

## Perchlorates(VII) removal on Dowex™ PSR-2 resin

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Lately there has been observed the increased presence of perchlorates(VII) in the natural environment which can affect human health negatively. Therefore the removal of perchlorate(VII) ions using the gel type resin functionalized with the tri-n-butyl ammonium (Dowex™ PSR-2) from waters was studied. The main aim was to evaluate the effects of experimental conditions including contact time, initial solution concentration, pH and temperature on perchlorate(VII) ions removal as well as the anion exchanger properties on perchlorate(VII) ions sorption. It was found that only the pseudo second order model described the experimental data well and the intraparticle diffusion was not the rate-limiting step. According to the Freundlich model, the  $q_e$  value was to be 69.26 mg/g at optimum conditions (pH 7.0 at 25°C).

**Keywords:** perchlorates, removal, ion exchange, Dowex™ PSR-2

### 1. INTRODUCTION

Recently perchlorate as an inorganic-contaminant has been detected in the surface and ground waters as well as food. The main source of perchlorate(VII) ions in the environment is ammonium perchlorate(VII) as an oxidizing agent (it constitutes about 50% of perchlorate(VII) amounts), fertilizers, ammunition, signal rockets, pyrotechnical mixtures

and fireworks production. They are also used as additives for technical oils, production of fabrics, paints, vanishes, catalysts, electrochemical bath components [1–3].

Due to the fact that most salts of perchloric(VII) acid are well soluble and mobile in natural waters, perchlorates(VII) are present in surface and underground waters as well as in potable waters in some states of USA. In 2005 it was found in the USA that 65% of surface waters containing perchlorates(VII) were contaminated due to rocket fuel burning as well as testing bombs and pyrotechnical materials on military resting grounds. Now it is believed that 5–17 million Americans can be exposed to perchlorates(VII) in 25 states (data from 2005) and even in 46 states (data from 2010) [4]. It is worth noting that the presence of source of their release into the environment is not known in some regions e.g. in North Carolina and Minnesota.

The same problem occurs in the European Union countries. Recently this problem has been discussed during the meeting of the section of the Regular Committee for the Food Provision and Well Being of Animals (toxicological section) of European Commission.

Most perchlorates(VII) are well soluble in water and under ordinary conditions where they remain for a long time [2]. Only potassium ( $15 \text{ mg/dm}^3$ ), ammonium ( $200 \text{ mg/dm}^3$ ) rubidium and cesium perchlorates(VII) are characterized by lower solubility compared to sodium perchlorate(VII) ( $2096 \text{ mg/dm}^3$ ) which can be made use of during the analysis of suitable cations. This imposes potential hazard for human health and life.

In the case of potable water another important factor is the use of chlorine dioxide and sodium chlorate(III) for its disinfection where  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  ions are main side products of water disinfection and  $\text{ClO}_4^-$  ions can also occur in it [5].

It should be mentioned that in most countries admissible concentration of  $\text{ClO}_2^-$  and  $\text{ClO}_3^-$  in the potable water is  $200 \text{ } \mu\text{g/dm}^3$ . However, in Poland the Decree of Health Minister of 2000 does not include admissible contents of these compounds. They are enumerated the decrees of 2002 and 2007. The American Agency of Environmental Protection (USEPA) established the perchlorates(VII) content in portable water not to exceed  $24.5 \text{ } \mu\text{g/dm}^3$  but for the purified water  $2 \text{ } \mu\text{g/dm}^3$  (the state of Massachusetts) and  $6 \text{ } \mu\text{g/dm}^3$  (the state of California) [6]. It should be noted that there are no norms for perchlorates(VII).

The problem of perchlorate(VII) in fruit and vegetables was dealt with by the Food Code Committee for Food Contamination (JECFA). The toxicological estimation of perchlorates(VII), was made and the value BMDL<sub>50</sub> (the lowest 95 % of the trust limit) which is 0.1 mg/kg m.c./day was accepted. Based on it there were determined temporary, maximal, tolerated daily uptake (PMTDI) of perchlorate(VII) 0.01 mg/kg m.c./day.

According to the data of American Food and Drug Agency (US FDA) the uptake of perchlorates(VII) along with the diet is on the average 0.1 µg/kg m.c./day for people over 14 years old and on the average 0.44 µg/kg m.c./day for two year old children.

Based on the estimated PMTDI, it was found that the presence of perchlorate(VII) does not impose threat for human health. However, the UE regulations do not deal with perchlorate(VII) in food. At present general regulations of the decree UE No. 178/2002 and the decree No. 315/93 can be followed.

