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# Application of Pyrolox sorbent for vanadium(V) ions removal

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**Abstract:** The sorption of vanadium(V) ions from acidic solutions using the Pyrolox sorbent was studied at varying ions concentrations, pH, contact time and temperature. The investigated ions were determined by means of graphite-furnace atomic absorption spectrometry (GF-AAS). The sorption capacity of vanadium(V) ions was examined in the pH range 2-10. The adsorption capacities of vanadium(V) ions depend on the pH values. Therefore, the initial pH 2 of vanadium(V) results in the highest adsorption capacities. The sorption vanadium(V) kinetics was investigated. The experimental data were analyzed using the pseudo-first-order, pseudo-second-order forms, Elovich, and intraparticle diffusion models. The kinetics of vanadium(V) sorption is described by the pseudo-first-order in the best way. The results indicate the endothermic process of V(V) ions sorption. The presented results of vanadium ions recovery from the solutions obtained as a result of spent catalysts leaching indicate the possibility of vanadium recovery.

Keywords: vanadium(V), kinetics, removal, sorption, Pyrolox

## 1. Introduction

Vanadium(V) compounds are used in numerous industries, such as: metallurgical, ceramic, glass, chemical and pigment production. This contributes to their emission into the environment. Due to the extensive use of vanadium, it tends to become a strategic metal. Taking into account the production and the increase in the vanadium demand, it becomes a more and more frequent object of investigations. The vanadium supply increased reaching 112kt V by 2020 from 83kt V in 2017 according to the source: TTP Squared, Credit Suisse research. The prices of min. 98% vanadium pentaoxide increased from 5.7 USD/lb as stated on 18 March, 2020 to 12.4 USD/lb on 18 March, 2022 according to vanadiumprice.com. In the regions where vanadium is industrially applied (Chengde in China) (Fang et al., 2017), its content can be determined in wastewaters being from 50 to 200 mg/dm<sup>3</sup> and in the groundwater 0.076-0.206 mg/dm<sup>3</sup> (Panzhihua in China) (Cao et al., 2017). Vanadium in the norm exciding doses can be toxic and accumulates in the circulatory and respiratory systems (Hao et al., 2015). The norm of vanadium concentration in blood is 0.07-0.11 mg/dm<sup>3</sup> but in the poisoned patients it was 6.22 mg/dm<sup>3</sup>. The main symptoms of poisoning were extensive abdominal pain, nausea, vomiting, and diarrhea (Miona et al., 1990). Additionally, it should be noted that the recovery of vanadium is promising due to the extensive research on the vanadium cells that will work as efficient electricity batteries (Barelli et al., 2019). Vanadium is a metal used in various types of catalysts. Its recovery is justified economically and in terms of environmental protection. It can be recovered from spent catalysts by the hydrometallurgical processes (Le et al., 2020). Precipitation was used for vanadium recovery from the solution after leaching the spent Al<sub>2</sub>O<sub>3</sub> vanadium catalyst (Chen et al., 2006). Precipitation was also used to remove the vanadium(V) ions at pH 6. (Cibati et al., 2015). Al, Mo, Ni and V were recovered from the exhausted hydrotreating catalysts using adsorption on the activated charcoal (Pagnanelli et al., 2011). The solvent extraction process with LIX-841 was applied for Al, V, Mo, Ni removal from the spent petroleum catalyst (Mishra et al., 2010). The similar extractant Cyanex 272 was used for SE of the spent vanadium pentaoxide catalyst containing V, Al, Fe, Ti (Painuly, 2015). Li et al., prepared an adsorbent with

