SORPTION OF VANADIUM(V) FROM MINERALIZED CHLORIDE-SULFATE SOLUTION BY FIBROUS IONITES MATERIALS

Nway Shwan Oo[1], I. D.Troshkina[2]

Abstract

In present work, the possibility of recovery of vanadium(V) from mineralized chloride-sulfate solutions by fibrous ionites materials of the FIBAN brand was investigated. (FIBAN is the abbreviation word for fibrous ionites brand which were produced by the Institute of Physical Organic Chemistry, Academy of Sciences of Republic Belarus). Equilibrium and kinetic characteristics of sorption of vanadium(V) by the fibrous ion exchangers (anionites and cationites) FIBAN brand, FIBAN AK-22, FIBAN A-6 and FIBAN K-1, which contain functional groups: $-NH_2$, $=NH$, $\equiv N$, $-COOH$, $-N^+\equiv$, $=NH$ and $-SO_3^- H^+$ had been studied. It is established that the maximal sorption capacity of FIBAN AK-22 and FIBAN A-6 with regard to kinetic sorption rate of vanadium (V) is observed at pH=4. Sorption isotherms of vanadium by using FIBAN AK-22 is convex shape being described by Langmuir constant $K_L = 190 \pm 9$mL/g (R^2 – 0.8) and FIBAN A-6 is linear shape by Henry constant $K_H = 2.09 \pm 0.20$ L/g (R^2 – 0.95), respectively. Integral sorption kinetic curves were found under conditions of a limited solution volume, and the order of effective diffusion coefficients of vanadium by using anion exchangers FIBAN AK-22 and FIBAN A-6 which are constituted 10^{-15} and 10^{-14} m^2/s respectively. The average apparent activation energies during the sorption of vanadium (V) for anion exchanger FIBAN AK-22 was 6.2 ± 2.0 kJ /mol and for FIBAN A-6, 19.9 ± 4.7 kJ/mol. It may be indicated that the flow of the sorption rate of vanadium and sorption process took place in the external diffusion region. Additionally, the maximum sorption capacity of fibrous cation exchanger FIBAN K-1 for sorption of vanadium(V) in the form of oxo-vanadate VO_2^+ was observed at pH = 1. From this study, it was found that cation exchanger has higher sorption rate than anion exchangers.

Keywords: vanadium(V), chloride-sulfate solution, sorption, FIBAN, fibrous ion exchangers, anionites, cationites

Introduction

Vanadium is an important rare metal which has been widely used in ferrous and non-ferrous alloys to improve its hardness, tensile strength, and fatigue resistance (Wang *et al*., 2013) for various purposes and the chemical industry. Recently vanadium is also known as "**new green element**". The need for clean and renewable sources of energy is generating increased interest in vanadium due to the recent development of the vanadium flow battery, also known as vanadium red-ox battery (VRB), and its utilization in the storage of energy produced by green sources such as wind and solar (Hammond, 2013).

The recovery of rare element—vanadium—from waste solutions, which are formed when processing natural mineral and organic complex raw materials, is an alternative process of increasing their mining, which promotes the improvement of environmental situation in the industrial zone of enterprises. The vanadium concentration in worked out solutions can reach 200 mg/L and higher (Mizin *et al*., 2005).

Vanadium is a heavy metal. Compounds of pentavalent vanadium are most toxic, since they retard the synthesis of fatty acids and inhibit certain ferment systems. The limiting

[1] Dr, Lecturer, Department of Chemistry, Myeik University

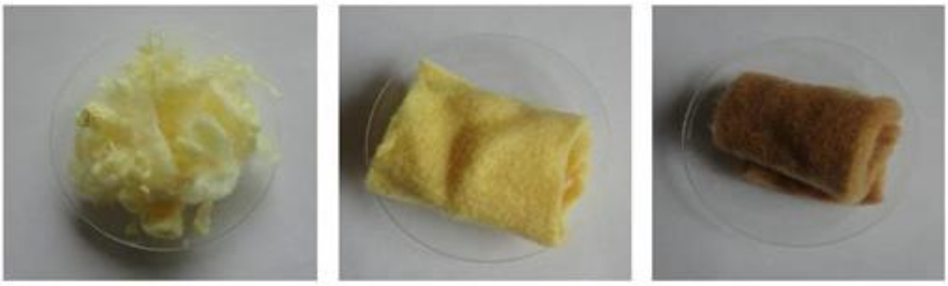
[2] Dr, Professor, Department of Technology of Rare Elements and Nanomaterials, D. Mendeleev University of Chemical Technology of Russia (MUCTR)

admissible concentration of vanadium in water of household and cultural–domestic water use is 0.1 mg/L (Sanitary-Epidemiological Rules and Standards, 2010), while its content in waste waters entering biological sewage purification facilities is normalized at a level of 5 mg/L. It is reasonable to apply the sorption method for the recovery of metals from solutions with their low content. Vanadium is preferentially recovered applying strongly basic and complexing ionites. The separation of these metals from water solutions can be also performed by sorption with fibrous ionites, for example, vanadium with cellulose - based fibers (TsM, TsM-A2, and TsM-A3 brands). It is known that fibrous ionites possess better kinetic characteristics than traditional granulated sorbents (Soldatov *et al*., 1990).

