THE STUDY OF THE SORPTION PROPERTIES OF FILTERING MATERIALS BASED ON TITANIUM PHOSPHATE - POROUS TITANIUM COMPOSITION

V. A. Shablovski[1], *A. V. Tuchkoskaya*[1], *V. A. Rukhlya*[1], *O. G. Pap*[1], *K. O. Kudelko* [2]
[1]Research Institute for Physical Chemical Problems of the Belarusian State University,
14 Leningradskaya st, 220006 Minsk, Belarus, shablovski@bsu.by
[2]V.I. Vernadskyy Institute of general and inorganic chemistry NAS of Ukraine, Ukraine
kathykudelko@gmail.com

DOI: https://doi.org/10.20535/2218-930032021244507

Inorganic sorbents are more selective in comparison with commercial ion exchange resins towards of metal ions. However, inorganic sorbents characterized not high kinetic properties. One of the way to increase the kinetic rate of inorganic sorbents is to reduce the particle size of these materials, other way is synthesizing inorganic sorbents as porous products from powder materials. A sample of such inorganic sorbents is titanium phosphate of various compositions.

Studying the properties of microfilters based on composition titanium phosphate - porous titanium has been developed. The sorbents based on acidic titanium phosphate $Ti(HPO_4)_2{\cdot}H_2O$ *were used for filtering solution with Fe(II) content. It is found that the number of impregnations with inorganic sorbent modificator is important and influence filtration process. The obtained results demonstrated that after the first impregnation of porous material with a smaller pore size, it is possible to obtain such sorbent as a mass content of powder material. By varying the ionic form of titanium phosphate, the porosity of titanium, the amount of impregnation, it could be possible effect on the sorption Fe(II). The sorption properties of titanium-titanium phosphate microfilters were studied by potentiometric titration in the NaCl-NaOH system, as well as the sorption of* Fe^{2+} *ions. The degree of purification for Fe(II) from solution with a concentration of 10 mg/l is 64 %. Application an electric potential to the microfilter of porous titanium - phosphate titanium increases the degree of purification of Fe(II) to 88 %.*

Keywords: *adsorption, inorganic sorbent, titanium phosphate, ion-exchange, microfilter, porous titanium*

Received: 26 November 2021 Revised: 18 December 2021 Accepted: 19 December 2021

---

1. Introduction

Inorganic sorbents (IS) are more selective of ion exchange in comparison with ion exchange resins towards of metal ions. However, ion exchange resins in comparison with IS has generally better kinetics. One of the known way to increase the rate of ion exchangers (IS) is to reduce the particle size of these materials, but practically, usage of dispersed materials for columns is impossible due to the high hydrodynamic resistance. This problem can be solved by synthesizing IS in porous products from powder materials, in particular, from sintered titanium powders (Shablovskyi, 1996).

In this work, acid titanium phosphate (TP) with the composition $Ti(HPO_4)_2{\cdot}H_2O$ has been used as sorbent (Chubar et al., 2016). This material is characterized as a highly acidic polyfunctional properties with a layered crystalline structure (Kumar, 2013). TP is suitable for application in separation process for heavy metals and ammonium from multicomponent solutions, as well as basic compounds from the gas phase (Somya, 2020). An important advantage of porous titanium materials is property of electrical conductivity. By changing the magnitude and sign of the electric potential to the material surface, it is possible to change the value of the isoelectric point of ionogenic groups of TF and, therefore, to change their sorption capacity and selectivity (Trublet et al., 2019, Shablovski, 2011).

Purpose research: studying the sorption properties of microfilters with composite titanium-titanium phosphate under an electric field.

2. Materials and methods

Microfilters based on porous titanium and titanium (IV) phosphate for research were obtained according to the following scheme**:**

1. The sieving process of the initial titanium powder and pressing of porous samples. The pressing was carried out at a pressure of 50-100 MPa.
2. The sintering process of porous samples was carried out in vacuum chamber at temperature 1200 °C, holding time - 2 hour.
3. Product titanium spongy powder was dissolved in low concentration orthophosphoric acid at 105 °C in the presence of a catalyst. As result, a homogeneous solution of titanium phosphate (III) was produced.
4. The technique of repeated impregnations of porous material with sintered titanium powder with solution TP (III) was used.
5. The process of oxidation on air of titanium (III) to tetravalent titanium with the formation of acidic titanium phosphate with composition $Ti(HPO_4)_2 \cdot H_2O$ was followed.

