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Development of a Modified Opoka-Bentonite Sorbent for Desalination of Highly Mineralized Water: Pore Structure, Adsorption Performance, and Influencing Factors

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ABSTRACT

The paper reports the results of research on creating a modified opoka-bentonite sorbent. The microstructures and chemical and mineralogical characteristics of the natural raw materials, opoka and bentonite clay from the West Kazakhstan deposit, are analyzed. All studied samples had a specific surface area close to 80 m^2/g and were characterized by the predominance of micro- and mesopores with a radius larger than 12 nm and a total pore volume around 0.2 cm^3/g. The obtained isotherms belong to type II, which is characteristic of porous materials and suggests the presence of meso- and micropores above 100 angstroms, and show H3-type hysteresis loops, observed in non-rigid aggregates of plate-like particles forming slit-like pores. The best characteristics of micro- and mesopores were observed for sorbent compositions with the following component ranges (wt%): 80-95 opoka and 5-20 bentonite clay. The relationship between desalination efficiency and sorbent particle size was investigated. The study found the degree of purification was higher for smaller sorbent fractions. Specifically, the degree of purification by the sorbent with a fraction size of 1-2 mm exceeds 50%, unlike the fractions of 3-5 mm. The patterns of desalination efficiency change were also analyzed in relation to water temperature. The degree of desalination increases at lower temperatures. With a water temperature of 50 ℃ and the starting salt content in the test water of 5.0 g/L, the purification effect of the sorbent with a fraction size of 1-3 mm was 49.6%, while at a temperature of 20 ℃, it reached 55.6%. The conducted comprehensive research demonstrates the potential of the developed opoka–bentonite compositions as effective sorbents for brackish water desalination.

1. INTRODUCTION

Water scarcity is an acute global problem exacerbated by population growth, rapid urbanization, climate change, and unsustainable water management practices [1], leading to high water demand [2]. A thorough understanding and optimization of desalination processes in a sustainable and economically feasible manner is crucial to meet the growing demand for fresh water.

Although water shortages are a worldwide problem [3], in many areas the cause of water scarcity is a lack of quality. A large share of groundwater and surface water are highly mineralized and not suitable for drinking and agricultural purposes. This is particularly important in arid and semi-arid areas, where the main water source consists of mineralized and brackish waters. Highly mineralized waters (that is, those with dissolved salts such as sodium, calcium, and magnesium) have an adverse effect on soil quality and plant growth, and are harmful to plants and animals. For this reason, cost-effective and efficient methods of desalination are essential.

Water salinity is a major obstacle in more than 100 countries, and the scale and spread of saline environments are likely to increase due to the growing salinization of irrigated soils, the use of poor-quality water, including seawater, for irrigation, and the impending climate change [4]. Water salinity is the result of sodium, calcium, magnesium, and potassium salts dissolved in water. Water salinity has been pinpointed as a growing public health problem in many parts of the world. It also has a major impact on food supply as saline water affects agricultural productivity [5].

Analyzing the situation with the provision of the population with quality water in Kazakhstan, it is important to note that the country ranks low in the world in terms of its water potential, as more than 50% of the water is unsuitable for drinking. Particularly affected are steppe-desert areas, most sensitive to natural factors, such as dramatic floods followed by drought. Over ¼ of Kazakhstan's territory has natural groundwater with mineralization of over 5 g/L. For example, the analysis of hydrological and hydrogeological indicators of water bodies in the West Kazakhstan Region indicates that six districts out of 12 have unsatisfactory water quality.

These territories are characterized by underdeveloped river networks and the presence of carbonate and chloride-type waters with heavy mineralization and high organic matter content.

Thus, adsorption is one of the most promising desalination techniques because it is simple, energy-efficient, and utilizes natural minerals that are abundant and cheap. The use of clay minerals as well as siliceous rocks and minerals as adsorbents for salt adsorption from brine has received increasing attention because of their abundance and low cost.

Desalination, the process of removing salts and other impurities from seawater or brackish water to produce drinking water, is a promising solution to mitigate water scarcity [6]. Therefore, affordable and locally available methods to remove these salts and reduce alkalinity have been drawing much research attention. Adsorption is considered a cost-effective method to reduce water alkalinity. Inexpensive adsorbents from natural sources, such as clays, are widely used to remove metal ions and other impurities from water [7-11].

In this regard, clay-like minerals can be highlighted as low-cost adsorbents for removing metal ions that can also be used to reduce water salinity [12]. Shokrolahzadeh et al. [13] used a clay material to remove arsenic from water. Similarly, Shokrian et al. [14] used natural zeolite clinoptilolite to remove NaCl from aqueous solutions, managing to extract 60%. Natural and activated bentonite has been used to remove metal ions (zinc, iron, manganese, potassium, and sodium) [15].

Innovative methods are also used to remove metals and salts from water. The study by Yang et al. [16] primarily aimed at reducing boron (B) and chloride (Cl^-) levels in brackish water to meet the water quality standards of B < 0.5 mg/L and Cl- < 250 mg/L. Towards this goal, the innovative adsorbent OQAS-AC@NGO was used to remove boron. It combines silicon, organic quaternary ammonium (OQAS), and chloride (OQAS) modified with activated carbon (AC) in a self-organizing nitrogen-doped graphene oxide (NGO) structure [17].