This study is aimed to find the sorption characteristics of fibrous ionites of the FIBAN series with the recovery of vanadium(V) from mineralized solutions and compare the kinetic sorption rate of vanadium metal ions on anionites and cationites.

Materials and Methods

Fibrous ionites FIBAN series of following brands: AK-22 and A-6 (anionites), and K-1(cationites), which were developed at the Institute of Physical Organic Chemistry, Academy of Sciences of Republic Belarus. These ionites have been synthesized by polymer and a similar transformation of polyacrylonitrile fibers (Palant *et al*., 2007). They are characterized by a developed system of meso-pores and micro-pores. Structure and surface appearance of fibrous ion exchangers FIBAN micrograph showed the heterogeneity of their surface and the cylindrical shape of the filaments with a diameter substantially the same length. Figure 1 is representative for fibrous ion exchanger FIBAN A-6 image and its electron micrograph is shown in Figure 2.



FIBAN AK-22 FIBAN A- 6 FIBAN K- 1

Figure 1 Fibrous ionites FIBAN series of brands anionites (AK-22), (A-6), and cationites (K-1)

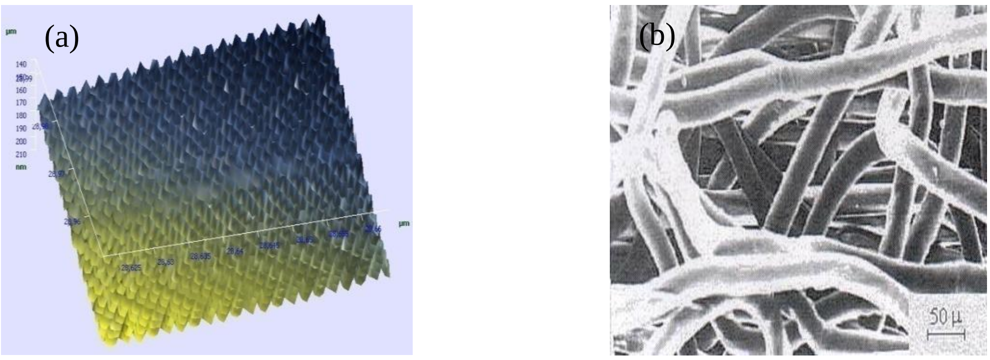


Figure 2 SEM micrographs of fibrous anionites (a) FIBAN AK- 22 (b)FIBAN A- 6 (Filament diameter 20-50 microns)

Electron micrographs of the starting monofilament polypropylene, and polypropylene grafted with 100 % monopolymer styrene (98 %) and divinylbenzene (2 %) and a schematic structure of a fibrous sorbents - sulfonic FIBAN K-1 are shown in Figure 3.

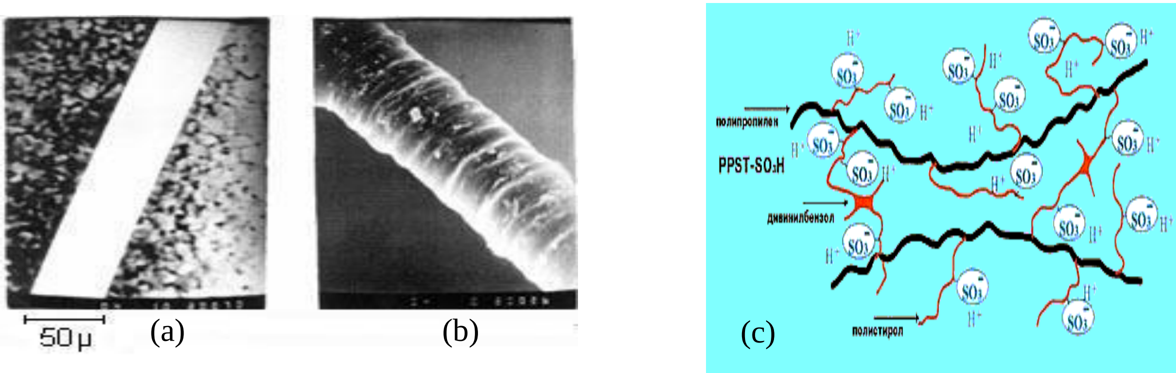


Figure 3 SEM micrographs of the filaments (a) FIBAN K-1 starting polypropylene and (b) polypropylene grafted with styrene and (c) divinyl benzene monopolymer and a diagram of the structure of fibrous sulfonic FIBAN K-1 (Soldatov *et al.*, 2004)

Ionites of the FIBAN series of brands AK-22, A-6, and K-1, the main physicochemical characteristics of which are presented in Table 1.