Moreover, there was established the temporary admissible amount of perchlorates(VII), which are to prevent difficulty in the trade among European Union countries. The established amounts are: 0.5 mg/kg for fruit and vegetables (except for citrus fruit, seedy fruits, tuber and root vegetables, table grapes, spinach, melon and water melon for which it was established 0.2 mg/kg) as well as foliaceous (except for spinach, fresh herbs, celery for which the perchlorate(VII) content could be 1 mg/kg) [7].

The presence of perchlorates(VII) in the environment is directly connected with their contents in soil. What is more, perchlorates(VII) penetrate into surface water along with flows from agricultural areas where artificial mineral resources with industrial wastes are used.

Moreover, the results of studies on perchlorates(VII) formation in the processes occurring in atmosphere are quite interesting. It is believed that perchlorates(VII) originating from sodium chloride react with atmospheric ozone forming perchlorates(VII) [8]. They are also formed during lightening striking against water [9]. These ions were also found on Mars [10].

### *1.1. Biological role of perchlorates(VII)*

Biological role of perchlorates(VII) is of great significance. It was proved that perchlorates(VII) present in potable water or food products affect negatively work of the thyroid gland hormone as they compete with iodide ions replacing them in the thyroid gland reducing its efficiency [11]. This is particularly dangerous for new-born children [1]. In adults they affect metabolism negatively. It is likely that perchlorates(VII) are

also responsible for brain damage [12]. Thus perchlorates(VII) are assayed not only in the thyroid gland but also in blood, human dehydrated fluids, urine and saliva.

The main way to get perchlorates(VII) is consumption of water and food contaminated with them. Perchlorate(VII) ions are readily and completely absorbed from the alimentary tract and excreted with urine in a short time. While inhaling them, the upper air passages are irritated and also skin getting in contact with them is irritated. Absorption of toxic amounts increases blood pressure, heart arrhythmia. Consumption of perchlorates(VII) can also damage alimentary tract [10].

In 2000 US EPA included perchlorates(VII) in the list of substances which should be investigated as the first due to their negative effect on health. In 2006 US EPA listed them as the substances which require constant monitoring in the environment.

The first investigations on perchlorates(VII) in potable water were carried out on a large scale in the USA. As a result, the individual states of the USA introduced some restrictions. The most rigorous requirements ( $1-2 \mu\text{g}/\text{dm}^3$ ) were applied in the states Maryland, New Mexico and Massachusetts [13]. The higher admissible concentrations 25 and  $18 \mu\text{g}/\text{dm}^3$  were applied in California and Nevada.

In order to determine proper activities against threats imposed by the presence of perchlorates(VII) in the environment, it is necessary to monitor their concentrations in water, soil, air and food. Their determination is also very important.

There are many methods used for determination of perchlorate(VII) ions but very few of them enable their determination with the required levels of concentration i.e.  $\mu\text{g}/\text{dm}^3$  [14]. One can distinguish gravimetric titration, spectrophotometric, calorimetric and based on ion chromatography and capillary electrophoresis methods.

Generally, perchlorates(VII) are well soluble in water therefore they are difficult to be determined by gravimetric methods. As follows from the literature data, they can be determined using nitron tetraphenylarsenic chloride or antipyrine. The obtained determinability limit is several  $\text{mg}/\text{dm}^3$  and it cannot be used for determination of perchlorates(VII) in environmental and food samples. Another group of methods are titration ones. In this case the obtained determinability is also worse than expected. The literature reports the cases of perchlorate(VII) ions determination by titration methods using such reagents as iodine, iron-ammonium sulfate or zinc amalgam in the presence of Mo(VI) ions [15, 16]. Better results are obtained applying spectrophotometric methods

based on reactions with some dyes for example methyl violet, natural red, rhodamine or triphenylmethane dye [17, 18].

Perchlorates(VII) can be also determined by means of spectroscopic and electrochemical [19, 20], ion chromatography and capillary electrophoresis methods. Capillary electrophoresis combined with membrane extraction was used for determination of perchlorates(VII) in biological samples [21].

