

INVESTIGATION OF SORPTION PROPERTIES OF NEW SORBENTS FOR WASTEWATER TREATMENT

¹Mukhtarova Nigora Bakhramovna, ²Aliev Bakhodir Abduganievich

¹Assistant, Tashkent State Technical University named after Islam Karimov

²Doctor of Technical Sciences, Professor, Tashkent State Technical University named after Islam Karimov

<https://doi.org/10.5281/zenodo.7889069>

Abstract. *The possibility of obtaining new selective sorbents from local bentonite clays is shown. The physicochemical and sorption properties of the obtained sorbents to ions of some metals have been studied. The use of the obtained sorbents in the treatment of wastewater from heavy metal ions and water softening has been established.*

Keywords: *bentonite clay, bentonite, sorption, phase composition, wastewater treatment, sorbent.*

Throughout the world, great importance is attached to the rational use of natural resources, especially water and land resources. The constant trend in the growth of water consumption and water use dictates the implementation of measures aimed at saving and rationally improving the system of management and use of water resources. At the present stage of development of society and production, water resources play a very important role as the main source of energy, carrier of energy, the main raw material component, means of purification, and other functions inherent in it. The introduction of closed water supply systems in industrial and technological processes, the research and development of new and highly efficient wastewater treatment technologies, dikutet on the application of new approaches to solving technical problems and the search for various methods and sources of wastewater treatment.

In this regard, there is a need to solve the following scientific solutions for the study of the process of wastewater treatment of various industries, the consideration of new adsorbing materials based on affordable and environmentally friendly natural raw materials, providing the maximum and effective degree of wastewater treatment from pollutants.

In the Republic of Uzbekistan, large-scale measures are being taken to protect nature, rational nature management and water use, the introduction of new technologies in the irrigation of crops in agriculture and closed water supply systems in the production and technological processes of industries. According to the fourth direction of the Action Strategies for the Further Development of the Republic of Uzbekistan, the main tasks aimed at “creating effective mechanisms for introducing into practice the promotion of research and innovation activities” have been identified. In this regard, it is of particular importance to study the processes of wastewater treatment from pollutants and toxic components, the creation of new adsorbent materials for wastewater treatment from locally available raw materials.

The literature widely covers issues related to the physicochemical study of wastewater treatment processes, the development of compositions and technologies for obtaining new types of adsorbents for wastewater treatment based on available mineral raw materials and secondary materials, as well as improving the improvement of their adsorbing and other functional properties. The aim of the study is to develop a technology for obtaining new types of sorbent materials based

on previously unused mineral resources and to study the processes of industrial wastewater treatment. The objects of study are samples of bentonite clays from the Shafirik deposit.

As objects of research, bentonite clays of the Shafirkan district of the Bukhara region, previously not studied for industrial wastewater treatment, are of great interest. Therefore, the study of their chemical and mineralogical composition, the main sorbing properties, the development of methods for chemical activation and modification is of particular interest. The results of chemical analysis (table) show that the samples of bentonites of the Shafirkan region differ from each other in terms of chemical composition and content of some elements. Table 1 shows that the silica content of all the studied samples are close and it ranges from 43.72 wt.% to 59.24 wt.%. Due to sand content, sample-3 and sample-4 have a high content of silica (SiO₂), the content of which decreases significantly during mechanical enrichment. And the content of aluminum oxide is in the range of 12.87-18.08%.

Table 1

Chemical composition of samples of bentonite clays of the Shafirkan region

Designation of bentonite samples	The content of oxides, wt.%									
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	SO ₃	ППП
Sample-1	57,65	0,87	13,69	5,77	1,81	3,08	1,12	1,72	2,59	11,21
Sample- 2	43,72	0,54	12,87	4,17	4,74	7,29	2,43	1,86	3,23	19,01
Sample-3	59,24	0,99	15,53	6,09	1,71	1,96	1,49	1,87	0,14	10,86
Sample-4	58,02	0,85	18,08	5,693	1,71	0,84	2,04	3,85	0,11	8,56

According to the data from table 1, it can be seen that the content of CaO in all the studied samples ranges from 0.84 to 7.29 wt.%. For bentonite clays, the content of alkaline oxides is of particular importance; therefore, sodium bentonites are of the highest quality in terms of their physicochemical properties. The amount of Na₂O also tends to change, so in sample-1 - 1.12%, in sample-4 its content reaches 2.04 wt.%.