Table 1 Characteristics of Fibrous Ionites FIBAN

Ionite	**FIBAN AK-22**	**FIBAN A-6**	**FIBAN K-1**
Functional group	$–NH_2$, $=NH$, $≡N$, -COOH	$(C_3H_5O)(CH_3)_2N^+Cl^-$, $–N(CH_3)_2$	$–SO_3^-\ H^+$
Basic of polymer	polyacrylonitrile fiber		Polypropylene fiber with a graft copolymer of styrene and divinyl benzene
Form (staple fiber)	Needle punched nonwoven fabric	woven fabric	Needle punched nonwoven fabric
optimal capacity, mg-equiv/g	3.5 - (amino), 1.0 - (–COOH)	2.0 ($–N^+≡$), 0.8 ($–NR_2$)	3.0
Swelling, g_{water}/g ion exchanger	0.7	1.2	1.0
Working pH range	0 – 8	0 – 13	0 − 14

The investigation into the sorption characteristics of fibrous ionites of the FIBAN A-6 series, which contain groups of quaternary and secondary amines, and FIBAN AK-22 ionites with amino-carboxyl groups was performed as applied to the recovery of vanadium (V) from diluted mineralized solutions which contained 0.1g/L Vanadium (V), 1.0 g/L Cl^- and 30.0 g/L SO_4^{2-}. The selection of ions is conditioned by their broad spread in natural and manufacturing solutions. The ion state of vanadium (V) largely depends on its concentration and acidic medium. It is reported that there are twelve vanadium (V) species in solution. These can be categorized as cationic species VO_2^+, neutral species $VO(OH)_3$ and anionic species.The anionic species are divided into decavanadate species ($V_{10}O_{26}(OH)_2^{4-}$, $V_{10}O_{27}(OH)^{5-}$ and $V_{10}O_{28}^{6-}$), mononuclear species ($VO_2(OH)_2^-$, $VO_3(OH)^{2-}$ and VO_4^{3-}) and other polyvanadate species ($V_2O_6(OH)^{3-}$, $V_2O_7^{4-}$, $V_3O_9^{3-}$ and $V_4O_{12}^{4-}$). In the ion exchange process, anion exchange resins are used for the adsorption of vanadium mostly in the form of anionic and poly-nuclear species, such as $V_{10}O_{28}^{6-}$, $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ (Zeng *et al*.2010).

In accordance with literature data in the pH range from 1 to 3, appropriate waste solutions of pH, ionic form of existence of vanadium ranges from a cation to anion. At a concentration of 200 mg/L and a pH of less than 1.5 in solution exists *oxo-cation* VO_2^+, and at higher pH exists *as decavanadates anion* $HV_{10}O_{28}^{5-}$ as shown in Figure.4. In connection with this, taking into account the acidity of waste solutions for the extraction of vanadium was used the anion ampholytes of different types.

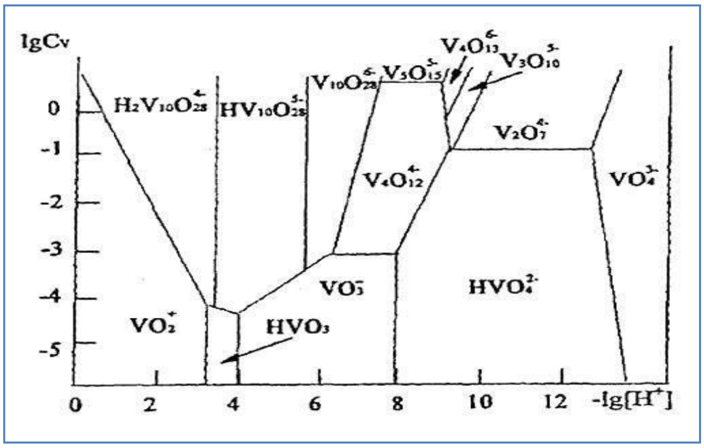


Figure 4 Dependence ion states of vanadium (V) on the pH of the aqueous solution (Mizin *et al*.,2005)

Effect of pH

The sorption of metals from solutions was investigated in static conditions with the ratio of fiber ionites (g) to solution volume (mL) equal to 1: 2000. After contacting the phases under intense stirring on a shaker and their separation, the concentration of metals in the solution (*C*) and the sorption capacity of ionites (SC) were determined by the balance relationship. The vanadium contents in solutions were determined by the photometric method.