As for the advantages of ion chromatography there can be distinguished possibility of simultaneous determination of several ions in short time, detectability and determinability in the range of  $\mu\text{g/L}$ , small amount of the sample needed for analysis, possibility of using different detectors, simple way of sample preparation and possibility of determination of ions of the same element with different degrees of oxidation (e.g.  $\text{Cl}^-$ ,  $\text{ClO}^-$ ,  $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$  and  $\text{ClO}_4^-$ ). At first the applied analytical systems using ion chromatography allowed to reach the detectability limits on the level of  $\mu\text{g/dm}^3$ . Better results were obtained using large volumes of injection. The best determination is achieved using combined techniques in which separation methods are joined with mass spectrometry detection including the tandem systems [22–24].

Assess availability of some analytical methods enabling their determination on required levels of concentrations, determine the best available technology for removal of perchlorates(VIII) from contaminated areas (bioremediation, ion exchange, reverse osmosis, adsorption on active carbon, membrane filtration, electrochemical reduction, phytoremediation) [25–27]. Among the above methods ion exchange is of significant importance as far as removal of perchlorate(VII) ions is concentrated.

To the group of commercially available ion exchangers these strongly basic anion exchangers (SBA) of quaternary ammonium groups type I (trimethylammonium), type II (dimethylhydroxyethylammonium) and type (III) (tripropylammonium), weakly basic anion exchangers (WBA) as well as chelating ion exchangers used as polymeric ligand exchangers, *PLE* should be mentioned.

Strong base ion exchange resin comprising a crosslinked styrene-divinylbenzene copolymer matrix with quaternary ammonium functionality are described in many US Patents [28, 29]. It should be noted that though SBA ion exchangers are selective toward perchlorate(VII) ions, their regeneration is difficult. On the contrary, the WBA group anion exchangers are not selective but their regeneration by

NaCl is relatively easy [30]. Moreover, it was proved that due to higher hydrophobicity polystyrene ion exchangers are more selective compared with the polyacrylic ion exchangers. Their common use also depends on the lower price.

It was also shown that with the increase of the length of hydrocarbon chain of anion exchange functional group, selectivity toward perchlorate(VII) increases but its total exchange capacity and ion exchange reaction rate decrease. These phenomena are due to the increase of hydrophobic character of the functional groups along with the increase which hindered diffusion of amines of larger molecular mass into the polymer structure during preparation of functional groups the result of which is decrease of an ion exchange rate with the chain length increase.


The most important ion exchangers used for perchlorates(VII) ions removal from waters and waste waters can be as follows: Dowex 1x4 with the trimethylammonium functional groups, NSR-1 with the triethylammonium functional groups or Dowex 66 with the tertiary amine functional groups (Dow Chemical Co.), Amberlite IRA 900 and Amberlite, IRA 958 with the trimethylammonium functional groups or Amberlite PWA2 with the trimethylammonium/trihexammonium functional groups (Rohm and Haas) as well as Purolite A 530E and Purolite A-532E with the trimethylammonium/quaternary ammonium functional groups (Purolite Ltd.).

The present study is focused on the removal of perchlorates(VII) using the gel-type resin functionalized with tri-n-butyl ammonium (Dowex<sup>TM</sup> PSR-2) from waters. The main aim was to evaluate the effects of experimental factors including contact time, initial solution concentration, pH and temperature on perchlorate(VII) ions removal as well as the anion exchanger properties on perchlorate(VII) ions sorption.

## 2. MATERIALS AND METHODS

Dowex<sup>TM</sup> PSR-2 is a strong base anion exchange resin designed for the selective removal of trace contaminants from potable water. It is a gel-type resin functionalized with tri-n-butyl ammonium. Its typical properties are presented in Table 1.

Table 1. Physicochemical properties of Dowex™ PSR-2.

Physicochemical properties	Dowex™ PSR-2
Manufacturer	Dowex Chemical Co.
% water cont.	40.0–47.5
Form	Cl <sup>-</sup>
Bead size [mm]	0.300–1.200
pH	0–14
Max.temp.[°C]	60
Image	

Before the use, the anion exchanger was rinsed with 1 M hydrochloric acid, deionized water, 1 M sodium hydroxide and deionized water.

The effect of contact time on the removal of perchlorate(VII) ions by Dowex™ PSR-2 was determined using 0.05 g of dry anion exchanger in a 100 cm<sup>3</sup> flask containing 20 cm<sup>3</sup> of deionized water for the appropriate time intervals (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 60, 120, 180 min.). The following initial concentrations were used: 5 mg/dm<sup>3</sup>, 10 mg/dm<sup>3</sup> and 20 mg/dm<sup>3</sup>. As follows from the literature data the most effective removal of perchlorate(VII) ions was at pH 7.0. The contents of the flask were shaken on a ELPIN+ 358A type shaker (Elpin, Poland) at A = 7,180 rpm and 25 ± 1°C. The samples were filtered.