decoration of nanosized hydrous zirconium oxide (HZrO) on the anion exchange resin D201 for efficient V(V) removal (Li et al., 2020). The maximum adsorption capacity of V(V) was 118.1 mg/g, due to the potential formation of inner sphere complexation between V(V) and HZrO. The weak macroporous base anion exchange resin (Dex-V) was used for vanadium(V) and chromium(VI) ions removal from wastewaters (Li et al., 2019). Besides the expensive anion exchangers, the low cost sorbent like Pyrolox can be used for ion metal removal form the wastewater. Pyrolox is a common sorbent used in industrial technology for the selective removal of iron(II) and manganese(II) ions from water. Pyrolox was applied as an adsorbent for La(III) and Cu(II) ions removal from the aqueous solutions (Kołodyńska et al., 2019). The sorption capacities for La(III) and Cu(II) were 3.47 mg/g and 6.82 mg/g, respectively. Gładysz-Płaska et al. used the sorbent Pyrolox for the Cu(II), Zn(II), Cd(II), and Pb(II) and U(VI) ions removal. The results indicate that adsorption of Cu(II), Zn(II), Cd(II), and Pb(II) and U(VI) ions is largely dependent on pH. The values of pH 4-7 were optimal for the adsorption (Gładysz-Płaska et al. 2017). The Pyrolox sorbent was not examined for the vanadium(V) removal according to the Web of Science data base. The main goal of this paper was investigation of Pyrolox applicability for the vanadium(V) ions removal from the solutions in the pH range 2-10. Moreover, the obtained research results allowed to use the sorbent for the vanadium(V) ions recovery from the spent catalyst.

## 2. Materials and methods

## 2.1. Materials

The Pyrolox sorbent is commercially available. It contains about 80% of pyrolusite ( $MnO_2$ ) and about 5% of quartz (SiO<sub>2</sub>). This is a uniform, brownish-black, granular material. The particle size of Pyrolox is in the range 0.42-0.84 mm, the bulk density is 1925 g/dm<sup>3</sup> (Kołodyńska et al., 2019). Sodium metavanadate 99.9% from Aldrich was used to prepare the stock solution. The pH value was adjusted with the NaOH and HCl solutions. The V(V) ion sorption studies were carried out at the initial concentration of metal ions equal to 50 mg/dm<sup>3</sup> and the pH in the range 2-10. All inorganic reagents were of analytical grade.

## 2.2. Conditions for vanadium ions concentration determination

The concentrations of vanadium(V) ions were determined by atomic absorption spectrometry in the GF-AAS graphite furnace. The apparatus is composed of the GTA 120 module and the Varian AA240Z spectrometer. This method is sensitive and allows the vanadium(V) ions determination in the concentration range from 1 to  $200 \,\mu g/dm^3$ . The calibration curve is shown in Fig 1.

The pH value was measured using a glass electrode connected to the Elmetron CP-401 pH meter. The sorbent samples were shaken using the laboratory shaker Elpin+ type 358, (Poland) at the amplitude 8 and speed 150 c.p.m.



Fig. 1. Calibration curve for the vanadium(V) ions determination by the GFAAS method

## 2.3. Experimental methods

0.5 g of Pyrolox was equilibrated with 20 cm<sup>3</sup> of vanadium(V) at the solution concentration 50 mg/ dm<sup>3</sup> in the shaker bath at 293 K. The samples were shaken in the contact time range 1 - 1440 min. In order to determine the isotherm 0.5g of sorbent was equilibrated at 293 K with 20 cm<sup>3</sup> of V(V) solutions in the concentration range 10 - 150 mg/dm<sup>3</sup> in the shaker bath for 24h. The desorption experiments were performed by contacting 0.5g of sorbent with the adsorbed metal ion with 20 cm<sup>3</sup> of 0.1M HCl, 0.1M NaCl, 0.1M NaNO<sub>3</sub> and 0.1M NaOH for the 24 hour contact time and shaken at the amplitude 8 and speed 150 c.p.m. 5 grams of the Montedison catalyst was digested in 5% hydrochloric acid at the ratio of 10 g of catalyst to 50 cm<sup>3</sup> of acid. The solution was stirred and contacted for 24 hours. Then it was drained from the residue and transferred to the 50 cm<sup>3</sup> flask. The sorption solution was prepared by the 1: 100 dilution.