Sorption Isotherm

Equilibrium sorption characteristics were studied under static conditions with the ratio of fiber ionites (g) to solution volume (mL) equal to 1: 2000 at pH 4. For determination of sorption isotherm for vanadium, the anionites FIBAN AK-22 and FIBAN A-6 were contacted with the solution for 48 h (including 4 hours at a stirring rate of 160 oscillations per minute) at room temperature. The experiment was carried out to complete saturation of the sorbent. After two days, the solution was analyzed for vanadium ion and was separated from the solution and contacted with a fresh portion of solution. The sorption is generally described by isothermal, that are functions relating the amount of sorbate on the ionites (sorbent). Langmuir and Henry models are used to describe the sorption process.

Kinetic Sorption Study

The same procedure was followed to investigate the effect of temperature on sorption process. The sorption kinetics of vanadium(V) with ionites FIBAN AK-22 and FIBAN A-6 were determined by the limited solution volume method using the installation of thermostated (temperature-controlled) cells at temperatures of 293, 313 and 333 K.

Results and Discussion

Effect of pH

Taking into account the complexity of behavior of vanadium in aqueous solutions, the influence of pH of solutions on the sorption of vanadium (V) with ionites FIBAN A-6 and FIBAN AK-22 was preliminarily studied. The dependence of SC on pH is presented in Figure. 5. It was shown that the largest sorption capacity for vanadium is attained at pH 4.

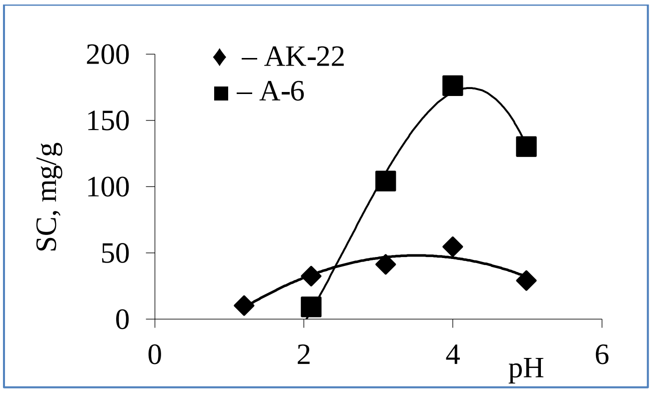


Figure 5 Dependence of capacity of the FIBAN series ionites on the solution pH

Vanadium was extracted and performed further investigations by using the FIBAN AK-22 and FIBAN A-6 ionite with the selected optimal acidity. At pH 4, vanadium is situated preferentially in the form of the anion as decavanadate-$HV_{10}O_{28}^{5-}$ ion which can be adsorbed by the FIBAN AK-22 and FIBAN A-6 anionites according to the following exchange reaction:

for sorption vanadium by FIBAN AK-22

$$5(R\text{-}NH_3)_2SO_4 + 2[HV_{10}O_{28}]^{5-} \longrightarrow 2(R\text{-}NH_3^+)_5[HV_{10}O_{28}]^{5-} + 5SO_4^{2-};$$

When decavanadate-ion interact with the functional groups of the anionites FIBAN A-6, the following reactions may occur:

with quaternary ammonium base groups

$$5(R_4N^+)_2SO_4 + 2[HV_{10}O_{28}]^{5-} \longrightarrow 2(R_4N^+)_5[HV_{10}O_{28}]^{5-} + 5SO_4^{2-},$$

with secondary amines groups

$$5[R\text{–}[N(CH_3)_2H]^+]_2SO_4^{2-} + 2[HV_{10}O_{28}]^{5-} \longrightarrow 2[R\text{–}[N(CH_3)_2H]^+]_5[HV_{10}O_{28}]^{5-} + 5SO_4^{2-}$$

Investigation of equilibrium characteristics of ionites (FIBAN AK-22 and FIBAN A-6) for sorption of vanadium(V) from mineralized solution

The results of the experiment are shown in Figure. 6. The isotherm obtained for the resulting vanadium concentration was a convex shape, which coincide with Langmuir equation.