Today, there are several other methods for removing dyes and heavy metals from wastewater, such as coagulation/flocculation, flotation, biological methods, and membrane filtration [18-20]. Each of these methods has advantages and disadvantages. However, among them, the adsorption method is still recognized as reliable because of its low energy consumption, lean running procedure, and high removal efficiency [21].

Despite the variety of the described treatment methods, Kazakhstan currently lacks efficient, cost-effective, and uncomplicated water treatment technologies. An important problem is to find technological solutions that account for territorial features and allow the creation of reliable schemes for purifying mineralized natural groundwater at minimum capital and operating costs.

The growing awareness of the use of inexpensive materials to create effective adsorbents and maintain environmental sustainability has sparked more attention to natural sorbent materials. The great potential of sorbents derived from various natural substances, such as zeolites, clay, chitosan, and red mud, as well as farm animal biomass and wastes, has been widely reported and is particularly relevant in today's conditions [22-29].

Therefore, the study focuses on compositions from locally sourced opoka and bentonite clay to reduce water mineralization. Opoka and bentonite are some of the potential raw materials that can be obtained at low cost from many sources. Our hypothesis about the potential utility of bentonite for water purification and desalination is based on several studies proving that bentonite clays have high specific surface area, porosity, and adsorption capacity [30, 31]. However, the opokas and bentonite clays of the West Kazakhstan deposit have not been sufficiently investigated to create modified sorbents for reducing water mineralization.

Therefore, the aim of this study is to develop and investigate modified mineral sorbents based on opoka and bentonite clay from the West Kazakhstan deposit for the desalination of highly mineralized water.

The specific objectives of the study are:

- to determine the optimal composition of the opoka–bentonite system;
- to analyze the relationship between pore structure characteristics (micro- and mesoporosity, specific surface area) and desalination efficiency;
- to evaluate the influence of operational parameters, including sorbent particle size and water temperature, on the degree of mineralization removal.

It is hypothesized that the combination of porous siliceous opoka and ion-exchange-active bentonite clay will provide a synergistic effect, leading to enhanced adsorption capacity and improved desalination performance.

2. METHODS

2.1 Studied filtration material and deposit

The raw materials used to obtain the modified mineral sorbent were siliceous rocks — opoka and bentonite clay from the West Kazakhstan deposit. Opoka is a light, finely porous, dense siliceous rock consisting of calcified opal flaps of diatom algae and their fragments [32, 33].

Opokas from the West Kazakhstan deposit are light and dense microporous rocks composed mainly of the smallest (< 0.005 mm) particles of opal-cristobalite silica. The chemical and mineralogical composition of opoka is given in Tables 1 and 2. Opoka has an average density of 1.32 g/cm^3 and is naturally porous (45-56%) [34-37].

The second modifying component chosen for the study was bentonite clay from the Pogodaevsky deposit, West Kazakhstan Region.

The chemical composition of bentonite clay from the Pogodaevsky deposit, West Kazakhstan Region, is provided in Table 3 [38-42]. The adsorption properties of the developed sorbents are closely related to the chemical and mineralogical composition of the initial components presented in Tables 1-3. Opoka from the West Kazakhstan deposit is characterized by a high content of silicon dioxide ($SiO_2 \approx 76\%$), predominantly represented by the opal–cristobalite phase and biogenic silica formed from the remains of diatom algae. Such a silica structure is characterized by a well-developed system of micropores and mesopores and provides a high specific surface area, which promotes the formation of a large number of active adsorption sites.

At the same time, bentonite clay contains montmorillonite, a layered aluminosilicate with a 2:1 structure, characterized by high cation-exchange capacity and the ability to swell in an aqueous medium. The presence of exchangeable cations and the developed surface of montmorillonite facilitate ion-exchange processes and the adsorption of dissolved salts.

The combined use of opoka and bentonite provides a synergistic effect. Opoka forms a porous siliceous framework with a developed pore system and high specific surface area, while bentonite increases the number of active adsorption sites due to the cation-exchange properties of montmorillonite. This explains the high efficiency of sorbents containing 80–90% opoka and 10–20% bentonite clay, which demonstrated the most favorable pore-structure characteristics and the highest degree of water mineralization reduction.

Table 1. Mineralogical composition of siliceous rock — opoka from the West Kazakhstan deposit, %

Rock	Opal-Cristobalite Silica	Clay Minerals	Calcite	Quartz	Mica	Glauconite	Biogenic Remains
Siliceous rock — opoka	54-78	15-22	< 6	4-7	2-4	2-3	< 12

Table 2. Chemical composition of opoka from the West Kazakhstan deposit, mass %

Raw Material	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	N_2O	K_2O
Opoka from the West Kazakhstan deposit	4.96	76.03	8.15	5.49	1.22	1.34	0.31	1.53	0.61

LOI: Loss on ignition.

Table 3. Chemical composition of bentonite clay from the Pogodaevsky deposit, West Kazakhstan Region, wt%

Raw Material	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	Na_2O	LOI
Bentonite clay from the Pogodaevsky deposit	61.51	17.06	2.27	3.21	6.36	1.27	3.57	6.75

The highest adsorption efficiency is observed for Composition containing 90 wt% opoka and 10 wt% bentonite, which is associated with the optimal balance between the developed siliceous porous structure of opoka and the high cation-exchange capacity of montmorillonite in bentonite clay.