All experiments were carried out on porous titanium materials (diameter of disc was 30 mm and thickness 2 mm) the average pore size 100, 60, 40 μm. Initial concentration of solution TP (III) for titanium was 5%.

3. Results and discussion

The mass changes of TP (IV) in porous titanium materials depending on the number of impregnations with a solution of TP (III) are given in Table 1. It was shown, that the mass content of TP (IV) in materials reaches 20 %.

The repeated impregnation of TP (III) leads to increasing in the content of TP (IV) in porous materials: with a pore size of 100 μm from 2.0 % to 12.9 %, with a pore size of 60 μm from 4.3 % to 18.3 %, and with a pore size of 40 microns from 7.0 % to 20.4 %.

The obtained results demonstrated that after the first impregnation of porous material with a smaller pore size with a TP (III) solution, it is possible to obtain such a mass content of TP (IV), which can be obtained for a filter with a large pore size only after the second or third impregnation. Based on these results, it can be concluded that TP (III) is precipitated primarily in smaller pores.

Table 1. *The mass changes of TP (IV) in porous titanium materials versus numbers of impregnations with a solution of TP (III) with an initial concentration of titanium* $C_{initial}$ *= 5 mg/l*

Pore diameter, µm - number of impregnations, times	m initial, g	∆m TP, g	Content PT, %
100 µm			
1 impregnation	6.05	0.12	2.0
2 impregnation	6.04	0.42	6.9
3 impregnation	6.65	0.71	12.5
4 impregnation	6.59	0.85	12.8
60 µm			
1 impregnation	5.36	0.38	7.0
2 impregnation	5.27	0.58	11.0
3 impregnation	5.62	0.79	14.0
4 impregnation	5.20	1.06	20.4
40 µm			
1 impregnation	5.07	0.22	4.3
2 impregnation	4.62	0.43	9.2
3 impregnation	4.69	0.69	14.6
4 impregnation	4.57	0.84	18.3

This conclusion is confirmed by the data presented in Table. 2. According the data, we could note the mass changes in the pore size from the number of repeated impregnations of the initial porous titanium with a TP (III) solution.

Table 2. *Dependence of the pore size of microfilters on the number of repeated impregnations with TP (III) solution*

Sample, Number of impregnations, times	Pore diameter $D_{max.}$, µm	Avarage pore diameter $D_{aver.}$, µm	$(D_{max}–D_{aver})/D_{max}$, %
Initial material	17.6	12.7	27.8
1 impregnation	11.2	8.2	26.8
2 impregnation	6.1	1.9	68.8
3 impregnation	3.7	0.5	86.8
Initial material	140	121	13.6
1 impregnation	140	96.4	31.1
2 impregnation	140	93.7	33.1
3 impregnation	49.2	22.9	53.5

As can be seen from Table 2, the maximum pore diameter of the porous element D_{max} = 140 μm practically does not change even after 2 impregnations, the average pore diameter changes insignificantly. And only after the third impregnation, the pore diameter decreases.

The picture is completely different for a titanium porous element with smaller pore diameters. For example, it is possible to reduce the initial maximum pore diameter from 17.6 μm to 3, μm, and the average diameter from 12.7 μm to 0.5 μm by three-fold impregnation with TP (III) solution.

The sorption properties of titanium-titanium phosphate microfilters were studied by potentiometric titration in the NaCl-NaOH system, as well as the sorption of Fe^{2+} ions in the concentration range 1-3 mg/l.

Typical curves of potentiometric titration are shown in Fig. 1. It can be seen that for TP the titration curves are characteristic of highly acidic polyfunctional ion exchangers.

It should be noted that, in contrast to the literature data (Chubar et al., 2016), which indicate that the process of exchange of H^+ for Na^+ in the initial area occurs in the pH range 3.5-4.0, in our study a similar process goes to 2-2.5 pH units are lower. This fact could be explained with the high dispersion of TP particles.

It was found that the exchange capacity (EC) of the materials in the acidic and neutral ranges is not directly dependent on the amount of TP introduced in pores. This fact is explained by the blockage of some of the ion-exchange sites in the pores of the initial material. Also, ion-exchange sites can be replaced by Na^+ ions only in the alkaline region.