## 3. Results and discussion

## 3.1. Effect of pH value

In order to determine the sorption properties of the Pyrolox sorbent in relation to vanadium(V) ions, the removal efficiency was tested in the pH range 2-10. The V(V) ion removal efficiency was calculated from the formula (1):

$$R_{V(V)} = \frac{c_{V(V)}}{c_o} \cdot 100\%$$
(1)

where  $C_{V(V)}$  is the concentration of V(V) ions in Pyrolox (calculated as the difference in the concentrations of V(V) ions (mg/dm<sup>3</sup>) in the solution before and after the vanadium(V) ion sorption process);  $C_o$  is the initial concentration of vanadium(V) ions (mg/dm<sup>3</sup>) in the solution before the sorption process.



Fig. 2. Influence of the pH value on the removal efficiency of vanadium(V) ions using Pyrolox (Co =  $50 \text{ mg/dm}^3$  and m / v =  $0.5g/20 \text{ cm}^3$ )

The influence of pH values on the removal efficiency is presented in Fig.2. As can be seen the pH value of vanadium solution has an enormous effect on the removal efficiency. The best sorption of vanadium(V) ions is observed at pH 2. In the pH range from 2 to 10 the values of removal efficiency decrease. This proves that the vanadium(V) ions sorption diminishes. The changes of pH after the vanadium(V) sorption process including the equilibrium pH vs. the initial pH are presented in Fig. 3. As can be seen in Fig. 3 in the range 2-6 the equilibrium pH is higher than the initial pH. On the other hand, the equilibrium pH is smaller than the initial pH being in the range 6-10. The observed changes in the pH values and removal efficiency depend on the interactions of ions with the Pyrolox surface.

The changes in the initial and equilibrium pH values are consistent with the literature reports. Kołodyńska et al., 2019 found out that the zero point values of Pyrolox determined by the titration and drift methods are similar and equal to 6.5 and 6.4, respectively.



Fig. 3. Effect of the initial pH on the equilibrium pH values



Fig. 4. Speciation of vanadium(V) forms in the pH range 0-14

In the range of pH 1-3, the cationic form of vanadium ions such as  $VO_2^+$  is present in the solution. At the pH values 3-6, the vanadate solutions are yellow which indicates the presence of anionic forms of decavanadates such as:  $V_{10}O_{26}(OH)_2^4$ ,  $V_{10}O_{27}(OH)^{5-}$ ,  $V_{10}O_{28}^{6-}$ , at pH 6-8 the forms  $V_3O_9^{3-}$ ,  $VO_2(OH)_2^-$ ,  $V_4O_{12}^{4-}$  occur and above pH 9 predominantly the  $VO_3(OH)^{2-}$  form is present, from pH 13 the  $VO_4^{3-}$  anion predominates. Taking into account the dependence of the vanadium ion removal coefficients on the pH value and their forms in the aqueous solutions, it can be seen that the Pyrolox sorbent adsorbs both cation in the form of  $VO_2^+$  in the pH 2-3 range and the anionic forms of decavanadates such as:  $V_{10}O_{26}(OH)_2^{4-}$ ,  $V_{10}O_{27}(OH)^{5-}$ ,  $V_{10}O_{28}^{6-}$ . Above the pH value of 6, the  $VO_3(OH)^{2-}$  form dominates, which reduces the removal efficiency to 7% at pH 10.

Considering the influence of the pH value on the vanadium ions sorption, it can be stated that it depends on two variables. The first is the change of vanadium ions speciation forms depending on the pH value. The other one is the change in the surface charge depending on the pH value.

#### 3.2. Mass dosage experiment

In order to determine the sorbent optimal mass, the study of Pyrolox mass effect on the vanadium removal efficiency ( $(R_{V(V)})$ ) was carried out. That investigation was performed at pH 2.

As can be seen in Fig. 5 the removal efficiency depends on the sorbent mass which was investigated in the range 0.05-0.75g. In the mass range from 0.05-0.5g the removal efficiency of vanadium ions increase from 1.25% to 63.25%. In the mass range 0.5-0.75g the removal efficiency is very similar being 63.25% for 0.5g and 63.8% for 0.75g. For this reason 0.5g of Pyrolox was used in further investigations.