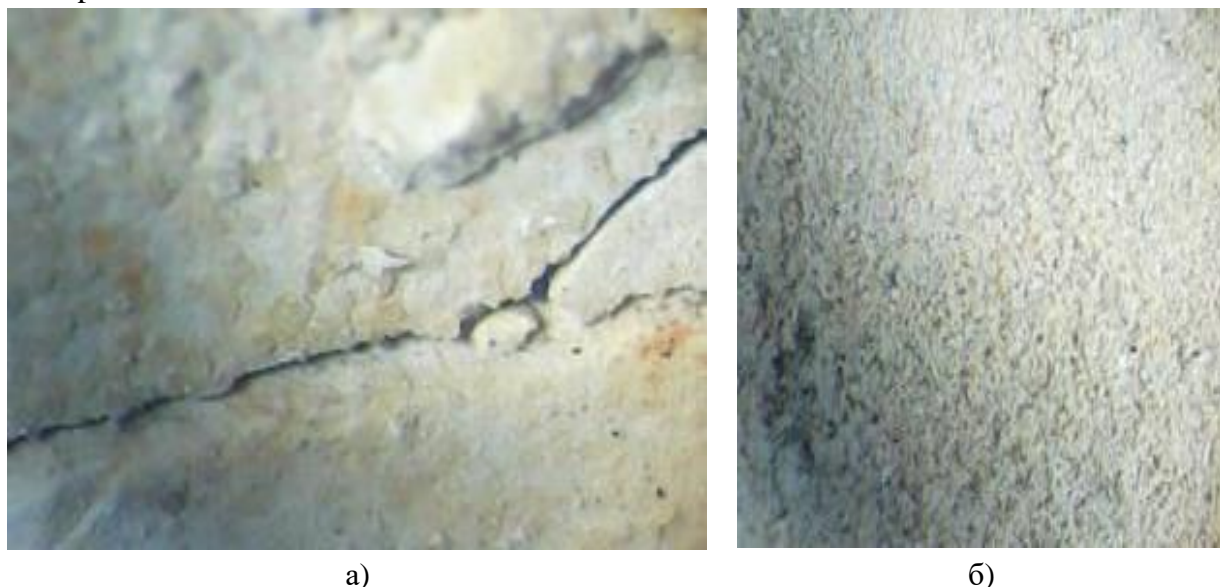


Fig. 1. A snapshot of a chip (a) and clay powder (b) of the Shafirkan deposit (x600 magnification)

Microscopic studies of samples of bentonite clays were carried out using an MBS-10 optical microscope in transmitted and polarized light with an installed digital camera with a

magnification factor of up to 600 s. Using this method, you can determine the appearance, shape, dimensions, the presence of anisotropy, pores, defects, the degree of swelling, etc.

As can be seen from the microphotographs (figure), large veinous inclusions of iron and quartz compounds, as well as minor gypsum inclusions in the form of gypsum dihydrate crystals, were found on rock chips and bentonite clays. In clay powders, a uniform distribution of these above inclusions is observed.

The study of the phase composition of samples of bentonite clays of the Shafirkanskoe deposit was carried out by the X-ray method of analysis. Diffraction patterns were obtained by the powder method on a DRON-4.0 setup at $\text{CuK}\alpha$ - and $\text{CoK}\alpha$ radiation, filter- Ni. For a more accurate determination of the content of montmorillonite in the studied bentonite clays, X-ray phase analysis of samples subjected to air drying, heat treatment at 580-600°C, and saturation with glycerin was carried out.