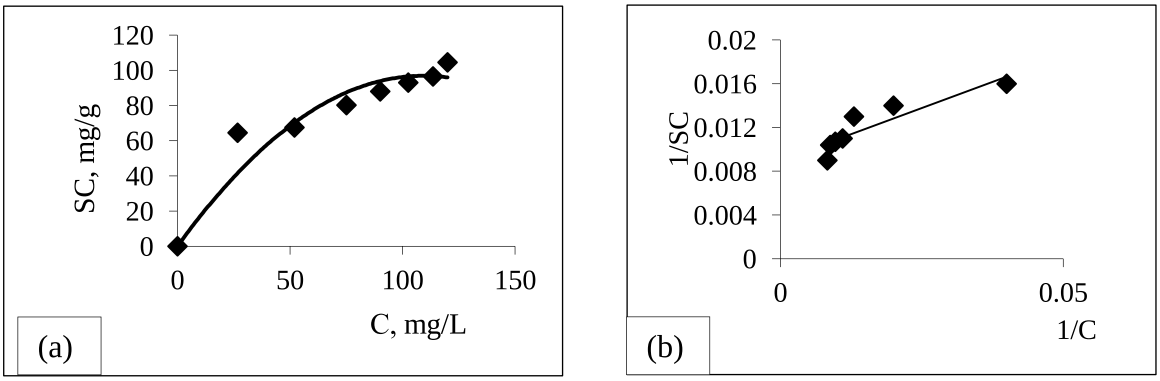


Figure 6 Langmuir isotherm of sorption for vanadium (V) from mineralized chloride-sulfate solution with anionite FIBAN AK-22.

Processing of data on the sorption equilibrium of vanadium with FIBAN AK-22 was carried out by the Langmuir equation in the coordinates "1/SC to 1/C, which describes the isotherm of this nature. Langmuir constant and maximum sorption capacity of the processing were calculated from linearized coordinates (Figure.6,b). The calculated Langmuir constant K_L and the maximum sorption capacity of the ion exchanger FIBAN AK-22 amounted to (190± 45) mL/g and 93.1 mg/g, respectively, with a correlation coefficient R^2 - 0,8.

Sorption isotherm of vanadium (V) with FIBANA-6 was studied by using the Henry equation (Frolov.,1982):

$$SC = K_H \cdot C ,$$

where SC – sorption capacity of the ionites for vanadium, mg /g;

K_H – Henry's law constant, mL/mg;

C –equilibrium concentration of vanadium, mg /L.

In the studied concentration range of vanadium (up to an equilibrium concentration of 110 mg/L) obtained isotherm is linear shape (Figure.7) and can be described by the Henry equation with constant: (2.09 ± 0.20) L/g (R^2= 0.955). The resulting equilibrium data were indicated that the fibrous FIBAN AK-22 has considerably better capacitive characteristics as compared with the ion exchanger FIBAN A-6.

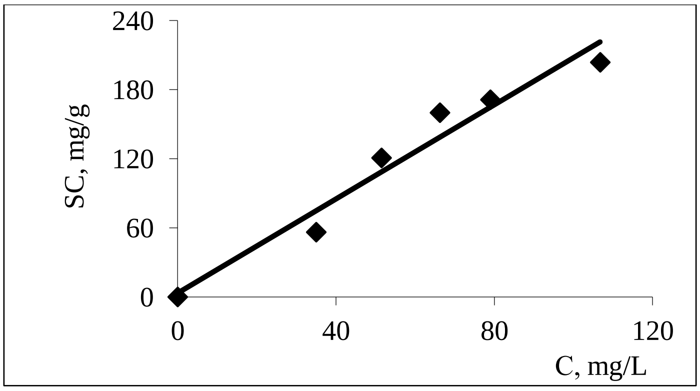
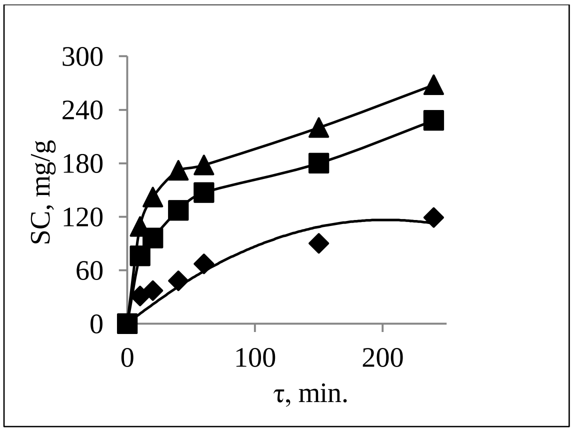


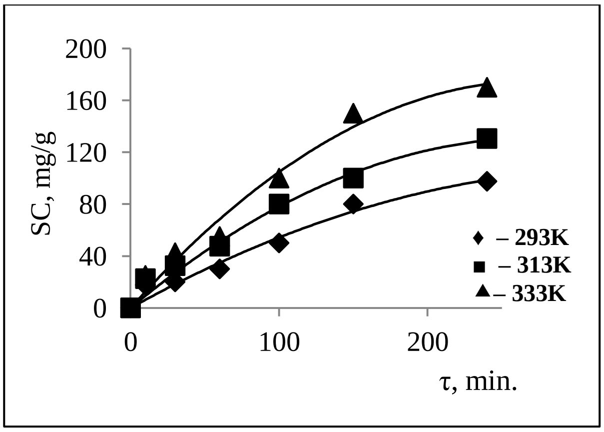
Figure 7 Henry isotherm of sorption for vanadium (V) from mineralized chloride -sulfate solution with anionite FIBAN A-6.

