Obtaining sorbents based on bentonite and wastewater treatment of hydrometallurgical plants

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Abstract. Methods of physico-chemical analysis of the composition of industrial wastewater and the use of sorption materials obtained on the basis of compositions of various chemical reagents with local minerals have been developed. The physicochemical and mechanical properties of the newly obtained composite materials have been studied. The composition of bentonite of the Navbakhor mine consists mainly of polygorskite carbonate, the general chemical composition consists of the following clays: $Mg_2Al_2[Si_8O_{20}](OH)_2 \cdot 8H_2O \cdot CaCO_3$. Bentonite also contains kaolinite $Al_4[Si].4O10] \cdot (OH)8$, polymorphic modification, polishplate $K[AlSi_3O_8] \cdot Na[AlSi_3O_8] \cdot Ca[Al_2Si_2O_8]$, silica SiO_2, beidellite (Na, Ca)·Al(Si, Al) present), calcite $CaCO_3$. Wastewater samples from a hydrometallurgical plant were used as an experimental object. It was found that the heat treatment of bentonite clay has practically no significant effect on the mineralogical composition and structure of the sorbents obtained from it, but has a positive effect on the mechanical strength of the granules. It has been established that the optimal firing temperature of bentonite sorbents is 550-800 °C, since at lower firing temperatures sorbent samples do not have sufficient strength limits. The effective effect of modified bentonites as a sorbent in wastewater treatment of “GMZ” has been determined, especially in the case of bentonite containing copper and aluminum oxides.

1 Introduction

From Water treatment for drinking and technical water supply is fundamentally different from other areas of chemical technology: water treatment processes are carried out with very small amounts of dissolved substances in large volumes of water. Due to the high requirements for the filtration of bulk materials, the possibilities of using natural adsorbents are very limited [1].

Currently, the scientific foundations of water purification technologies with naturally occurring aluminosilicate materials with unique adsorption properties are actively

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developing. These adsorbents mainly include bentonite clays. Bentonite clays have been used since ancient times to purify wine, oil and water. They are non-toxic and have a highly developed surface, which causes a significant adsorption capacity, that is, the ability to actively absorb various substances from solutions [2,3].

A limiting factor in the widespread use of natural bentonite sorbents for the purification of drinking water and industrial wastewater is the lack of effective granulation technologies, since clay minerals in the aquatic environment are susceptible to peptization, that is, they are dispersed [4,5].

Another source of exchange centers are weakly acidic hydroxyl groups (Si–OH) and basic (Al–OH) groups on the side faces and edges, which participate in pH-dependent ion exchange [6].

In the process of molecular sorption, the sorbed substances are located between the planes of the packages, and without changing the structure of the layers, the initial water complexes are destroyed. Thus, the presence of such active centers as exchange cations, hydroxyl groups, as well as the activation of bentonite clays by changing their surface makes it possible to significantly expand the practical application of layered silicates for the purification of aqueous media [7-8].

The main purpose of the work is to study the methods of obtaining multifunctional modified sorbent materials based on waste water treatment, as well as their structure and physico–chemical properties.

2 Materials and methods

Production of modified bentonite composites. Traditionally, the sorbent production process consists of the following stages: pyrolysis (carbonation) and activation. Carbonation and activation combustion are carried out in furnaces under the influence of high temperature and without air access. The mineral bentonite of the Navbakhor deposit was selected as a sorbent for the experiment. a) 80 g of bentonite powder was measured on analytical scales. The obtained samples were fired in an oven at a temperature of 300-800 ºC for 30-35 minutes. After the firing process, the samples were reduced from 80 g to 40 g and weighed. b) Bentonite was treated with 10, 20 and 30% solutions of salts of various metals to obtain a modified form. After mixing the treated bentonite with such concentrated solutions of Co^{2+}, Al^{3+} and Mn^{2+} salts, an NH_4OH solution is added to it and the metal is converted to a hydroxide form, from where it enters the solution in the form of NH_4Cl. NH_4Cl is removed from the reaction mixture by repeated washing of the bentonite mass with distilled water. After drying, it was fired at a temperature of 500-800 °C, metal oxides were formed in bentonite and a modified form was obtained.