2.2 Composition of the modified sorbent

The selection of component ratios in the opoka–bentonite clay composition was based on an analysis of the literature data and the results of preliminary laboratory experiments. It is well established that the incorporation of clay minerals containing montmorillonite into siliceous materials enhances adsorption capacity by increasing the number of active adsorption sites and the cation-exchange capacity of the material.

Preliminary tests showed that when the bentonite clay content is below 5 wt%, its effect on the sorption properties of the composition is negligible. At the same time, increasing the bentonite content above 20 wt% leads to deterioration of the filtration properties of the sorbent and a decrease in the mechanical strength of the granules.

Therefore, in this study, a bentonite clay content range of 5–20 wt% was selected, as it provides an optimal combination of the porous siliceous structure of opoka and the high cation-exchange capacity of montmorillonite. Within this range, four representative sorbent compositions (Table 4) were investigated, which made it possible to determine the influence of bentonite content on the pore structure and sorption properties of the material.

Table 4. Studied compositions of modified sorbents

Composition No.	Opoka, mass %	Bentonite, mass %
1	80	20
2	85	15
3	90	10
4	95	5

2.3 Equipment

1. The surface morphology of the studied sorbents was determined by microphotographs taken with a JSM-IT 200 scanning electron microscope. Microphotographs allow analyzing macroporous structures in the pore size range inaccessible by other methods.

2. A PoreMaster 60 mercury porosimeter was used to determine porosity, macropores, and mesopores. The mercury porosimeter determines macropores, micropores, mesopores, total pore volume, and specific surface area as a function of applied pressure based on mercury intrusion/extrusion measurements. The measurable pore size range of the PoreMaster 60 is 0.0036–1100 μm.

The equipment used to make the modified sorbent included: a drying cabinet, a porcelain ball mill, a DELTA ME 300 granulator, a 3Flex high-performance automatic micropore analyzer, and a SmartVacPrep degassing unit (Micromeritics, USA) equipped with a forevacuum pump.

2.4 Methods

In addition to porometry methods (microscopic, porosimetric, and X-ray diffraction (XRD)), the method of creating a polymer matrix using polyvinyl alcohol (PVA) was used to prepare the modified sorbent. The sorption properties of the sorbents in relation to mineralized waters were determined by the dynamic method. Studies were performed on test solutions with an initial mineralization of 5 g/L, pH = 7, T = 20 °C.

The pore structure of the samples was investigated using mercury porosimetry on a PoreMaster 60 instrument (Quantachrome Instruments, USA). Prior to analysis, the samples were dried at 105 °C for 4 hours to remove residual moisture. The mass of the analyzed samples ranged from 0.5 to 1.0 g.

Measurements were carried out in a pressure range of 0.1–60,000 psi (0.7–413 MPa), which allowed the determination of pore-size distribution in the range of 0.006–950 μm. The pore size was calculated using the Washburn equation, assuming a mercury surface tension of 0.485 N/m and a contact angle of 140°.

As a result of the analysis, the following pore-structure parameters were determined: specific surface area, total pore volume, pore-size distribution, and average pore radius.

All measurements were performed in at least three parallel experiments, and the results were averaged.

2.5 Stages of research on sorbent properties

After extracting opoka and bentonite clay samples from the deposit, electron microscopy of macropores was performed to obtain micrographs to identify their general pattern and model their structure. Next, mercury porometry based on capillary phenomena was applied to study the size distribution of opoka pores by forcing mercury into the pores. Liquid mercury did not wet the investigated material and hardly interacted with it. Each pressure level corresponds to a certain volume of mercury pressed into the pores of a certain radius. By increasing the pressure and simultaneously measuring the volume of mercury pressed into the pores, an integral curve of the distribution of specific pore volume by pore diameters was plotted, and the porosity and specific surface area were determined. Next, XRD was applied as a reliable method of identification of crystalline phases to determine the mineral composition of the samples. The subsequent stage of the study was to investigate the composition of the opoka-bentonite system to create the modified sorbent.

2.6 Stages of preparing the modified sorbent

To prepare the modified sorbent, opoka and bentonite clay samples were first dried in a drying oven at 80-95 °C to a residual moisture content of 5-7%. The samples were then ground in a porcelain ball mill until they passed completely through a 0.14 mm sieve. The obtained opoka and bentonite clay powders were purified with distilled water by soaking until the complete removal of soluble salts. The purified powders were dried again at 80-95 °C to a residual moisture content of 5-7% and then subjected to thermal modification at 500 °C. These technological modification solutions are consistent with prior research connected with the development of sorbents for water purification [43, 44].

The grinding of the raw materials (opoka and bentonite clay) was carried out in a laboratory porcelain ball mill for 60 minutes to obtain a homogeneous powder. The milling duration was selected to ensure a uniform particle size distribution and to increase the specific surface area of the particles. After grinding, the material was sieved through a 0.14 mm mesh to obtain a fraction with a consistent granulometric composition for further analysis.

The milling time was controlled to ensure complete passage of the material through the 0.14 mm sieve. The obtained powders were then subjected to dry sieving using a laboratory vibrating sieve with the same mesh size (0.14 mm) for 10 minutes, which ensured the removal of larger particles and the formation of a uniformly dispersed fraction.

