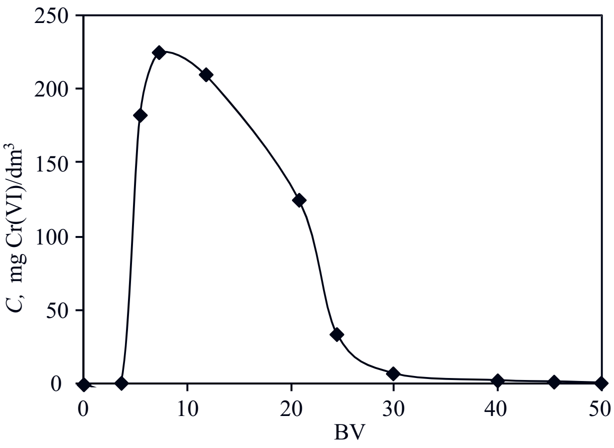

Fig. 5. Chromate elution curve (0.1 M NaOH solution, flow rate 3.5 BV/h)

column process was 1.6 % of total Fe content in the hybrid polymer, and this amount was much less than the potential Fe(II) and Fe(III) load in the retained sulfonic groups of the polymer, it can be stated that the presence of iron ions in the effluent was probably the result of their removal from the functional groups and not from dissolution of iron oxide. These results suggest that iron oxide was quite firmly deposited in the polymer matrix and did not undergo dissolution under these adsorption conditions.

After the sorption process, the bed of the hybrid polymer was treated with 0.1 M NaOH (Fig. 5). The effectiveness of Cr(VI) desorption was found to be 93 % and resulted in a chromate solution with concentration of 84 mg Cr(VI)/dm^3. Due to the adsorption – desorption process it is possible to reduce the wastewater volume and the obtained chromate solution can be evaluated for reuse.

The consecutive hybrid polymer fixed-bed column run was carried out using a solution containing Cr(VI) anions in the concentration of 10 mg/dm^3 and sulfate and chloride anions in concentrations of 1000 mg/dm^3 and 500 mg/dm^3, respectively. The breakthrough curve shows that the hybrid polymer exhibited chromate sorption capacity even in the presence of high concentrations of competing anions. The breakthrough point was achieved after 25 bed volumes resulting in 340 cm^3 of purified water.

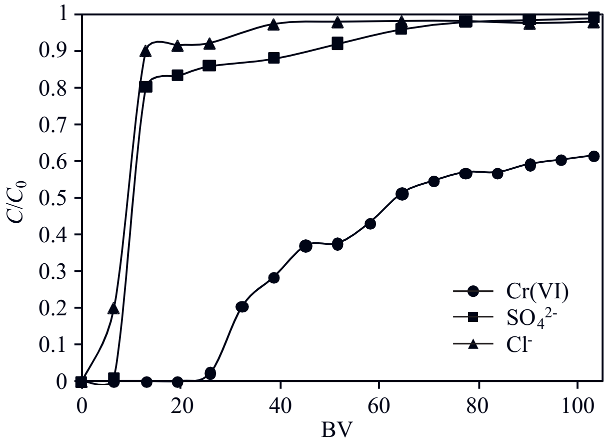

Fig. 6. Breakthrough curve for hybrid polymer bed at 10 mg Cr(VI)/dm^3, 500 mg Cl$^-$/dm^3 and 1000 mg SO$_4^{2-}$/dm^3 (BV = 15.5 cm^3, flow rate 3.5 BV/h)

As can be seen from Fig. 6, Cl$^-$ broke through immediately in the first fraction of the effluent. In the second fraction chloride concentration in the effluent approximated its concentration in the influent. In the case of sulfate, the breakthrough point was achieved in the second fraction and its concentration reached 80 % of the SO$_4^{2-}$ concentration in the influent. These results showed that both anions competed with chromate anions for the active surface of iron oxide deposited within the polymer matrix. The greater competitive effect of SO$_4^{2-}$ anions can be explained by the mechanism of adsorption. The sulfate forms both stronger outer-sphere complexes and weaker inner-sphere complexes on the iron oxide surface in contrast to chloride, which is a poor ligand and forms outer-sphere complexes [28, 30]. Noticeable is the fact that although the concentration of Cr(VI) was two orders of magnitude lower than the concentration of competing anions, the hybrid polymer exhibited higher affinity toward chromate due to the specific mechanism of adsorption on the iron oxide surface via inner-sphere complexation [7, 28].