The perchlorate(VII) ions concentration and pH of the solutions of the samples were measured. pHM 85 Precision, Radiometer Copenhagen was applied for pH measurements. For perchlorate(VII) ions determination the ion chromatograph 940 Professional IC Vario (Metrohm) was used. The following parameters were applied: Metrosep A SUPP5, 250/4.0 column (250 mm × 4.0 mm ID), suppressed conductivity detector, eluent speed 0,7 cm<sup>3</sup>/min, pressure 11,2 MPa, temperature 46.1°C, conductivity 1,2 µS/cm, loop volume 100 mm<sup>3</sup>. As the eluent the mixture of 20 mmol/dm<sup>3</sup> Na<sub>2</sub>CO<sub>3</sub>, 35% acetonitrile and deionized water

was used. For suppressor regeneration 100 mmol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> was used. The limit detection was equal to 4 µg/dm<sup>3</sup>.

Adsorption of perchlorate(VII) ions on the resin obtained under controlled pH was carried out applying the above procedure. The desired pH was controlled using HNO<sub>3</sub> and NaOH while the equilibrium time was equal to 3 h. All experiments were carried out in triplicate and the deviation from the mean value was less than 5% in all cases.

The adsorption amount ( $q_t$ ) and the adsorption percentage ( $S\%$ ) were calculated according to Eqs. (1) and (2):

$$q_t = (c_0 - c_t) \times \frac{V}{m} \quad (1)$$

$$S\% = \frac{c_0 - c_t}{c_t} \times 100 \quad (2)$$

where:  $q_t$  is the adsorption amount of perchlorate(VII) ions at time  $t$  (mg/g),  $m$  is the weight of Dowex™ PSR-2 (g),  $V$  is the volume of solution (dm<sup>3</sup>), and  $c_0$  and  $c_t$  are the initial and at time  $t$  concentrations of perchlorate(VII) ions in solution, respectively (mg/dm<sup>3</sup>).

Based on the obtained results the distribution coefficients  $K_d$ , (cm<sup>3</sup>/g) were also determined:

$$K_d = \frac{c_0 - c_t}{c_t} \times \frac{V}{m} \quad (3)$$

where:  $c_0$  and  $c_t$  are the initial and at time  $t$  concentrations of perchlorate(VII) ions in solution, respectively (mg/dm<sup>3</sup>),  $V$  is the volume of the solution (cm<sup>3</sup>) and  $m$  is the amount (g) of ion exchanger.

When  $t$  is equal to the equilibrium contact time,  $c_t = c_e$ ,  $q_t = q_e$ , and the amount of perchlorate(VII) ions adsorbed at equilibrium,  $q_e$ , is calculated using Eq.(1).

Kinetic investigations with ion exchange resins usually apply the pseudo first order (PFO) and the pseudo second order (PSO) reaction models (Eqs. 4 and 5) [31, 32]:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (4)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (5)$$



where:  $q_e$  is the amount of perchlorate(VII) ions sorbed at equilibrium (also denoted as  $q_1$  and  $q_2$  for the PFO and PSO models, respectively) (mg/g),  $q_t$  is the amount of perchlorate(VII) ions sorbed at time  $t$  (mg/g),  $k_1, k_2$  are the equilibrium rate constants (1/min).

The comparison with other mass transfer model like the intraparticle diffusion one of Morris and Weber [33] is also presented. The *Weber and Morris model* or intraparticle diffusion model is of major interest because the internal diffusion determines the adsorption rate in most of the liquid systems.

$$q_t = k_i t^{1/2} + C \quad (6)$$

where:  $k_i$  is the rate constant of diffusion (mg/g·min<sup>-1/2</sup>) and  $C$  is the intercept.

The Elovich equation is one of the most useful models for describing chemisorption, which is given as [34]:

$$q_t = \frac{1}{B}(\ln AB) + \frac{1}{B} \ln(t) \quad (7)$$

where:  $A$  (mg/g min) is the initial sorption rate and  $B$  (g/mg) is related to the extent of surface coverage and activation energy for chemisorption (desorption constant).

Based on the linear plots of  $q_t$  versus  $\ln t$  the Elovich parameters can be calculated.