Fig. 5. Influence of Pyrolox mass on the removal efficiency at pH 2, Co=50 mg/dm<sup>3</sup>

## 3.3. Effect of contact time and kinetic parameters

The rate at which ions are removed from the solution has an effect on the time sorption process. The influence of contact time on vanadium(V) ions sorption is shown in Fig. 6.



Fig. 6. Influence of contact time on the vanadium(V) ions removal efficiency, Co=50 mg/dm3 and pH=2

As can be seen in Fig. 6 the removal efficiency of vanadium ions depends on the phase contact time. Its values increase in the period 0-1440 min. The plateau is reached after the 720 min contact time. The value of removal efficiency is about 61% as the result of the 1440 min contact time.

Several kinetic models were used to describe the vanadium(V) ions sorption on Pyrolox. The most common are: the pseudo-first-order, pseudo-second-order, Elovich and intra-particle kinetic models. The kinetic models are presented in Table 1 (Ghasemi et al., 2013; Ho & McKay, 1998).

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

Table 1.	Linear	forms	of	kinetic	models
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Table 2. Killetic parameters for the variadium(v) fors sorption						
DEO	$k_1$ (1/min)	$q_1 (\mathrm{mg}/\mathrm{g})$	$R^2$			
FFO	0.003167	1.466	0.9879			
	$k_2$ (g/mg min)	$q_e (\mathrm{mg}/\mathrm{g})$	$R^2$			
1501	0.005346	1.277	0.9414			
	$k_2$ (g/mg min)	$q_e (\mathrm{mg}/\mathrm{g})$	$R^2$			
PSO 2 —	22.19254	0.363	0.8687			
	$k_2$ (g/mg min)	$q_e (\mathrm{mg}/\mathrm{g})$	$R^2$			
150.5	0.09654	0.602	0.4025			
	$k_2$ (g/mg min)	$q_e (\mathrm{mg}/\mathrm{g})$	$R^2$			
150 4	0.02626	0.891	0.4025			
Floorial	a (g/mg min)	$\beta$ (mg/g)	$R^2$			
Elovich	0.081142	6.576	0.8220			
Intra-particle	$k (mg/g min^{0.5})$	<i>C</i> (mg/g)	$R^2$			
diffusion	0.03342	0.056	0.9771			

Based on the equations presented in Table 1 the kinetic parameters were calculated and the results are given in Table 2.

Table 2. Kinetic parameters for the vanadium(V) ions sorption

The kinetic parameters are presented for V(V) ions in Table 2. They were calculated using the pseudo-first-order PFO, pseudo-second-order PSO1, PSO2, PRO3, PSO4, Elovich and intra-particle diffusion kinetic models. The smallest values of the determination coefficient were obtained for the PSO3 and PSO4 models and the R<sup>2</sup> values were about 0.4. The best results were found applying the pseudo-first order model, PFO. The determination coefficients for the PFO model are relatively large being up to 0.98. The smaller value of the determination coefficient (R<sup>2</sup>-0.977) for vanadium(V) ions was obtained based on the intra particle diffusion model. This indicates that the V(V) ions sorption is partly limited by the intra-particle diffusion. The sorption capacity calculated from PFO -1.466 mg/g is higher than that for PSO1- 1.277 mg/g at pH 2 and at the initial concentration of vanadium ions 50 mg/dm<sup>3</sup>.

## 3.4. Sorption isotherm

The isotherm of vanadium(V) ions sorption on Pyrolox is shown in Fig. 7. The equilibrium data were analyzed by the most commonly used Langmuir (Langmuir, 1917), Freundlich (Freundlich, 1906), and Dubinin-Radushkevich (D-R) (Dubinin et al., 1947) isotherm models.