This procedure provided a consistent granulometric composition of the raw materials, which is essential for the reliable comparison of the structural and sorption properties of the samples. Particles that did not pass through the sieve were returned for re-grinding.

The purification of opoka and bentonite powders from soluble salts was carried out by repeated soaking and washing with distilled water. The completeness of salt removal was controlled by measuring the electrical conductivity of the wash water.

The washing process was continued until the conductivity of the wash water approached that of distilled water (no more than 5–10 μS/cm), indicating the near-complete removal of soluble salts. After washing, the samples were dried again at 80–95 °C to a residual moisture content of 5–7%.

Each washing step was accompanied by stirring the suspension for 20–30 minutes.

The thermal modification temperature of 500 °C was selected based on literature data and the mineralogical characteristics of the materials. It is known that in the temperature range of 400–600 °C, the removal of adsorbed and interlayer water from clay minerals occurs, along with partial dehydroxylation of montmorillonite, which leads to an increase in specific surface area and the development of pore structure.

At this temperature, activation of the aluminosilicate surface takes place, resulting in the formation of additional active adsorption sites, while the siliceous framework of opoka is preserved without significant sintering. Therefore, a temperature of 500 °C provides optimal conditions for thermal activation of the composite material and enhancement of its sorption properties.

The selection of sample preparation conditions, including mechanical grinding, washing with distilled water, and subsequent thermal modification, was based on both literature analysis [43, 44] and the results of preliminary laboratory experiments.

According to the literature, these treatment methods contribute to an increase in specific surface area, removal of soluble impurities, and the formation of a well-developed pore structure in aluminosilicate materials. At the same time, the specific preparation parameters were refined through preliminary experiments conducted by the authors to ensure a uniform granulometric composition, effective removal of soluble salts, and improved sorption properties of the resulting materials.

The preliminary experiments demonstrated that the selected preparation conditions provide the formation of a highly developed pore structure and stable sorption properties of the composite material.

Next, we proceeded to the creation of a polymer matrix using PVA. A hydrogel was prepared based on PVA by boiling in distilled water. As a water-soluble synthetic polymer, PVA forms a stable and crystallizable hydrogel. PVA-based hydrogel has high mechanical strength and biocompatibility and is viscoelastic, non-toxic, and cost-effective.

PVA was used as a polymer binder to ensure the formation of a mechanically stable granulated structure of the sorbent and to improve the water resistance of the granules during filtration.

A 5% aqueous PVA solution was used to prepare the hydrogel, obtained by dissolving PVA in distilled water under heating with continuous stirring until complete dissolution of the polymer.

The resulting PVA solution was added to the mineral mixture (opoka–bentonite) in an amount of 8–10 wt% relative to the mass of the dry mineral mixture. The use of the polymer binder in this proportion ensured the formation of strong sorbent granules and prevented their destruction during water filtration.

The incorporation of PVA makes it possible to form a polymer–mineral matrix that stabilizes the pore structure of the sorbent and improves its mechanical stability.

Following this, four formulations (Table 4) of granulated modified sorbent with particle sizes of 1-2 mm and 3-5 mm were prepared from the thermally modified powders using the PVA-based hydrogel.

The resulting modified sorbent has 100% water resistance, which guarantees that it can filter water without degradation (Figure 1).

To determine the optimal composition of sorbents, micro- and mesopore studies were conducted using a 3Flex micropore physisorption and chemisorption analyzer.

All samples were pre-degassed on a SmartVacPrep unit before measurement. The degassing conditions were as follows:

Temperature 1 — 90 °C, time — 60 min;

Temperature 2 — 200 °C, time — 720 min, pressure — < 0.02 mmHg

After degassing with SmartVacPrep, the samples were weighed to account for mass loss. For subsequent filtering, the samples were also degassed using the 3Flex unit under the following conditions: Temperature — 200 °C, time — 300 min; pressure — < 0.0006 mmHg.

Point counting started from a value of 1×10^{-7} p/p0 and ended at p/p0 = 0.995. Free space or void volume was measured after helium-based analysis to prevent the micropores from filling with helium prematurely. All samples were first degassed for 60 minutes. Pore volume was calculated using both the isotherm curve (the Gurvich rule) and the desorption curve (the BJH method).

Figure 1. General appearance of the obtained modified sorbents in the opoka-bentonite composition