Investigation of Kinetic Characteristics of Ionites (FIBAN AK-22 and FIBAN A-6) for the Sorption of Vanadium(V) from Mineralized Solution

Integral kinetic curves of sorption of vanadium at different temperatures are shown in Figure. 8 (a, b). Integral characteristic kinetic curves of sorption of vanadium ion by FIBAN AK-22 and FIBAN A-6 in the coordinates (sorption capacity SC - time τ) and (saturation F - time τ) are shown in Figures 8 and 9, respectively, and data for their processing are presented in Table 2.

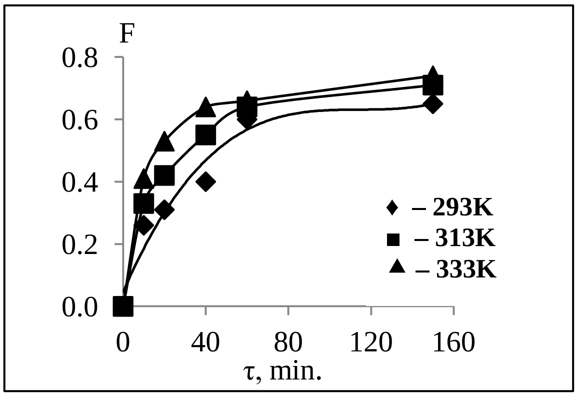
Effective diffusion coefficients of vanadium on the fibrous ionite FIBAN AK-22 and FIBAN A-6 are calculated allowing for the half-transformation time ($\tau_{0.5}$).



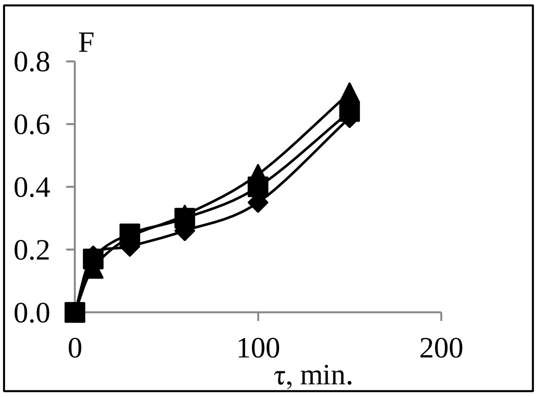


(a) (b)

Figure 8 Integral kinetic curves of sorption of vanadium from mineralized chloride - sulfate solution by using (a) anionites FIBAN AK-22 and (b) anionites FIBAN A-6.



(a)



(b)

Figure 9 Time dependence of the saturation degree (F) of the (a) FIBAN AK-22 and (b) FIBAN A-6 anionites with vanadium

According to the integral kinetic curves of sorption of vanadium in the coordinates of the (degree of saturation (F) - time (τ)),half-transformation time, $\tau_{0.5}$ was graphically calculated (Table 2).

Effective diffusion coefficient of vanadium on the fibrous ionite were calculated, taking into account the half- transformation time. The calculation was performed using the formula (Kokotov, 1979):

$$D_{eff} = (0.065 \cdot R^2) / \tau_{0.5} ,$$

where D_{eff} – effective diffusion coefficients of vanadium on the fibrous ionite, (m^2/s), $\tau_{0.5}$– half-transformation time, (s) , and R – the fiber radius, (m) (its average magnitude is 30 microns meter.)

Table 2 Kinetic Characteristics of Vanadium (V) by FIBAN AK-22 and FIBAN A-6

Temperature (K)	Half time sorption $\tau_{0.5}$ (s)		Effective diffusion coefficient (m^2/s)	
	AK-22	**A-6**	**AK-22**	**A-6**
293	8100	3300	$3.2x10^{-15}$	$7.9x10^{-15}$
313	7800	2100	$3.3x10^{-15}$	$1.2x10^{-14}$
333	6000	1200	$4.3x10^{-15}$	$2.1x10^{-14}$

Table 2 shows that the order of effective diffusion coefficients of vanadium are in the range of 10^{-15} – 10^{-14} m^2/s. Using the calculated effective diffusion coefficients of vanadium ionites,the apparent activation energy of adsorption of vanadium by ionites FIBAN AK-22 and FIBAN A-6 are calculated by an equation similar to the Arrhenius equation (Kokotov, 1979):

$$D= D_0 . e^{-E act./RT}$$

where $E_{act.}$ − the apparent activation energy (J/mol), D_o − constant (m^2/s), D – effective diffusion coefficient of vanadium ionites (m^2/s), R – universal gas constant (8.3144 J/mol), T – Temperature (K).