The Langmuir isotherm was calculated based on equation 2:



Fig 7. Isotherm of vanadium(V) ions on Pyrolox at pH 2

where,  $q_e$  is the amount of vanadium ions in the Pyrolox (mg/g);  $C_e$  is the equilibrium concentration (mg/dm<sup>3</sup>); b is the Langmuir isotherm constant (dm<sup>3</sup>/mg);  $Q_0$  is the maximum monolayer coverage capacity (mg/g).

The values of the determination coefficient ( $R^2$ ) in the D-R isotherm for vanadium(V) are about 0.997 and indicate that this model describes the experimental data better than the Freundlich and Langmuir ones. The value of the sorption capacity  $Q_0$  calculated based on the Langmuir model for vanadium(V) is 2.92 mg/g at pH 2. Moreover, the Langmuir isotherm allows to estimate the  $R_L$  parameter. It can be calculated using equation 3.

$$R_L = \frac{1}{1 + b \cdot C_i} \tag{3}$$

where  $C_i$  is the initial concentration of metal ions in the solution (mg/dm<sup>3</sup>)

The  $R_L$  parameter calculated from the Langmuir isotherm for vanadium(V) is presented in Table 3. As can be seen the value of  $R_L$  is 0.0253. This points out to favourable sorption of vanadium(V) on Pyrolox.

The Freundlich isotherm was calculated according to equation (4):

$$logq_e = logK_F + \frac{1}{n}logC_e \tag{4}$$

where  $q_e$  is the amount of vanadium(V) ions in the adsorbent (mg/g); K<sub>F</sub> is the characteristic constant related to the adsorption capacity (mg/g); n is the adsorption intensity; C<sub>e</sub> is the equilibrium concentration (mg/dm<sup>3</sup>).

The values of the determination coefficient for the Freundlich isotherm are smaller than those for the D-R one (Table 3). This indicates that the Freundlich model does not describe the vanadium(V) ions sorption as well as the D-R one.

The linear form of the Dubinin-Radushkevich (D-R) model is presented in equation (5):

$$lnq_e = lnq_m - \beta \cdot \varepsilon^2 \tag{5}$$

where  $q_m$  is the maximum amount of vanadium(V) ions in Pyrolox (mol/g);  $\beta$  is related to the adsorption energy (mol<sup>2</sup>/kJ<sup>2</sup>),  $\varepsilon$  is the Polanyi potential which can be calculated from equation (6):

$$\varepsilon = RT ln \left[ 1 + \frac{1}{c_e} \right] \tag{6}$$

Taking into account the  $\beta$  parameter, the D-R model allows to calculate the adsorption free energy E (kJ/mol):

$$E = \frac{1}{\sqrt{2\beta}} \tag{7}$$

The results of the Dubinin-Radushkevich parameter calculated for vanadium(V) are presented in Table 3. The values of the determination coefficients are higher for the D-R isotherm than those for the Langmuir and Freundlich isotherms. The Dubinin-Radushkevich isotherm is very useful because it allows to calculate the adsorption energy E which is 8.882 kJ/mol for V(V) ions. The calculated values are in the range of 8–16 kJ/mol which indicates the chemisorption mechanism.

Table 4 compares the sorbents of various types with Pyrolox. As can be seen from the comparison, the sorption capacity of Pyrolox is the smallest compared to that of the other sorbents. However, it should be noted that, despite the small capacity, Pyrolox is one of the cheap sorbents.

## 3.5. Thermodynamic parameters

The thermodynamic parameters like: the  $\Delta G^{\circ}$  Gibbs free energy (kJ/mol),  $\Delta H^{\circ}$  enthalpy (kJ/mol) and  $\Delta S^{\circ}$  entropy (kJ/K·mol) were calculated for V(V) ions. They allow to predict the nature of investigated ions adsorption on Pyrolox. They were determined from the equations:

$$\Delta G^0 = -RTln(K_D) \tag{8}$$

$$\ln(K_D) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{T}$$
(9)

The values of  $\Delta$ H<sup>o</sup> enthalpy (kJ/mol) and  $\Delta$ S<sup>o</sup> entropy (kJ/K·mol) were obtained from the slope and intercept of the plot ln(K<sub>D</sub>) vs 1/T, K<sub>D</sub> is the distribution coefficient (dm<sup>3</sup>/g), R is the universal gas constant (8.314 · 10<sup>-3</sup> kJ/K·mol). The values of the thermodynamic parameters are presented in Table 5.