The adsorption data of perchlorate(VII) ions on the Dowex™ PSR-2 were analyzed using the Langmuir (Eq. 8) and Freundlich isotherm (Eq. 9) models. The Langmuir model [35]:

$$q_e = \frac{q_0 K_L c_e}{1 + K_L c_e} \quad (8)$$

where:  $c_e$  is the equilibrium concentration of the perchlorate(VII) ions (mg/dm<sup>3</sup>),  $q_e$  is the adsorption capacity at equilibrium (mg/g), the constant  $q_0$  (mg/g) and  $K_L$  are the characteristics of the Langmuir equation (L/mg) and can be determined from its linearized form (plots of  $c_e/q_e$  vs.  $c_e$ ).

The Freundlich model [36]:

$$q_e = K_F c_e^{1/n} \quad (9)$$

where:  $K_F$  is the Freundlich adsorption capacity (mg/g),  $1/n$  is the Freundlich constant related to the surface heterogeneity. The above equation can be linearized to calculate the parameters  $K_F$  and  $n$ .

The FTIR analysis of Dowex™ PSR-2 before and after the sorption process was performed using Cary 630 FTIR instrument (Agilent Technologies).

All reagents were analytical grade and used without further purification. Demineralized water was used in preparation of all sample solutions (Hydrolab, Poland).

### 3. RESULTS

#### 3.1. FTIR spectra

Comparing the spectra of Dowex™ PSR-2 before and after the sorption of perchlorate(VII) ions new band near  $1085\text{ cm}^{-1}$  is observed. This is connected with the presence of perchlorate(VII) ions in the anion exchange resin phase (Fig. 1). Other bands are connected with the polystyrene-divinylbenzene matrix of the anion exchanger.

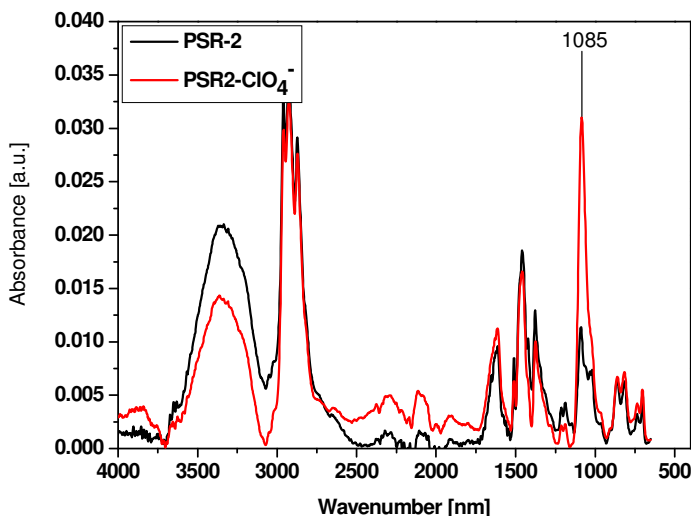


Fig.1. FT-IR spectra of Dowex™ PSR-2 before and after the sorption process.

#### 3.2. Removal studies using batch method – kinetics

As shown in Fig. 2a, it can be observed that the sorption of chloride(VII) ions achieves equilibrium within 3 h and the maximum sorption percentages reach almost 100 % for the solutions of perchlorate(VII) ions with the concentration from  $5\text{ to }20\text{ mg/dm}^3$ . It was

found that for  $5 \text{ mg/dm}^3$ ,  $10 \text{ mg/dm}^3$  and  $20 \text{ mg/dm}^3$  initial concentration, the maximum amounts of  $1.95 \text{ mg/g}$ ,  $3.98 \text{ mg/g}$  and  $8.01 \text{ mg/g}$  of perchlorate(VII) ions were removed by the anion exchanger. These values correspond to a  $98.91\%$ ,  $99.92\%$  and  $99.99\%$  removal efficiency. The highest percentage perchlorate(VII) removal was observed with the interaction of  $0.05 \text{ g}$  Dowex™ PSR-2 with  $20 \text{ cm}^3$  of a  $20 \text{ mg/dm}^3$  perchlorate(VII) solution.