In samples subjected to air drying, the width of the basal lines of X-ray patterns increases and the lines of beidellite $d = 0.725$ and 0.359 nm, as well as the lines of palygorskite $d = 1.05$ n, are more clearly manifested. Saturation with glycerol and heating to 580-600°C leads to a shift of the basal lines towards smaller angles from $d=1.025$; 0.263 nm to $d=1.426$; 0.180 nm

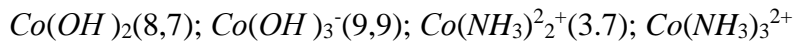
Based on the generally accepted methodology for studying clays, in order to clarify the presence of montmorillonite, X-ray patterns of bentonite samples were taken in an air-dry state, when heated to 330°C and saturated with glycerin, and during heat treatment at 580°C. It is known from the literature that upon saturation with glycerol, the X-ray effects of montmorillonite are shifted towards smaller angles. Heat treatment at a temperature of 580°C is necessary to distinguish montmorillonite from other clay minerals such as chlorite, vermiculite, etc.

In the course of experimental studies, the processes of distribution of trace elements between the solution, the solid phase of hydroxides and oxides were studied both for the practical purposes of concentrating, separating and deep purification of substances, and for elucidating the mechanism of elementary acts leading to the sorption of microcomponents.

At present, the role of individual factors that ultimately determine the magnitude of sorption, for example, the pH of the medium within narrow limits, has been revealed. However, many of them have not been studied enough. The data on the influence of the composition and concentration of the “background” electrolyte are very contradictory, the behavior of microcomponents with a change in their concentration over a wide range, and the state of sorbents under sorption conditions have been little studied. At the same time, the dependence between the state of the sorbent, such as, for example, natural clay adsorbents such as montmorillonite, and the sorption value of 3d elements and dyes under the same conditions [8] has been studied least of all.

In our case, the study of the sorption of Cr(III, VI), Zn, Ni, Co, and a number of organic dyes on montmorillonite in a wide range of solution pH and concentration of sorted components ($C_{\text{me}}=2,5 \cdot 10^{-5}$ - $4,5 \cdot 10^{-4}$) mg/l was sent to solve a number of problems to determine the state of microcomponents in aqueous solutions, search for various chemical concentration conditions, and determine them on natural clay adsorbents bentonite clays.

A systematic study of the sorption of cobalt (II) depending on a number of factors simultaneously acting on its sorption on montmorillonite has not been carried out, including the influence of the pH of the medium, the composition and concentration of the salt background, etc. In the presence of ammonia (up to 1.08 mol/l Co(II) the following complexes and hydro complexes are formed: $\text{Co}(\text{OH})_2$ (8.70).



According to the literature data [9], active Co(II) ions can have the shape of octahedral $Co(H_2O)_6^{2+}$ and partially tetrahedral $Co(H_2O)_4^{2+}$ structures, and these forms are in balance. Apparently, a similar phenomenon takes place during the formation of Co(II) ammoniates. Considering all the factors, we have studied the effect of the pH of the medium, the presence of ammonia and nitrate anions on the coprecipitation of Co(II) at its concentration from $4,5 \times 10^{-4}$ mol/l.

The salt background was KNO_3 , NH_4 , NaO_3 , NH_4Cl , and NHO_2 solutions. In this case, a different order of mixing the reagents was used:

- a) carrier - montmorillonite (1.25 g) was isolated from an acidic environment together with cobalt (co-precipitation);
- b) cobalt salt was added to montmorillonite (sorption);
- c) under the same conditions, loss of Co(II) due to precipitation of its solid phase, sorption by vessel walls, etc. conditionally besieged by us.

The value of sorption was estimated by the radioactivity of the centrifugate using $^{57.58}Co$ isotopes; the contact time of the precipitate with the solution was 30 min. Other experimental conditions and their procedure were described earlier [90].

Sorption of cobalt (II) on bentonite clays in 1M KNO_3 begins at pH values coinciding with the beginning of Co(II) hydrolysis, that is, at pH=5 and is complete in the pH range of 8.3-9 (Fig. 14.), in under these conditions, concentration of Co (II) is possible, followed by its separation from the carrier, reprecipitation of the latter at pH = 5, or pouring the solution obtained by dissolving the sorted microcomponent in a minimum amount of acid into a concentrated ammonia solution. In the presence of ammonium nitrate, two maxima are observed with precipitation: at pH 7-7.5 and pH 10; with increasing concentration NH_4NO_3 from 1 to 3 moles co-precipitation decreases in the pH range of 7-10. Sorption of Co (II) drops to zero $b > 3$ mol NH_4NO_3 from pH 8.