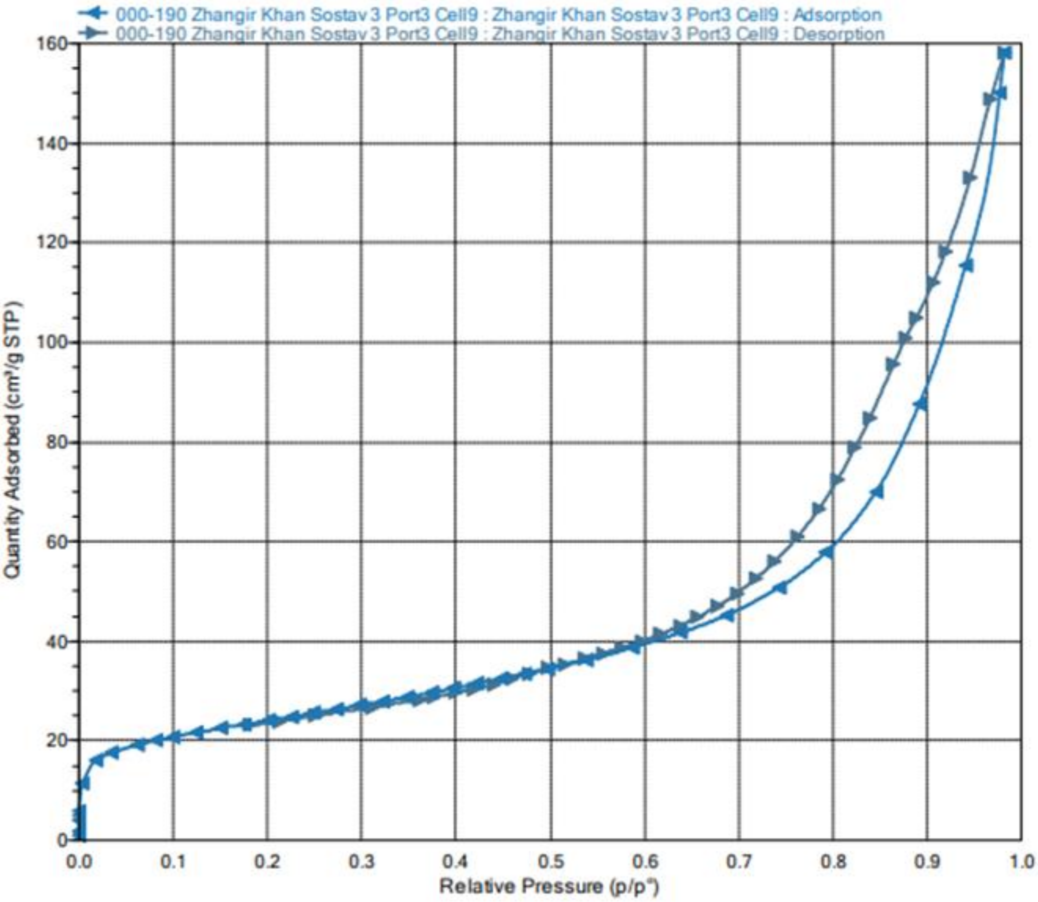


Figure 2. Adsorption–desorption isotherm for Composition 3 of the modified sorbent (90% opoka, 10% bentonite)

The isotherm corresponds to Type II according to the IUPAC classification and exhibits an H3-type hysteresis loop, indicating the presence of a mesoporous structure with slit-shaped pores (Figure 2).

The next stage of work on obtaining the sorbent was to study the technological parameters of the selected raw material, such as its sorption properties, hydrodynamic modes of operation, sorption capacity, etc.

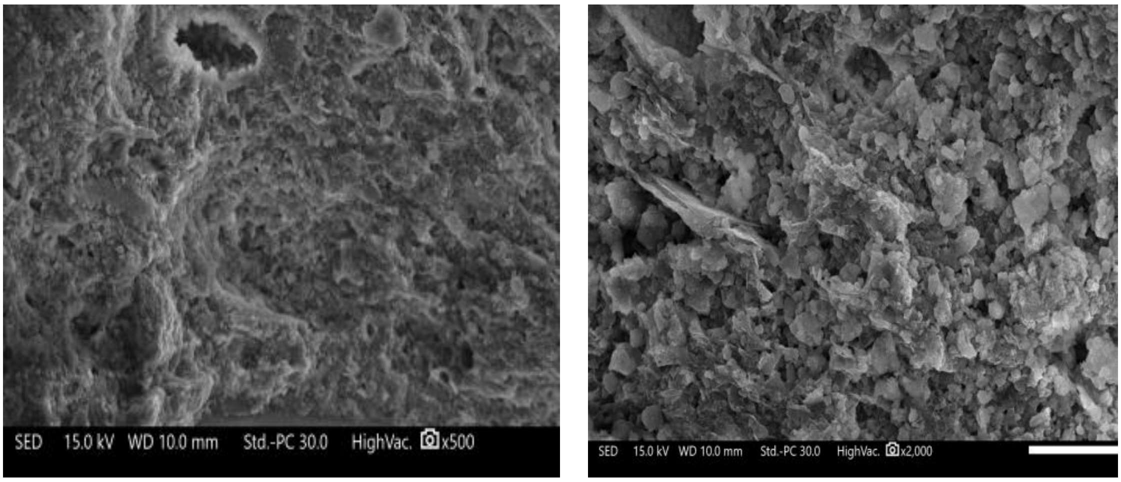
The test solution was passed through an adsorption column with the sorbent (20 g). The particle sizes of the sorbents used were 1-2 mm and 3-5 mm.

Since groundwater used for agriculture experiences temperature changes depending on climatic and seasonal conditions, at the final stage of the study of the properties of modified sorbents, we investigated the effect of water temperature on the filtering parameters.

3. RESULTS AND DISCUSSION

Macrostructure analysis shows that the studied opoka mainly consists of amorphous silica particles cemented by finely dispersed porous particles. Furthermore, the analyzed opoka consists of a mass of sponge skipulae and calcified opal flaps of diatom algae and their fragments. Clay particles and organic remains were also found. Under the microscope, the sponge skipulae, the calcified opal flaps of diatoms and their fragments, and their porous structure were clearly visible (Figure 3).

The studied opoka has high porosity and, in the natural state (43-47%), relatively low average density in the range of 1,200-1,350 kg/m^3 and is distinguished by great water holding capacity and high hydraulic and sorption activity.