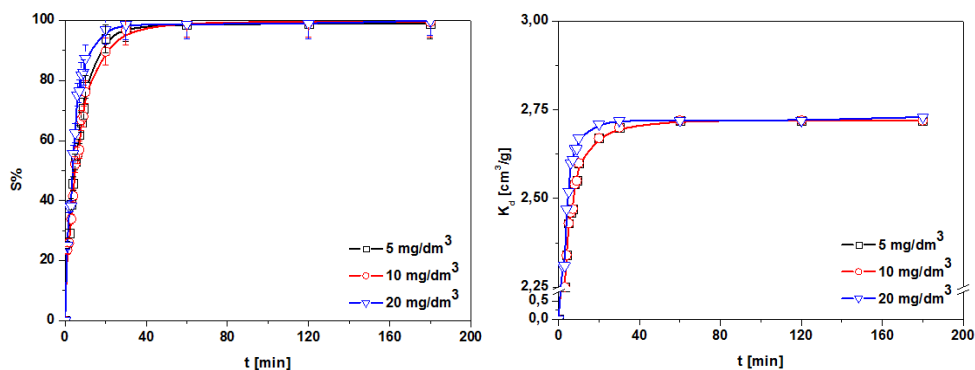


Fig. 2. Comparison of the sorption percentage(S%) (a) and the distribution coefficients ( $\log K_d$ ) (b) for the initial concentrations  $5 \text{ mg/dm}^3$ ,  $10 \text{ mg/dm}^3$  and  $20 \text{ mg/dm}^3$  of perchlorate(VII) ions during their removal on Dowex™ PSR-2 depending on the time ( $A = 7$ ,  $\text{rpm} = 180$ ,  $\text{Ph} = 7$ ,  $T = 25^\circ\text{C}$ ).

It was also found that the  $\log K_d$  values increase up to  $2.69$  for the perchlorates concentration  $20 \text{ mg/dm}^3$  (Fig.2b). High values of the distribution coefficient indicate the ion exchange mechanism of the perchlorate(VII) ions removal.

In the next stage the kinetic parameters for the adsorption process were studied by batch method. The effect of increasing initial perchlorate(VII) ions concentration on the kinetics sorption was investigated and presented in Fig. 3a whereas Fig. 3b shows the changes of the pH values of the solution after the sorption process. The curves fitted by the pseudo first order and pseudo second order kinetic models are shown in Figs. 4a-b. The parameter values obtained from the application of kinetic models are presented in Table 2.

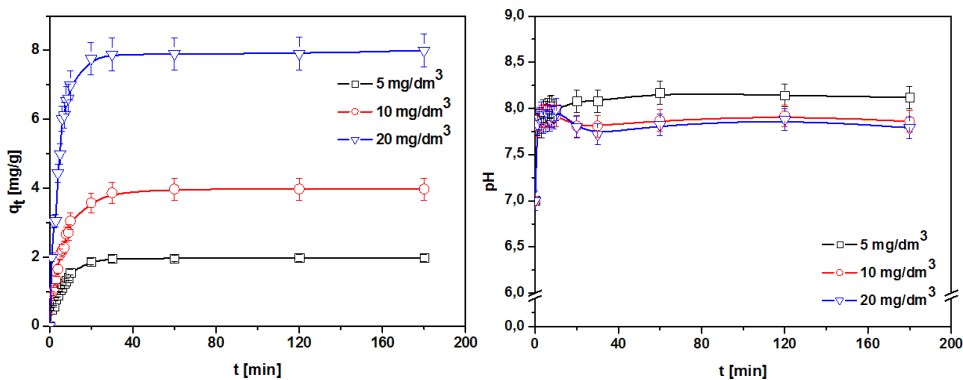


Fig. 3. Comparison of the maximum sorption capacity ( $q_t$ ) (a) and pH changes of the solutions (b) for the initial concentrations 5 mg/dm<sup>3</sup>, 10 mg/dm<sup>3</sup> and 20 mg/dm<sup>3</sup> of perchlorate(VII) ions during their removal on Dowex™ PSR-2 depending on the time ( $A = 7$ , rpm = 180, pH = 7,  $T = 25^\circ\text{C}$ ).