At the same time, with increasing salt concentration, age-related sorptions are observed at pH=7, that is, in the region of cobalt (II) hydrolysis (Fig. 15). These data are in good agreement with the literature data [10,11]:

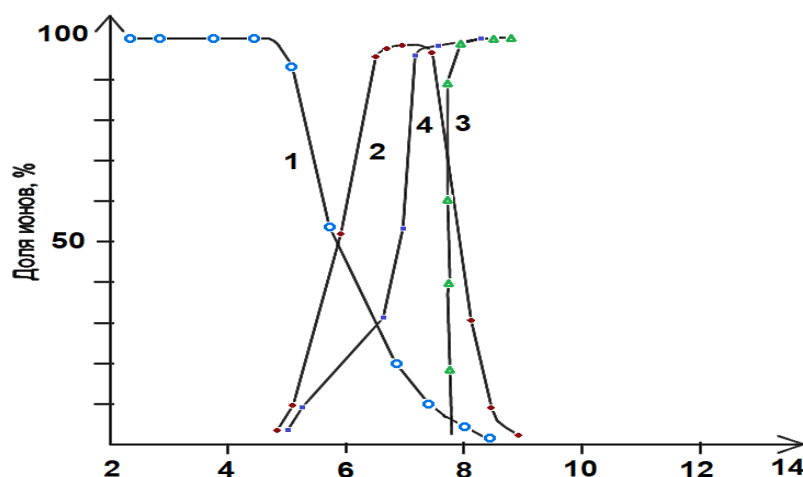


Fig. 14. Condition and sorption Co (II) в 1M KNO_3 1 and 2 - fraction of ions Co^{2+} and $Co_4(OH)_4^{4+}$, respectively; 3 and 4 - hydroxide precipitation Co (II), respectively

The co-precipitation of nickel (II) with metal hydroxides was studied in order to elucidate the mechanism of sorption and separation of nickel from other elements [12], as well as its concentration when determined in wastewater.

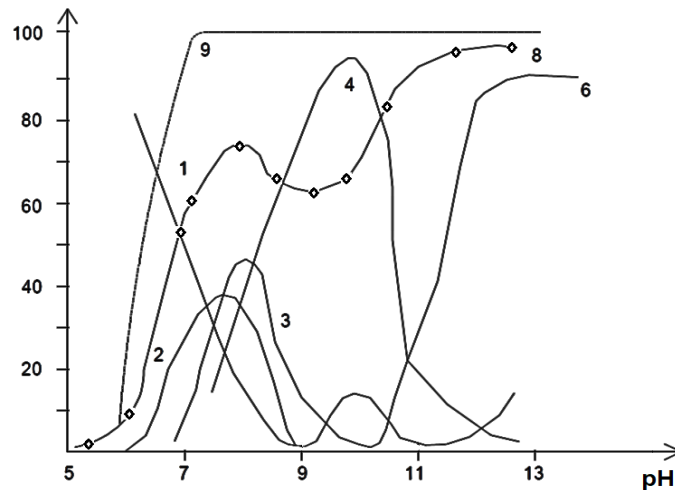


Fig. 15. Condition and sorption Co (II) in 1M NH₄NO₃
 1-7 – fraction of ions Co (NH₃)₂²⁺, Co(NH₃)₃²⁺, Co(NH₃)₄²⁺, Co (NH₃)₆²⁺, Co(NH₃)₂(OH)₂ and Co(OH)₃⁻ respectively, 8 – sorption 2,5·10⁻⁴ g-l/ion Co(II) в 1M NH₄NO₃, 9 – same, in 1M KNO₃.

Under other conditions, it was taken into account that nickel (II) ions in aqueous solutions undergo hydrolysis with the formation of hydrox cations:

NiOH⁻ (lgK₁=5,0; K₁ – hydrolysis constant), Ni₂(OH)³⁺ (lgβ_{1,2}=9,0) and Ni₄(OH)₄⁴⁺(lgβ_{4,4}=27,82), respectively [13, 14].