During this column run the effluent fractions were also analyzed for content of Fe(II) and Fe(III) ions. In comparison to the previous experiment, their content in the first six fractions was higher, 7.5 mg and 31.0 mg (Total), respectively. Total iron loss in the whole process was 4.02 % and still did not exceed the amount of Fe(II) and Fe(III) potentially loaded in retained sulfonic groups (about 5 %). High ionic strength of the used solution did not favor dissolution of precipitates such as iron oxide but enhanced the ion exchange reaction. This confirmed the supposition that the presence of leached Fe(II) and Fe(III) ions in the effluent was a result of their release from retained functional sulfonic groups.

CONCLUSIONS

Adsorption of Cr(VI) on the hybrid polymer containing iron oxide was highly pH dependent and the best sorption capacity was obtained at pH 2.5—5.5.

Comparable sorption capacity in strongly and weakly acidic environments was a result of the relatively high value of pH$_{PZC}$ of ferrihydrite. The kinetic studies showed that the pseudo-second order model described best the adsorption of chromate onto the hybrid polymer surface, indicating the chemisorption mechanism of this process, but the intraparticle diffusion was also an important rate-limiting step of the adsorption. The equilibrium adsorption data fitted well with the Freundlich isotherm equation (pH = 2.5 and 7.5) and Langmuir isotherm equation (pH = 5.5). The column studies showed that the obtained product combining high porous, mechanical and hydraulic properties with good selectivity toward Cr(VI) anions allowed efficient removal of chromate, even from solutions containing other anions in high concentrations, significantly exceeding their concentrations in pretreated wastewaters or ground waters. The acidification property of hybrid adsorbent during the adsorption process enabled us to obtain conditions which favored Cr(VI) removal. Due to the desorption process with NaOH solution, it is possible to recover Cr(VI) anions and the obtained concentrated solution can be considered for reuse.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— *P. Król, P. Chmielarz* — Synteza kopolimerów poli(uretanowo-metakrylowych) z zastosowaniem makroinicjatora tetrafenyloetanouretanowego metodą polimeryzacji kontrolowanej ARGET ATRP

— *B. Szczepaniak, P. Jankowski, J. Sołtysiak* — Reakcja małocząsteczkowej dianowej żywicy epoksydowej z poli(1,3-fenyleno metylofosfonianem)

— *A. Brzozowska-Stanuch, S. Rabiej, J. Fabia, J. Nowak* — Zmiany właściwości termicznych izotaktycznego polipropylenu z różnymi dodatkami poddanego procesowi starzenia (*j. ang*.)

— *A. Gnatowski, M. Chyra, W. Baranowski* — Badania właściwości termomechanicznych i morfologii rur z polietylenu poddanych procesowi starzenia za pomocą promieniowania UV

— *M. Żenkiewicz, T. Żuk* —Fizyczne podstawy tryboelektryzacji i rozdzielania elektrostatycznego tworzyw polimerowych

— *K. Formela, M. Cysewska, J. Haponiuk* — Wpływ kolejności dozowania surowców oraz sił ścinających na właściwości mieszanin polietylen dużej gęstości/miał gumowy, wytwarzanych przy użyciu współbieżnej wytłaczarki dwuślimakowej

— *A. Fridrihsone-Girone, U. Stirna* — Charakterystyka sieci poliuretanowych na bazie poliolu otrzymanego z oleju rzepakowego (*j. ang*.)

— *G. Mitchener* — Czy nanopianka poliizocyjanurowa może rzucić wyzwanie aerożelom? (*j. ang*.)