Table 3	. Constant of the	Langmuir,	Freundlich	and D-R	isotherm	models a	nd their	determination	coefficients	for
			the V(	V) ion sor	ption on I	Pyrolox				

Langmuir			Freundlich			Du	Dubinin-Radushkevich			
$Q_0$	b	$R_{L}$	R <sup>2</sup>	$K_{\mathrm{f}}$	n	R <sup>2</sup>	β	$q_{m}$	Е	R <sup>2</sup>
(mg/g)	(dm³/mg)	-	-	(mg/g)	-	-	$(mol^2/kJ^2)$	(mol/g)	(kJ/mol)	-
2.92	0.07678	0.0253	0.9867	0.36312	2.1227	0.9849	6.34 ·10-9	0.000454	8.882	0.997

Table 4. Comparison of Pyrolox capacities with the literature data

Sorbent	Capacity	Literature
anion exchange resin D201	118.1 mg/g	Li et al., 2020
amino-functionalized magnetic macroporous copolymer	11.23 mg/g	Suručić et al., 2021
lignin-based spherical particles (L- CTAB)	10.79 mg/g	Stanisz et al., 2021
modified manocellulose obtained from coconut coir	32.88 mg/g	Daniel et al., 2021
coal waste	55.56 mg/g	Kajjumba et al., 2018
Pyrolox	2.92 mg/g	presented paper

Table 5. Values of the thermodynamic parameters for V(V) ions

ΔHº (kJ/mol)	$\mathbf{AC}_{2} = (\mathbf{I}_{1} \mathbf{I}_{1} / \mathbf{I}_{2} + \mathbf{m}_{2} \mathbf{I}_{1})$	ΔG° (kJ/mol)			
	$\Delta S^{o}$ (KJ/K·mol) -	293K	313K	333K	
7.14	-0.0214	13.42	13.85	14.28	

For the vanadium(V) ions sorption on Pyrolox the positive  $\Delta H^{\circ}$  value indicates the endothermic interactions at 293 - 333 K. The insignificantly negative  $\Delta S^{\circ}$  value indicates the randomness decrease at the solid-solution interface during the vanadium(V) sorption. The positive  $\Delta G^{\circ}$  values exhibit the existence of an energy barrier and that the reaction is a non-spontaneous process. The values of free enthalpy increase insignificantly with the increasing temperature in the range 293-333K. Summing up, the vanadium(V) ions sorption proceeds more efficiently with the increasing temperature of solution.

## 3.6. Influence of foreign ions

As real solutions contain foreign ions like those of sodium, potassium, iron, chloride and sulphate, it is necessary to establish their influence on the vanadium(V) ion sorption process on the Pyrolox sorbent. Therefore the influence of such electrolytes as 0.1M NaCl, 0.1M KCl, 0.1M Na<sub>2</sub>SO<sub>4</sub> and 0.1M FeCl<sub>3</sub> on the vanadium(V) ions sorption was investigated.

As can be seen in Fig. 8 all electrolytes 0.1M NaCl, 0.1M KCl, 0.1M Na<sub>2</sub>SO<sub>4</sub> and 0.1M FeCl<sub>3</sub> affect the vanadium ions sorption. The removal efficiency for vanadium ions without the addition of electrolytes was 38.5%. Sodium chloride and potassium chloride resulted in a decrease in the removal efficiency value to 30.0% and 26.4%, respectively. Sodium sulphate had a much greater effect on the vanadium(V) ions adsorption using Pyrolox than sodium chloride and potassium chloride. The removal efficiency of vanadium(V) ions in the 0.1M sodium sulphate solution was 12.6%. Iron(III) chloride had the greatest effect on the vanadium ions sorption using Pyrolox. The removal efficiency was only 2.51%. Iron(III) ions are more strongly sorbed by Pyrolox and compete with vanadium ions. This sorbent is recommended by the manufacturer for removing iron ions from water.