In pH = 8 precipitated Ni₂(OH)₂, lgIIP which, according to various authors, is: 13,81; 14,5; 15,21; 18,06; 17,19, respectively [15].

In the presence of ammonia (>1.08 mol/l), nickel (II) forms amine complexes, lg formation constants are indicated in parentheses [93]: Ni(NH₃)²⁺(2,80); Ni(NH₃)₂²⁺(5,04); Ni(NH₃)₃²⁺(6,77); Ni(NH₃)₄²⁺(7,96); Ni(NH₃)₅²⁺(8,71) and Ni(NH₃)₆²⁺(8,74) [16].

We have studied the sorption of nickel (II) depending on the pH of the medium, in the presence of ions in the ammonia solution Cl⁻, CO₃²⁻, ClO₄⁻ and NO₃⁻, at different concentrations of the sorbed component and background electrolyte, on bentonite clays. In this case, the salt background was the solutions KNO₃, NaClO₄, NH₄NO₃ and KNO₃+K₂CO₃. The order of displacement of reagents under the conditions of this experiment was changed as follows:

a) the carrier of bentonite clays (1 g 25 mg) was isolated from an acidic medium together with the sorbed component (co-precipitation);

b) the sorbed component was added to the sediment of bentonite clays (sorption);

c) under the same conditions, the loss of nickel was determined due to the precipitation of its solid phase, sorption by vessel walls, etc. conventionally called by us precipitation. The amount of precipitation was determined from the nickel content in the centrifuge by the photometric method using dimethylglyoxime; the contact time of the precipitate with the solution was 20 min. The rest of the conditions were the same as described previously. Nickel sorption 4,5·10⁻⁵ gr-ion/l in 1m KNO₃ on bentonite clays it starts at pH=5 and is complete in the range of pH=7.5-10. Under these conditions, it is possible to concentrate nickel with its subsequent separation from the carrier by reprecipitation, the latter at pH=5 or by pouring a concentrated ammonia solution into the precipitate of bentonite clays, followed by desorption of nickel on the surface of the precipitate. Sorption of nickel in 1 mol KNO₃, 1 mol NaClO₄ and 1 mol KNO₃+0,5 mol K₂CO₃ practically the same. In 1mol NH₄NO₃ the maximum co-precipitation is observed at pH> 7.9 (Fig. 3.6.) with increasing concentration NH₄NO₃ to 5M decreases with precipitation and sorption in the areas of

pH = 8.9-10.5, as well as its value and the position of the first maximum on the pH axis. With an increase in the alkalinity of the solution, the sorption of nickel drops to zero in a 2.5 solution NH_4NO_3 in interval pH = 8,9-11 (fig.16). These data are in agreement with the data of [13].

The data obtained can be most satisfactorily explained by the following processes. In a weakly acidic medium at pH=5, the hydrolysis of nickel ions begins with the formation, predominantly, of ions $\text{Ni}_4(\text{OH})_4^{4+}$, which is confirmed by calculations of the change in the proportion of hydrolyzed forms with an increase in the pH of the medium. Calculations were performed according to the balance equation using the available constants for the formation of hydroxocations: $C_{\text{Ni}}=[\text{Ni}^{2+}]+[\text{NiOH}^+]+2[\text{Ni}_2\text{OH}^{3+}]+4[\text{Ni}_4(\text{OH})_4^{4+}]$

Proportion NiOH^+ and $\text{Ni}_2\text{OH}^{3+}$ negligible compared to a fraction of a tetramer $\text{Ni}(\text{OH})_4^{4+}$. Sorption of nickel on montmorillonite begins only when $\text{Ni}(\text{OH})_4^{2+}$, and does not occur if only aquilons are present in the solution [13].