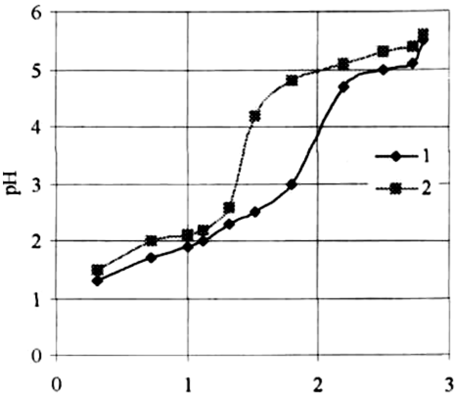

Fig. 1. *Potentiometric titration curves of microfilters titanium-titanium phosphate in 0.1 N HCI - NaOH: solution system: 1 and 2 – is mark 3-times and 4-times impregnation of the titanium framework 60 μm pores with a solution of TP (III)*

The results of process of sorption of Fe(II) ions on microfilters with TP in H^+ and Na^+ forms given in Table 3.

As could be seen from Table 3 the varying the ionic form of TP, the pore diameter of porous titanium, as well as the amount of impregnations, it is possible to reduce the content of Fe(II) of the concentration from 10 mg/l to 3.55 mg/l. The removal degree for Fe(II) from the initial solution was found 64 %.

When an electric potential is applied to the titanium-titanium phosphate microfilter, the degree of solution purification from Fe(II) increases to 88 % (Table 4).

Since TP has a positive surface charge, for the three-phase system: electrode-ionite-solution in the pores of the microfilter during cathodic polarization, OH-ions are generated, which leads to an increase in the diffusion coefficient of ions and, consequently, to an increase in the sorption of Fe(II) ions.

Table 3. *Results of sorption of Fe(II) ions on microfilters titanium-titanium phosphate,* $C_{init.}$*= 10 mg/l*

Pore diameter, µm - number of impregnations, times	**C** $_{\mathbf{equl,}}$ **mg/l**	**EC, mg/l**	**Adsorption, %**
H-form 100-3	4.60	0.380	54
60-1	5.26	0.980	47
60-2	5.00	0.640	50
60-3	4.60	0.450	54
40-1	4.80	0.500	52
40-2	4.60	0.480	54
40-3	4.48	0.320	55
Na-form 100-1	5.26	1.970	47
100-2	5.71	0.510	43
60-2	4.80	0.600	52
60-3	4.60	0.390	54
60-4	4.60	0.320	54
40-1	5.26	0.620	47
40-2	3.55	0.560	64
40-3	4.50	9.350	55

Table 4. *Sorption Fe(II) on microfilters titanium-titanium phosphate (pore diameter 60* μ*m, 1 time and 2 time impregnation,* Na^+*- form,* $C_{initial}$*= 5 mg/l) at different values of potentials*

Filter – 1 impregnation, potential 500 mV				
1	2	3	4	5
2.85	2.34	2.10	0.96	1.74
43	53.2	58	80.8	65.2
Filter – 1 impregnation, potential 600 mV				
2.49	2.43	1.35	1.28	0.90
50.2	51.4	73	74.4	82
Filter – 1 impregnation, potential 700 mV				
1.80	1.74	1.20	0.93	0.60
64	65.2	76	81.4	88
Filter – 2 impregnation, potential 500 mV				
2.10	2.49	2.04	1.20	0.93
58	50.2	59.2	76	81.4
Filter – 2 impregnation, potential 600 mV				
1.35	0.93	0.90	2.25	1.65
Filter – 2 impregnation, potential 700 mV				
3.0	2.10	1.83	1.74	1.20
40	58	63.4	65.2	76

4. Conclusions

The effect of the pore structure of titanium-titanium phosphate microfilters and application of electric potential on sorption Fe(II) during filtration has been studied. A process of impregnating porous material of sintered titanium powder with a titanium (III) phosphate solution with an active inorganic sorbent (acidic titanium (IV) orthophosphate) has been developed for microfilters. It was shown that the usage of titanium - titanium phosphate microfilters allow to reduce the content of Fe(II) in the solution to 64 %, and with application electric potential to 88 %.

Acknowledgment

We are grateful to PhD Kudelko K. O. for assistance with translation into Ukrainian and English.