(a) (b)

Figure 3. Porous structure of opoka from the West Kazakhstan deposit: (a) magnification 500×, (b) magnification 2,000×
SEM images acquired using a JEOL JSM-IT200 scanning electron microscope.

Research found that opoka has high sorption capacity for ammonium, potassium, rubidium, cesium, iron, cobalt, nickel, manganese (II), chromium (III), zinc, cadmium, lead, mercury, copper, alkaline-earth and rare-earth elements, and a wide range of organic substances [45].

The second object of our research was to create the modified sorbent, bentonite clay. Scientific and experimental studies established that the clay is highly plastic, "greasy" to the touch, and notable for its good water holding capacity and high hydraulic and adsorption activity [46].

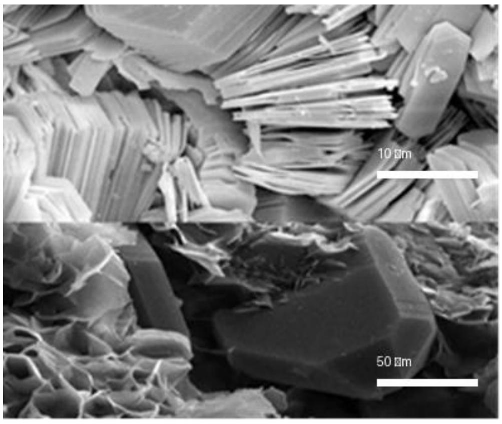


Figure 4. Microscopic image of montmorillonite mineral in the structure of bentonite clay from the Pogodaevsky deposit (magnification 5,000×)

XRD results show that the mineralogical composition of bentonite clay from the Pogadaevsky deposit is dominated by montmorillonite d/n=5.06; 4.46; 3.79; 3.06; 2.45; 2.28; 2.12; 1.97; 1.81; 1.67 Å (Figure 4).

In addition, the clay contained quartz (SiO_2) d/n =4.24; 3.34; 2.45; 2.28; 2.12; 1.98; 1.81; 1.66; 1.33 Å, hematite (Fe_2O_3) d/n= 2.69; 1.83; 1.68; 1.59 Å, and hydrous mica d/n= 3.21; 2.57; 2.12; 1.49 Å.

This clay was chosen because of the basic physicochemical properties of montmorillonite, such as high adsorption capacity, high concentration of exchangeable cations, enveloping capacity, high plasticity, hydrophilicity, and alkalinity, which are owed to its crystal lattice structure, large specific surface area of the particles, and electrokinetic potential. This clay belongs to 2:1 layered nanosilicates with a swelling crystal lattice, where each elementary cell has a width of 0.94 nm [41, 47].

Micropores and transitional pores play the leading role in the sorption process, defining the technical value and applications of the sorbent. The pattern of the porous structure of adsorbents determines their specific surface area, which dictates the amount of adsorbed substance and is used to calculate adsorption, work, and the heat of adsorption and wetting per unit surface area. The total porosity estimation is derived from the total pore volume of the sorbent. Given that the porosity of sorbents results from the presence of pores with different radius sizes, there is an objective need to study the porous structure of the studied sorbent compositions [48]. The results of this study are presented in Table 5.

Table 5. Parameters of the micro- and mesopores of the studied modified sorbent compositions

Pore Parameter	Composition 1 80% Opoka, 20% Bentonite Clay	Composition 2 85% Opoka, 15% Bentonite Clay	Composition 3 90% Opoka, 10% Bentonite Clay	Composition 4 95% Opoka, 5% Bentonite Clay
Specific surface area of mesopores, m^2/g	82.3	83.2	85.8	79.2
Average width of mesopores, nm	12.5	12.7	12.8	12.9
Specific surface area of micropores, m^2/g	11.2	10.4	12.1	8.5
Volume of micropores, cm^3	0.011	0.012	0.015	0.010
Total pore volume, cm^3	0.19	0.21	0.25	0.15

The results suggest that all isotherms belong to type II, which is characteristic of porous materials and suggests the presence of meso- and micropores above 100 angstroms, and show H3-type hysteresis loops, observed in non-rigid aggregates of plate-like particles forming slit-like pores.

The pore structure is predominantly governed by the mesoporous region, with a maximum in the distribution at around 100 Å (≈10 nm), confirming the predominance of mesopores (Figures 5 and 6).