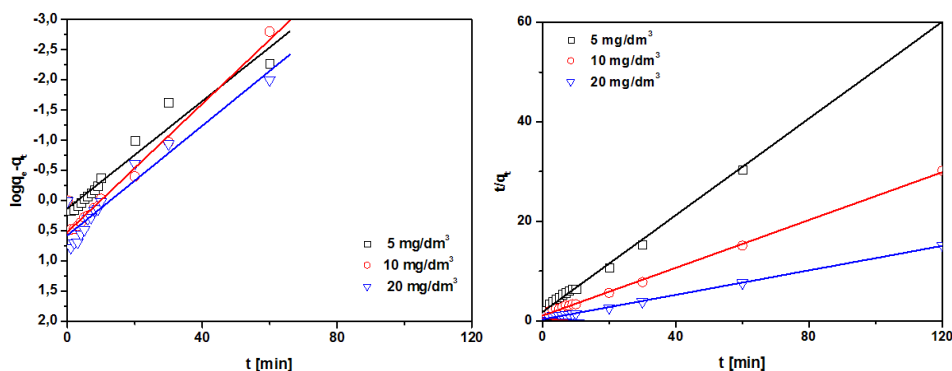


Fig. 4. Comparison of the plots obtained based on the pseudo first order model (a) and the pseudo second order model (b) for the initial concentrations 5 mg/dm<sup>3</sup>, 10 mg/dm<sup>3</sup> and 20 mg/dm<sup>3</sup> of perchlorate(VII) ions during their removal on Dowex™ PSR-2 depending on the time ( $A = 7$ , rpm = 180, pH = 7,  $T = 25^\circ\text{C}$ ).

According to Table 2, although the pseudo first order model provides quite good fit to the experimental data. Fewer relative errors and higher determination coefficients, the pseudo second order model indicates that the latter can better describe the sorption of perchlorate(VII) ions on Dowex™ PSR-2. The pseudo second kinetic model is based on the assumption that the rate of sorption is determined by the square of the number of vacancies [37].

Moreover, compared to the experimental data, the calculated ( $q_{e,cal}$ ) values from the pseudo second order equation are in good agreement with the experimental values of sorption capacities ( $q_{e,exp}$ ). The obtained results also suggest that the rate limiting step can be intraparticle diffusion. Based on the Weber-Morris kinetic model, the values of  $k_i$  at different metal concentrations are shown in Table 2 along with their determination coefficients values. The observed multi-linearity in the shape of the intraparticle diffusion plots has also been confirmed by other authors [38, 39]. The results indicate that the intraparticle diffusion rate decreased from 0.48 to 0.0026; from 0.93 to 0.0029 and from 1.19 to 0.0032 with increase of the initial concentration from 5 to 20 mg/dm<sup>3</sup>, respectively. Additionally, the overall line for each concentration of perchlorates(VII) does not pass through the origin (data not presented). Therefore it can be stated that surface adsorption and intraparticle diffusion were concurrently control the adsorption onto Dowex™ PSR-2 .

Table 2. Kinetic parameters of perchlorate(VII) ions removal on Dowex™ PSR-2 for the initial concentrations 5 mg/dm<sup>3</sup>, 10 mg/dm<sup>3</sup> and 20 mg/dm<sup>3</sup>.

Parameters	Perchlorate(VII) ions concentration		
	5 mg/dm <sup>3</sup>	10 mg/dm <sup>3</sup>	20 mg/dm <sup>3</sup>
PFO			
$q_{e,exp}$	1.95	3.98	7.98
$q_{1,cal}$	0.36	0.92	0.90
$k_1$	0.146	0.063	0.023
$t_{1/2}$	0.106	0.069	0.049
$R^2$	0.8600	0.8632	0.8754
PSO			
$q_{2,cal}$	2.03	4.01	8.01
$k_2$	0.131	0.201	0.232
$h$	0.541	3.242	14.865
$t_{1/2}$	0.064	0.050	0.029
$R^2$	0.9999	0.9999	1.0000

Cont. Table 2.

IPD			
$k_{i1}$	0.48	0.93	1.19
$k_{i3}$	0.21	0.21	0.21
$k_{i3}$	0.0026	0.0029	0.0032
$R_{i,1}^2$	0.9930	0.8215	0.9883
$R_{i,3}^2$	0.9184	0.9185	0.9185
$R_{i,3}^2$	0.7463	0.7464	0.7464
Elovich			
$A$	0.62	30.65	56.11
$B$	2.18	1.84	1.72
$R^2$	0.9411	0.9851	0.9622

As for the Elovich equation the parameters  $(1/B)$  and  $(1/B)\ln(AB)$  can be obtained from the slope and intercept of the linear plot of  $q_t$  versus  $\ln t$ . The value of  $(1/B)$  indicative of the number of sites accessible for adsorption while the  $(1/B)\ln(AB)$  is the adsorption quantity when  $\ln t$  is equal to zero. This value is helpful in understanding the adsorption behaviour of the first step [40].