Table 3 Activation Energy During the Sorption of Vanadium with FIBAN AK-22 and FIBAN A-6

Interval Temperature (K)	Activation energy of sorption of vanadium $E_{act.}$ (kJ/mol)		Mean value of the apparent activation energy (kJ/mol)	
	AK-22	**A-6**	**AK-22**	**A-6**
293-313	1.2±0.5	15.9± 4.5		
293-333	6.0±1.8	19.8± 4.8	6.2±2.0	19.9± 4.7
313-333	11.5±3.3	24.2± 7.7		

As shown in Table 3, the average apparent activation energy of FIBAN AK-22 was calculated by an equation similar to the Arrhenius equation, is equal to (6.2 ± 2.0) kJ /mol, which may be indicated the flow of the sorption of vanadium by the external field. For FIBAN A-6, the average apparent activation energy was (19.9 ± 4.7) kJ/mol, which may be indicative of the flow of the sorption of vanadium by the external field (Rakov *et al*.,1993). According to the resulting data, the sorption rate of FIBAN A-6 is a mite higher than AK-22 by the above resulting data, elution characteristics for sorbent FIBAN AK-22. Proceedings integral kinetic curves and the data on the effective diffusion coefficient of vanadium(V) by using fibrous ion exchangers FIBAN AK-22 and FIBAN A-6 show that the low speed (rate) of the sorption of vanadium present in the acidic condition, mainly in the form of large-ion decavanadate $HV_{10}O_{28}^{5-}$. Delayed kinetics of sorption of vanadium fibrous ion exchanger can be apparently explained by lower mobility due to sufficiently large size decavanadate $HV_{10}O_{28}^{5-}$ adsorbed ion, which has a considerable charge, and rather large size and by the necessity of spatial orientation during the sorption.

Furthermore, sorption of vanadium(V) was investigated at acidic medium- oxo-cations VO_2^+ state, which is smaller than decavanadate $HV_{10}O_{28}^{5-}$ ion size. For this purpose, strong-fibrous cation exchanger FIBAN K-1 containing sulfonic groups was used as a sorbent for sorption of vanadium(V) by changing pH. Preliminary study of the effect of pH on the sorption of vanadium cation exchanger FIBAN K-1 is shown in (Figures 10 and 11). It can be seen the distribution ratio of vanadium(V), decreases with increasing the pH of the solution. The distribution coefficient of vanadium in ionities was calculated as the ratio of the equilibrium sorption capacity of the ion exchanger to the equilibrium concentration in the solution.

$$K_d = SC/C_V,$$

where, K_d – distribution ratio of vanadium (mL/g), SC – equilibrium sorption capacity (mg /g), C_V–the equilibrium concentration of vanadium in the solution in mg /L.

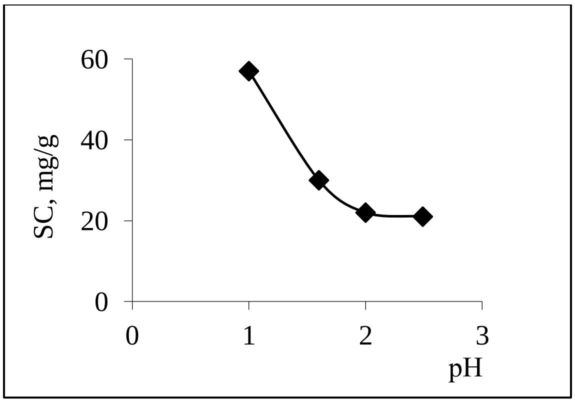


Figure 10 Dependence of the sorption capacity of cationites FIBAN K-1 on pH

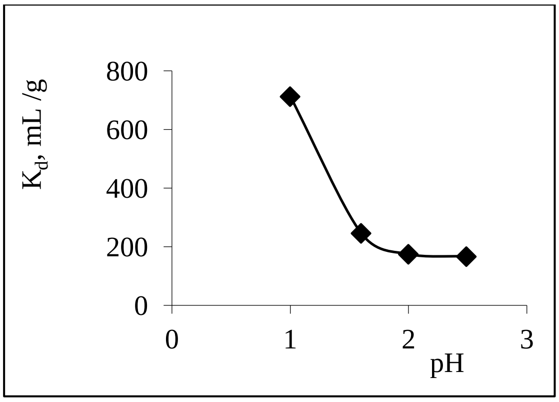


Figure 11 Dependence of distribution ratio of the cationites FIBAN K-1 on pH

The maximum distribution coefficient of vanadium in ionite FIBAN K-1 was observed at pH of 1 (Figure 11). Integral sorption kinetic curve of vanadium(V) by using cationites FIBAN K-1 at this pH in the coordinates of the “degree of saturation of the F – time τ” is shown in Figure 12.