The study of the amount of certain ions in the solutions taken for the study. 500 g of analyzed water is measured. Then put 2-3 layers of gauze in the mixing funnel, and then put 40 grams of bentonite. First, we pass 50 g of distilled water, and then we pass a 500 g sample. We use Marjonbulok and "GMZ-3" waters as samples and pass them through the resulting sorbents.

3 Results and discussion

The results obtained and their discussion. The composition of bentonite of the Navbakhor mine consists mainly of carbonate-palygorskite, and the general chemical composition consists of the following clays: $Mg_2Al_2[Si_8O_{20}](OH)_2 \cdot 8H_2O \cdot CaCO_3$.

Table 1. Chemical composition of bentonite from the Navbakhor deposit.

Mineral	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	CaO
Quantity, %	58.25	14.27	4.37	3.62	2.25	1.20	2.07

Montmorillonite $(Ca,Na)(Mg,Al,Fe)_2[(Si, Al)_4O_{10}](OH)_2$ nH_2O and bentonite also contains kaolinite $Al_4[Si_4O_{10}](OH)_8$, polymorphic modification, feldspar $K[AlSi_3O_8]$-$Na[AlSi_3O_8]$-$Ca[Al_2Si_2O_8]$, silica SiO_2, beidellite (Na, Ca) Al (Si, Al), calcite $CaCO_3$.

In order to determine the points of temperature difference during thermal carbonization and activation, preliminary studies of raw bentonite from the Navbakhor mine were studied. Carbonation and activation combustion are carried out in furnaces under the influence of high temperature and without air access.

Table 2. Porous structure of bentonite clay samples after high-temperature firing.

№	**Samples**	**Specific surface area** ***S*****, m^2/g**	**Total volume** ***V*****, cm^3/g**	**Distribution of holes by radii, %**			
				1.5-2.0 nm	**2.0-4.0 nm**	**4.0-8.0 nm**	**10.0-52.0 nm**
1	Bentonite powder	51	0.061	9	21	21	49
2	Firing *t* = 550 °C	37	0.092	6	16	23	55
3	Firing *t* = 600 °C	36	0.096	6	17	23	54
4	Firing *t* = 650 °C	35	0.100	5	13	5	57
5	Firing *t* = 700 °C	26	0.090	4	14	24	58
6	Firing *t* = 800 °C	12	0.031	5	15	24	56

A). The results of the chemical analysis of the composition of Marjonbulok water (GMZ-4) passed through calcined bentonite at various temperatures are shown in the following tables.

Table 3. The number of primary ions in the selected sample, mg/dm^3.

№	**Water ions GMZ-4**	**Ca^{2+}**	**SO_4^{-2}**	**Cl^-**	**Mg^{2+}**
1	Content	275.53	1.48	1158.15	131.24

Analyzing the transferred water for ions Ca+2, SO4-2, Cl-, Mg+2, it was noticed that the number of ions decreased. As can be seen from the table, the number of ions that increase water hardness decreased as follows: Analysis of GMZ-4 water passed through bentonite B-2 300-500 oC: The number of Ca+2 ions decreased from 275.53 mg/dm3 to 17.03 mg/dm3.The number of Mg+2 ions decreased from 131.24 mg/dm3 to 9.11 mg/dm3. The content of Cl-ions decreased from 1158.15 mg/dm3 to 140.38 mg/dm3.The content of SO4-2 ions decreased from 1.48 mg/dm3 to 0.0040 mg/dm3.

Analysis of GMZ-4 water passed through bentonite B-2 800 oC: The number of Ca+2 ions decreased from 275.53 mg/dm3 to 20.04 mg/dm3. The number of Mg+2 ions decreased from 131.24 mg/dm3 to 7.29 mg/dm3. The content of Cl-ions decreased from 1158.15 mg/dm3 to 105.28 mg/dm3. The content of SO4-2ions decreased from 1.48 mg/dm3 to 0.0045 mg/dm3.

Table 4. The number of ions in the selected sample after passing through the sorbent is mg/dm^3.