REFERENCES

1. Арипов Э.А., Закиров М.З., Ахмедов К.С. Монтмориллонит-гидрослюдистые глины Узбекистана. ФАН,-1976,-136 с.
2. Закиров М.З., Либензон Е.С., Арипов Э.А., Галимов Р.З., Мирсаидов М.М., Асанова А.П. Керменинское месторождение опоквидных глин. В сб. Опоквидные глины Кермене. ФАН,-1970,- с.4-34.
3. Sabirov B.T., Javloniy C., Kadirova Z.R., Usmanov H.L. Prospects and problems of industrial use of bentonite clays of the Zerafshan region Prospects and problems of industrial use of bentonite clays of the Zerafshan region. Proceeding of the International conference on “Integrated innovative development of Zerafshan region: achievements, challenges and prospects”. Uzbekistan, Navoi.-2017.-p.197-202.
4. Сабилов Б.Т. Определение коэффициента набухания бентонитовых глин Южных областей Узбекистана. «Кимё ва озиқ-овқат саноатлари ҳамда нефт-газ қайта ишлашнинг инновацион технологияларини долзарб муаммолари» Республика илмий-техника анжуманининг мақолалар тўплами. Тошкент кимё-технология институти, Т.: -2011.-С.193-194.
5. Мирзаев А.У., Чиникулов Х. Новое месторождение бентонитовых глин Навбахор. Ж. Геология и минеральные ресурсы.-1999.-№5.-с.23-30.
6. Сабилов Б.Т., Намазов Ш.С., Кадырова З.Р. Определение коэффициента фильтрации гидроизоляционных композиций на основе бентонитовых глин. Узбекский научно-технический и производственный журнал «Композиционные материалы», Ташкент.-2019.-№2.-С.131-134.
7. Кариев А.Р., Джамолов А.А., Комилов Д.К. Бентониты, их использование в народном хозяйстве. // Рекламно-информационный буклет /. – Душанбе, 1997.
8. Бокиев Б.Р. К расчету искусственно аэрируемых биологических прудов. // Вестник Таджикского технического университета им.акад. М.С.Осими (научный журнал), №1 (5).–Душанбе: ТТУ, 2009. – С. 64 – 69.
9. Microwave Fast Sintering of Ceramic Materials. Romualdo R. Menezes1, Pollyane M. Souto, Ruth H.G.A. Kiminami. // Sintering of Ceramics – New Emerging Techniques.. Edited by Arunachalam Lakshmanan. Опубликовано: InTech Janeza Trdine 9, 51000, Риека, Хорватия.-2012.-pp.624.

10. Hassan Hassanien Mohamed Darweesh. Nanoceramics: Materials, Properties, Methods and Applications-Part II. Submitted to Nanoscience.-2018.-pp. 40-66. (Published: 09.03.2018).
11. В.А. Смолко, Е.Г. Антошкина. Кинетика набухания бентонита Зырянского месторождения. Вестник Южно-Уральского Государственного Университета. Серия «Металлургия».-2014.-Том 14.-№2.-С.89-91.
12. Кариев А.Р., Джамолов А.А., Комилов Д.К. Бентониты, их использование в народном хозяйстве. // Рекламно-информационный буклет /. – Душанбе, 1997.
13. Назарова З.А. Использование бентонитовых глин Узбекистана в производстве мазей. - Тез. докл. конференции «Состояние и перспективы развития и исследования вспомогательных веществ». - Харьков, 1982. - С. 75.
14. Forteza V., Galan E., Gornejo J. Interaction of dexametasone and montmorillonite – adsorbtion – degradation process. // Appl – Clay Sci, 1989, №4 (5-6). –P. 437-438.
15. Sabirov B.T., Javloniy S., Kadirova Z.R., Usmanov H.L. Prospects and problems of industrial use of bentonite clays of the Zerafshan region Prospects and problems of industrial use of bentonite clays of the Zerafshan region. Proceeding of the International conference on “Integrated innovative development of Zarafshan region: achievements, challenges and prospects”. Uzbekistan, Navoi.-2017.-p.197-202.
16. Bakatula E.N., Cukrowska E.M., Weiersbye I.M., Mihaly-Cozmuta L., Tutu H. Removal of toxic elements from aqueous solution using bentonite modified with L-histidine// W ater Science and Technology. - 2014. - Т. 70. - Вып. 12. - С. 2022-2030.