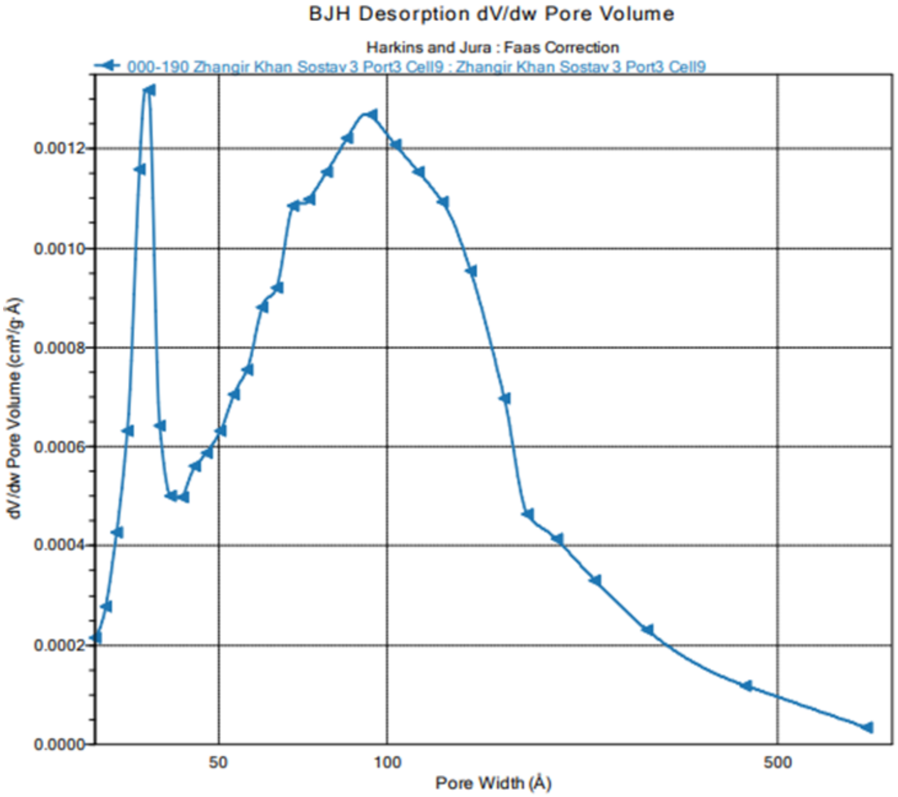


Figure 5. Pore-size distribution for Composition 3 calculated using the BJH method from the desorption branch

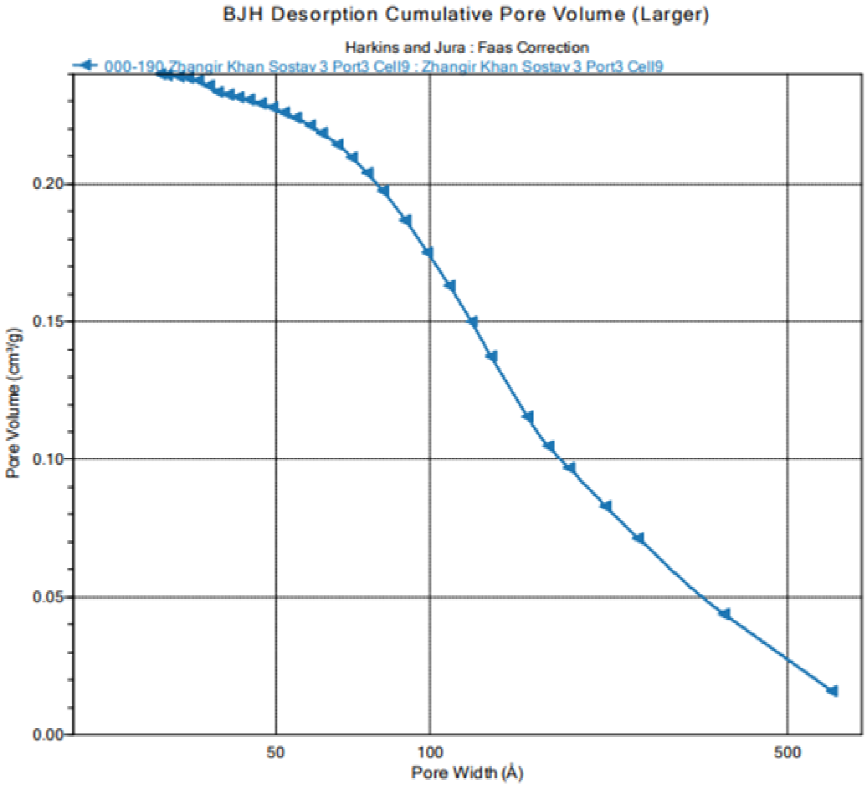


Figure 6. Cumulative pore volume distribution for Composition 3 (90 wt% opoka, 10 wt% bentonite clay), calculated using the BJH method from the desorption branch of the N_2 adsorption–desorption isotherm

Based on the data, we can conclude that the samples predominantly have meso- and micropores. All samples have a specific surface area close to 80 m^2/g and are characterized by the predominance of micro- and mesopores with a radius larger than 12 nm and a total pore volume around 0.2 cm^3/g.

The best characteristics of micro- and mesopores are observed in sorbent compositions confined to the following concentrations of components, in mass %: 80-90% opoka, 10-20% bentonite clay. Accordingly, further studies were carried out using these sorbent compositions.

The study of the sorption of test solutions by the investigated material shows that the degree of purification varies depending on specific water consumption.

The fractions of the studied sorbents used in the experiment are listed in Table 6. Sorbent particle sizes were selected based on the results of preliminary laboratory tests. The results of these experimental studies are presented in Table 6.