№	**Title of bentonite**	**Ca^{2+}**	**SO_4^{2-}**	**Cl^-**	**Mg^{2+}**
1	B-1 bentonite 300-500 °C	17.03	0.0040	140.38	9.11
2	B-2 bentonite 800 °C	20.04	0.0045	105.28	7.29
3	Enriched bentonite 1200 °C	14.03	0.0053	70.19	1.21

Analysis of GMZ-4 water passed through bentonite enriched with Al_2O_3: The number of Ca^{+2} ions decreased from 275.53 mg/dm^3 to 14.03 mg/dm^3. The number of Mg^{+2} ions decreased from 131.24 mg/dm^3 to 7.29 mg/dm^3. The content of Cl^- ions decreased from 1158.15 mg/dm^3 to 1.21 mg/dm^3.The content of SO_4^{-2} ions decreased from 1.48 mg/dm^3 to 0.0053 mg/dm^3.

B). When obtaining a modified bentonite composite, the following reactions occur:

$$\text{Bent.} + MeCl_n\ (n=2,3) \rightarrow \text{Bent.}MeCl_n$$

$$\text{Bent.}MeCl_n + nNH_4OH \rightarrow \text{Bent.}Me\,(OH)_n + nNH_4Cl$$

$$\text{Bent.}Me\,(OH)n\ \text{heating}(500\text{-}800\ ^\circ C) \rightarrow \text{Bent.}Me_xO_y + H_2O$$

As can be seen from the diagram, when modifying bentonite, porous and selective sorbents containing oxides of various metals are obtained. They can simultaneously precipitate anions and cations or holds cations and anions by chemisorption.

Figures 1-2 show the results of wastewater treatment of GMZ-3 using modified bentonite. It can be seen from the graphs that modified bentonite with the addition of metal oxides reduces the amount of both cations and anions in wastewater. These results show that the continuation of scientific research in this direction in the future has a unique perspective.

In all forms, the sorbents obtained have a good effect on wastewater treatment from various cations and anions, which satisfy the requirement for the reverse use of these waters in the technological process. The effective effect of modified sorbents is observed in the case of bentonite containing copper and aluminum oxides.

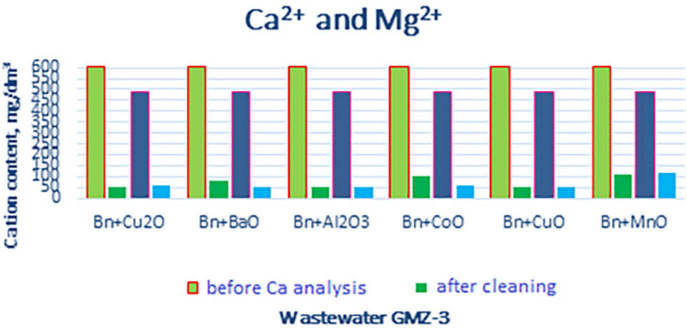

Fig. 1. Graph of the dependence of the cation content on the composition of modified bentonite.

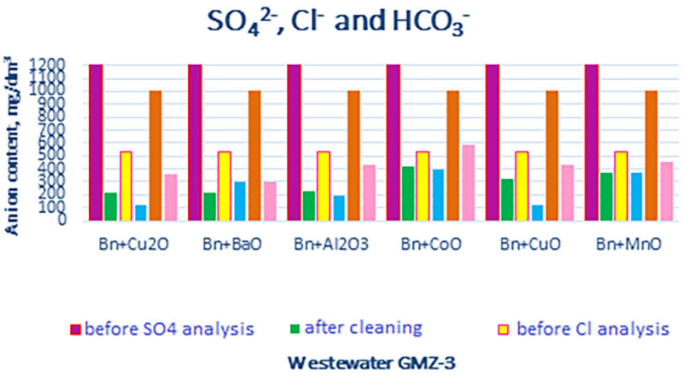

Fig. 2. Graph of the dependence of the anion content on the composition of modified bentonite.

4 Conclusion

It has been established that the heat treatment of bentonite clay has practically no significant effect on the mineralogical composition and structure of the sorbents obtained from it, but has a positive effect on the mechanical strength of the granules. It has been established that the optimal firing temperature of bentonite sorbents is 550-800 °C, since at lower firing temperatures sorbent samples do not have sufficient strength limits.

It has been observed that bentonite granules have very effective sorption properties of some ions, especially sulfate, chloride, calcium, and magnesium ions from water.

The effective effect of modified bentonites as a sorbent in wastewater treatment of GMZ has been determined, especially in the case of bentonite containing copper and aluminum oxides.

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