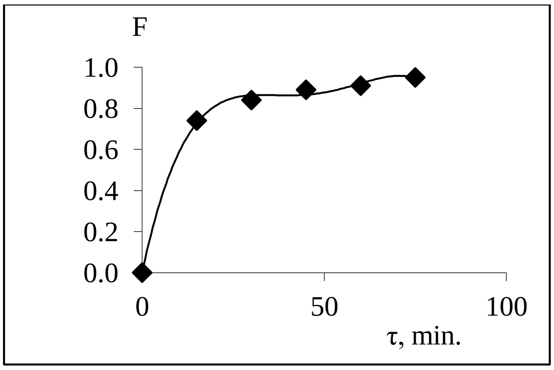


Figure 12 Integral kinetic curves of sorption of vanadium(V) by cationites FIBAN K-1 from the mineralized chloride-sulfate solutions (pH 1).

Integral kinetic sorption curves were obtained in conditions of limited volume of the solution. According to the integral kinetic curves of sorption of vanadium in the coordinates of the (degree of saturation (F) – time (τ)), half-transformation time, $\tau_{0.5}$ was graphically calculated. For FIBAN K-1, effective coefficient of vanadium diffusion (5.4×10^{-14} m^2/s) was calculated, taking into account the time of half-reaction in Table 4.

Table 4 Comparison of Effective Diffusion Coefficients of Vanadium(V) during the Sorption of Ion Exchangers FIBAN

Mark of the ion exchanger FIBAN	pH	Half-transformation time, $\tau_{0.5}$ (s)	The effective diffusion coefficient (m^2/s)
AK-22	4.0	8100	3.2×10^{-15}
K-1	1.0	480	5.4×10^{-14}

A comparison of the effective diffusion coefficients of vanadium on the fibrous ionites FIBAN AK-22 and FIBAN K-1, as well as the integral of the kinetic curves in the coordinates of the (degree of saturation of F – time τ), obtained by the sorption it these ion exchangers shows that a decrease in the size of the adsorbed ion vanadium(V) sorption rate increases significantly: the effective diffusion coefficient increases by more than an order of magnitude.

Conclusion

Recovery of vanadium(V) from mineralized chloride-sulfate solutions by fibrous materials of the FIBAN series (anionites and cationites), (FIBAN AK-22), (FIBAN A-6) and (FIBAN K-1) which contain functional groups: (-NH_2, =NH, ≡N, -COOH), (–N^+≡, =NH), and (-SO_3^- H^+) respectively were studied. The maxium sorption rate for vanadium (V) of decavanadate $HV_{10}O_{28}^{5-}$ and oxo-vanadate VO_2^+ was observed in the pH range 1 – 4. Sorption isotherms of vanadium from mineralized solution by using ionites FIBAN AK-22 has a convex shape. Langmuir constant K_L is (190 ± 9) mL/g (R^2–0.8), the maximum sorption capacity – 93.1 mg /g. Sorption isotherm of ion exchanger FIBAN A-6 has a linear shape and is described by Henry constant K_H (2.09 ± 0.20) L/g (R^2 – 0.955). For methods of limiting the volume of solution, integral kinetic curves of sorption of vanadium(V) ion by using exchangers FIBAN were obtained. It was found that the sorption of vanadium(V) in the form of decavanadate ion from the chloride- sulfate solution (pH ≥ 2) by using nitrogen-containing fibrous ion exchangers (FIBAN AK-22 and FIBAN A-6) took place in the external diffusion region. The effective diffusion coefficients of vanadium on the fibrous ionite FIBAN AK-22 increases from 3.2 x 10^{-15} to 4.3 x 10^{-15} m^2/s, ion exchanger FIBAN A-6, 7.9 x 10^{-15} to 2.1 x 10^{-14} m^2/s over the temperature range 293 – 333 K. The activation energy of sorption of vanadium(V) by ion exchanger FIBAN AK-22 is (6.2 ± 2.1) kJ/mol, that of ion exchanger FIBAN A-6 (19.9 ± 4.7) kJ/mol. It is established that the diffusion of oxo-vanadate VO_2^+ in the strongly acidic condition by cationites FIBAN K-1 occurs at a higher sorption rate than the diffusion of decavanadate ions $HV_{10}O_{28}^{5-}$ by anionites FIBAN AK-22 and FIBAN A-6.

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