Table 6. Dependence of the residual mineralization of test solutions as a function of their specific consumption rate

Experiment	Water Flux, $m^3/(m^2 \cdot h)$	Residual Mineralization of Treated Water, g/L	
		Sorbent Particle Size 1-2 mm	Sorbent Particle Size 3-5 mm
1	0.5	2.2	4.1
2	1.0	2.22	4.12
3	1.5	2.28	4.17
4	2.0	2.31	4.20
5	2.5	2.34	4.22
6	3.0	2.36	4.25
7	3.5	2.39	4.28
8	4.0	2.43	4.30
9	4.5	2.46	4.33
10	5.0	2.48	4.36
11	5.5	2.49	4.37
12	6.0	2.51	4.39
13	6.5	2.53	4.59
14	7.0	2.54	4.60
15	7.5	2.56	4.63
16	8.0	2.58	4.64
17	8.5	2.59	4.66
18	9.0	2.61	4.69
19	9.5	2.61	4.70
20	10.0	2.62	4.72

The results demonstrate that smaller fractions of the opoka-bentonite sorbents increase the degree of desalination: filtration through a layer of sorbent with a particle size of 1-2 mm reduces mineralization to 2.2-2.62 g/L, and the particle size of 3-5 mm allows purification to 4.1-4.72 g/L with the same specific water consumption up to 7 $m^3/m^2 \cdot h$. In this case, the degree of purification (with a 150 mm layer) amounts to 47.6-56.0% with the particle size of 1-2 mm and 6.0-18.0% with 3-5 mm sorbent particles.

The reason behind the efficiency of purification with finer fractions is the following. The process of groundwater desalination using natural mineral raw materials relies on the absorption of dissolved mineral salts by the surface of opoka and bentonite clay grains. In this case, the finer the sorbent particles, the larger the interface area between the sorbent and the filtered water.

Due to the fact that different points on the mineral grain vary in hydrophilicity, the surface of the sorbent is a "mosaic", and mineral salts are retained in the places on the surface where the hydrophilic properties are weak and near which the hydration shell is minimal.

The theoretical and practical aspects of mesoporous structures of sorbents using finely dispersed bentonite particles in the composition of siliceous components to improve their sorption properties have been covered extensively [49-51].

The results on the influence of test water temperature on the sorptive desalination process (Table 7) demonstrate that the degree of desalination increases with lower water temperatures.

Table 7. The influence of water temperature on filtering parameters

Filtering Parameters	Particle Size, mm	Water Temperature, °C		
		50	40	20
Filter cycle duration, h	1-3	2.6	12.6	16.5
	3-5	3.4	13.7	17.1
Mineralization of treated water, g/L	1-3	2.52	2.43	2.22
	3-5	4.79	4.83	4.72

With a specific consumption of 5.0 $m^3/m^2 \cdot h$ and an initial salt content of test water equaling 5.0 g/L, the effect of filtering using the sorbent with a particle size of 1-3 mm amounts to 49.6% for test water at a temperature of 50 °C and to 55.6% for water at 20 °C.

Under the same conditions, the effect of purification with the sorbent with a particle size of 3-5 mm reaches only 4.2% for water at 50 °C and 5.6% for water at 20 °C.

This result can be explained by the fact that higher temperatures intensify such processes as dissociation and diffusion and facilitate the transfer of previously absorbed substances from the surface of the sorbent material to lower layers in the direction of the flow in the course of filtration [52-55].

Although this effect allows the entire volume of filter media to be more fully utilized, it also results in lower efficiency of purification [56].

Thus, the data show that at a specific consumption rate of test solutions equaling 2 $m^3/m^2 \cdot h$ and a water temperature of 20 °C, the mineralization of the filtrate drops from 2.20 mg/L to the concentration permissible for household drinking water. Even better results can be achieved by increasing the contact time of the treated water with the sorbent or by increasing the thickness of the sorption layer.

4. CONCLUSIONS

The results of the laboratory studies allow us to draw the following conclusions:

- Studies were carried out to examine the microstructure and chemical and mineralogical characteristics of two natural raw materials — opoka and bentonite clay from the West Kazakhstan deposit;
- Studies on the porous structure of different opoka-bentonite clay sorbent compositions have found that all samples had a specific surface area close to 80 m^2/g and were characterized by the predominance of micro- and mesopores with a radius larger than 12 nm and a total pore volume around 0.2 cm^3/g;
- The obtained isotherms were found to belong to type II, characteristic of porous materials, and suggest the presence of meso- and micropores above 100 angstroms, and the observed H3-type hysteresis loops can be found in non-rigid aggregates of plate-like particles forming slit-like pores;
- The best characteristics of micro- and mesopores were observed in sorbent compositions confined to the following concentrations of components, in wt%: 80-90 opoka and 10-20 bentonite clay.
- Studies on the patterns of changes in desalination efficiency depending on sorbent particle size established that the degree of purification is higher, the smaller the sorbent particle size. Specifically, the degree of purification of the sorbent with a particle size of 1-2 mm exceeded 50%, in

contrast to the particle size of 3-5 mm;

- Studies on the patterns of changes in desalination efficiency depending on water temperature showed that the degree of desalination increases with lower temperatures. With an initial test water salt content of 5.0 g/L, the effect of purification using the sorbent with a fraction size of 1-3 amounted to 49.6% at a water temperature of 50 °C compared to 55.6% at 20 °C.

The experimental studies have shown that the developed sorbents can be used in practice for the treatment of mineralized water, which is particularly important for Kazakhstan, where groundwater water has high salinity and cannot be used directly. The materials used (opoka and bentonite) are available in Kazakhstan and therefore do not require additional costs for transportation, and hence, the proposed sorbents are a financially favorable option for improving the quality of drinking water, where there is a shortage of fresh water.

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