The parameters  $A$  and  $B$  are constants,  $A$  as mentioned earlier is the initial sorption rate of the Elovich equation ( $g/g \text{ min}$ ),  $B$  is the adsorption constant ( $g/g$ ) and  $q_t$  is the amount of metal adsorbed/desorbed at time  $t$  ( $g/g$ ), and  $t$  is the reaction time ( $\text{min}$ ). The results indicated that the Elovich model was more suitable for estimation of perchlorate(VII) ions at higher concentration levels as confirmed by the determination coefficients that range from 0.9411 at the concentration of  $5 \text{ mg/dm}^3$  to 0.9822 at  $20 \text{ mg/dm}^3$ . Analogous results were obtained in [41] when kinetics of perchlorate(VII) adsorption by calcined iron-based layered sorbent was analyzed.

### 3.3. Removal studies using batch method – adsorption equilibrium

Adsorption isotherms describe how adsorbates interact with adsorbents. In Fig. 5 the adsorption isotherm of perchlorate(VII) ions is presented. The linear least-squares method with linearly transformed isotherm equations was applied to confirm the experimental data.

The Langmuir model is based on the assumption that all adsorption sites are equivalent and adsorption in an active site is independent of whether the adjacent sites are occupied or not. The Langmuir parameters can be calculated by plotting  $c_e/q_e$  versus  $c_e$ . Moreover, based on it is possible to determine if the sorption is favourable. According to the value of the dimensionless separation factor ( $R_L$ ), it can be stated that: the isotherm is unsuitable for  $R_L$  greater than 1.0, the isotherm is linear for  $R_L$  equal to 1.0, the isotherm is suitable for  $R_L$  greater than 0 and lesser than 1.0 as well as the isotherm is irreversible for  $R_L$  equal to null.

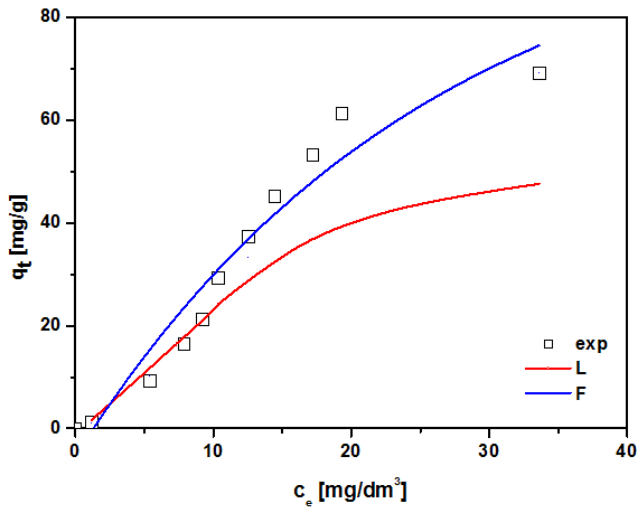


Fig. 5. Comparison of the adsorption isotherms of perchlorate(VII) ions during their removal on Dowex™ PSR-2 ( $A = 7$ , rpm = 180, pH = 7,  $T = 25^\circ\text{C}$ ,  $t = 3\text{h}$ ,  $c_0$  from 5 to 120 mg/dm<sup>3</sup>).

The Freundlich isotherm is an empirical model that proposes a monolayer sorption with heterogeneous energetic distribution of active sites. The applicability of the Freundlich sorption isotherm was also analyzed by plotting  $\log(q_e)$  versus  $\log(c_e)$ . The Freundlich isotherm constant,  $K_F$ ,  $1/n$ , and the coefficients of determination are presented in Table 3. The magnitude of the exponent ( $1/n$ ) represents the adsorption favourability. The values of  $n > 1$  represent favourable adsorption.

Based on the sorption parameters it was found that the  $R^2$  values indicate that the model Freundlich fit the experimental data better than the Langmuir model.

**Table 3.** Isotherm parameters for perchlorate(VII) ions removal on Dowex™ PSR-2 calculated based on the Langmuir and Freundlich isotherm models.

Parameter	Value
$q_{e,exp}$	69.31
$iq_{0,cal}$	22.27
$K_L$	0.064
$R_L$	0.344
$R^2$	0.9042
$q_{e,cal}$	69.26
$K_F$	0.99
$n$	0.719
$R^2$	0.9946

#### 4. CONCLUSIONS

The ion exchange mechanism was predominant for perchlorate(VII) ions removal on Dowex™ PSR-2. Only the pseudo second order model described the experimental data well and the intraparticle diffusion was not the rate-limiting step. According to the Freundlich model, the  $q_e$  value was calculated to be 69.26 mg/g under the optimum conditions (pH = 7.0 at 25°C).

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