Fig 8. Influence of the electrolytes on the vanadium(V) sorption using Pyrolox (0.1M electrolytes, Co =  $50 \text{ mg/dm}^3$ , pH=2, t=6h)

## 3.7. Desorption of vanadium(V) ions

The desorption process is very important for the recovery of vanadium ions. The low cost of the sorbent and the possibility of ion desorption make the sorbent economically advantageous. Therefore, the possibility of vanadium ions desorption was tested.

The desorption (D%) was calculated from equation (10):

$$D\% = \frac{c_d}{c_o - c_s} \cdot 100\% \tag{10}$$

where  $C_d$ - the concentration of vanadium ions after the desorption mg/dm<sup>3</sup>,  $C_o$ - the concentration of vanadium ions before the sorption mg/dm<sup>3</sup>,  $C_s$ - the concentration of vanadium ions after the sorption mg/dm<sup>3</sup>.

There were selected the following reagents: 0.1M HCl, 0.1M NaCl, 0.1M NaNO<sub>3</sub> and 0.1M NaOH. The results of the desorption process are shown in Fig. 9.



Fig 9. Desorption of vanadium(V) ions from the Pyrolox sorbent

As can be seen in Fig 9 the following reagents: 0.1M HCl, 0.1M NaCl, 0.1M NaNO<sub>3</sub> and 0.1M NaOH desorbed vanadium(V) ions with a varying efficiency. The smallest desorption efficiency was obtained for 0.1M NaCl and 0.1M NaNO<sub>3</sub> which was 35.3% and 39.8%, respectively. 0.1M HCl exhibited a better desorption efficiency that is 58.1% than 0.1M NaCl and 0.1M NaNO<sub>3</sub>. 0.1M NaOH showed the best desorption efficiency of all tested reagents. It was stated that 93.2% of vanadium ions was desorbed from Pyrolox. This behaviour is consistent with the effect of pH on the vanadium ion sorption using the Pyrolox sorbent presented in section 3.1.

## 3.8. Recovery of vanadium (V) ions from the spent catalyst

Vanadium is used as a catalyst in the chemical industry for the oxidation of sulfur oxides in the process of obtaining sulfuric(VI) acid. Therefore, Pyrolox was applied to recover vanadium from the spent

catalyst Montedison. The catalyst digestion procedure is described in the Experimental methods section. After the catalyst digestion the solution contained  $3.29 \text{ g/dm}^3$  of vanadium(V) ions. The solution was diluted and the pH was adjusted to the value 2. The vanadium(V) ions concentration in the diluted solution was  $32.9 \text{ mg/dm}^3$ . 20 cm<sup>3</sup> of the vanadium(V) solution was contacted with 0.5g of the Pyrolox sorbent. After the sorption process the efficiency removal of vanadium(V) ions was 55.8%.

The removal efficiency of vanadium(V) ions was slightly smaller than that in the model solution at pH2 63.25%. The research on the vanadium(V) ions recovery from the spent catalyst proved that the sorbent Pyrolox can be used for its recovery.

## 3. Conclusions

The research on the vanadium(V) ions removal proved the possibility of using the Pyrolox sorbent for ions removal from various types of solutions. Better vanadium(V) ion sorption efficiency was obtained for the chloride solutions than for the sulfate ones. The maximum of sorption capacity of vanadium(V) ions was obtained at pH 2. The Pyrolox sorbent can be used for vanadium recovery from the solution prepared by the digestion of the exhausted vanadium catalyst. The desorption of vanadium(V) ions sorption the sorbent was demonstrated using 0.1M sodium hydroxide. It was proved that the vanadium(V) ions sorption on Pyrolox is the endothermic process. Its advantage is the low price compared to that of the ion exchangers.

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