References

1. Somya, A. Hybrid Ion Exchangers. *Hybrid Nanomaterials - Flexible Electronics Materials* **2020**. https://doi.org/10.5772/intechopen.92116

2. Chubar, N.; Gerda, V.; Omastova, M.; Micusic, M.; Heister, K.; Man, P.; Fraissard, J. Next generation inorganic layered structure (an)ion exchangers: Synthesis, properties and applicability for water treatment. https://researchonline.gcu.ac.uk/en/publications/next-generation-inorganic-layered-structure-anion-exchangers-synt (accessed Dec 17, 2021).

3. Trublet, M.; Scukins, E.; Carabante, I.; Rusanova, D. Competitive Sorption of Metal Ions on Titanium Phosphate Sorbent (TIP1) in Fixed-Bed Columns: A Closed-Mine Waters Study. *ACS Sustainable Chemistry & Engineering* **2019**, *7* (9), 8145–8154. https://doi.org/10.1021/acssuschemeng.8b05971

4. Kumar, S.; Jain, S. History, Introduction, and Kinetics of Ion Exchange Materials. *Journal of Chemistry* **2013**, 1–13. https://doi.org/10.1155/2013/957647

5. Shablovskyi, V. O.; Tykavyi, V.F.; Myklush, S. A.; Poluchenye y modyfytsyrovanye neorhanycheskykh sorbytov na poverkhnosty y v porakh razlychnykh nosytelei. *Avtoreferaty dokladov 1-oi Mezhdunarodnoi konferentsyy Khymyia vesokoorhanyzovannykh veshchestv i nauchnye osnovy nanotekhnolohyi, S-Pb*., **1996**, 35-37.

6. Shablovski, V. A.; Tuchkovskaya, A. V.; Belyakov, V. N.; Vasilyuk, S. L. Treating microbiological fluids with metal filters, characterized by variable sign and magnitude charge of surface. *Water and water purification technologies. Scientific and technical news* **2011**, *1* (3), 67-72.

ДОСЛІДЖЕННЯ СОРБЦІЙНИХ ВЛАСТИВОСТЕЙ ФІЛЬТРУЮЧИХ МАТЕРІАЛІВ НА ОСНОВІ КОМПОЗИЦІЙ ФОСФАТ ТИТАНУ – ПОРИСТИЙ ТИТАН

Шабловський В. О.[1], *Тучковська А. В.*[1], *Рухля В. А.*[1], *Пап О. Г.*[1], *Куделко К. О.*[2]

[1]НДІ фізико-хімічних проблем БДУ, вул. Ленінградська 14, 220006, Мінськ, Білорусь,
shablovski@bsu.by

[2] Інститут загальної та неорганічної хімії ім. В. І. Вернадського НАН України, Україна
kathykudelko@gmail.com

По відношенню до іонів металів неорганічні сорбенти є селективнішими порівняно з промисловими іонообмінними смолами, але ці сорбенти характеризуються невисокими кінетичними властивостями. Одним із способів підвищення кінетичної швидкості неорганічних сорбентів є зменшення розміру частинок цих матеріалів, іншим способом є синтез неорганічних сорбентів у вигляді пористих продуктів на основі порошкових матеріалів. Зразком таких неорганічних сорбентів є фосфат титану різного складу.

Розроблено спосіб модифікації мікрофільтрів на основі композицій фосфат титану – пористий титан. В дослідженні було використано сорбент на основі кислого фосфату титану (ФТ) складу $Ti(HPO_4)_2 \cdot H_2O$*. Знайдено, що важливим є кількість просочень (імпрегнувань) модифікатором поверхні пористого мікрофільтра. Варіюючи іонну форму фосфат титану, пористість титану, кількість просочень (імпрегнувань), можна впливати на ступінь сорбції Fe(II) з розчинів під час фільтрації. Сорбційні властивості титан-титанфосфатних мікрофільтрів досліджували шляхом потенціометричного титрування в системі NaCl-NaOH, а також сорбції іонів Fe(II). Ступінь очищення від Fe(II) розчинів, концентрація яких складала 10 мг/дм*^{3}*, становить 64 %. При накладанні електричного потенціалу до мікрофильтру пористий титан - фосфат титана, можна підвищити ступінь очищення Fe(II) до 88 %.*

Ключові слова: *адсорбція, неорганічний сорбент, фосфат титану, іонний обмін, мікрофільтр, пористий титан*