Using the sorption properties of diatomite from the Aktobe deposit in improving the quality of drinking water in Western Kazakhstan

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Abstract. The paper describes the results of monitoring studies of the quality of tap water in the city of Uralsk. A solution was found to use natural reserves of the mineral diatomite in the purification of drinking water. The natural sorbent diatomite was modified with hydrochloric acid before testing. Natural and modified diatomite samples were studied using X-ray fluorescence analysis and electron microscopy. In acid-activated diatomite, the specific surface area and porosity increase by 2.5 times. X-ray fluorescence analysis of the elemental composition showed an increase in the silicon content in the sorbent. Organoleptic and physicochemical properties were studied in the original and diatomite-treated water: turbidity, taste, smell, color, hardness, permanganate oxidation, pH, iron and copper ions. The efficiency of sorption with respect to heavy metals was tested using the model toxicant copper sulfate. Determinations of copper and iron ions were carried out using the atomic spectrometry method. Hardness, permanganate oxidation, pH and organoleptic parameters were determined by standard methods. Treatment of water with natural and modified diatomite made it possible to significantly reduce water pollution according to the studied parameters. Filtering water with a modified diatomite sorbent allows you not only to purify water from unwanted impurities, but also to adjust its salt composition due to the intake of silicon. Based on the results of the work, we can conclude that, compared to natural, modified diatomite has higher adsorption properties in relation to copper and iron cations, increases pH, and also contributes to more effective water purification from unwanted impurities.

1 Introduction

The large natural reserve of diatomite and its unique sorption properties fully make it possible to provide the region with high-quality drinking water.

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Currently, heavy metals such as copper, cadmium and zinc are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. The high adsorption capacity of diatomite makes it a fairly cheap material for removing various heavy metals from aqueous solutions [1]. Diatomite has a number of unique physical properties and is widely used as an adsorbent in wastewater treatment [2].

The sorption activity of diatomite is due to the interaction of hydroxyl groups of the clay mineral with lead cations. The absorption capacity of diatomite is related to the reactive activity of silane groups and their quantity. This is determined by the degree of hydration of silicon dioxide. Chemical modification of the sorbent surface makes it possible to increase the sorption characteristics of diatomite [3]. It was found that its efficiency in removing arsenic, ammonia nitrogen and phosphates from wastewater was low and remained unsatisfactory even when the dose of natural sorbent was increased to 500 mg/l. When using modified diatomite, the removal efficiency of all target components was increased by 20-50% [4]. Heavy metal contamination of water is a global problem that requires an inexpensive and simple solution. In this context, the unique properties of diatomite and its abundance in many regions of the world have led to the current widespread interest in this material for water purification purposes [5]. Diatomite is a siliceous sedimentary rock consisting of an amorphous form of silica ($SiO_2 \cdot nH_2O$) containing small amounts of microcrystalline material. It has a unique combination of physical and chemical properties such as high porosity, high permeability, small particle size, large surface area and low thermal conductivity. Thanks to these properties, diatomite is successfully used for the purification of drinking water, industrial and sewage waste [6-7]. It has been established that diatomite is a mesoporous sorbent. The permeability of diatomite can be increased by granulating the rock [8]. The use of natural minerals for wastewater treatment is acceptable from environmental and economic points of view, but often such materials do not have the necessary sorption properties and require modification [9]. During the acid modification process, SiO_2 gel powder was partially adsorbed in pure diatomite, blocking macropores and large mesopores of diatomite, which led to a significant increase in the specific surface area and SiO_2 content in diatomite [10]. The adsorption effect of Cr(VI) on acid-modified diatomite was better than that on the original diatomite [11]. The ability to adsorb fluorine in the acid-activated form is higher than that of natural forms of adsorbents [12]. Treatment of diatomite with sulfuric acid improves its characteristics as a phenol adsorbent, and also increases the adsorption capacity after chemical treatment [13]. There are quite a few different methods for treating industrial wastewater, but the most promising are methods based on the use of natural minerals as adsorbents [14]. Diatomite can effectively adsorb organic pollutants in water, so it can be used as an industrial water purifier [15]. Analysis of data on the use of the sorption qualities of the natural mineral diatomite showed the need for further research in the direction of finding effective ways to purify drinking water.

2 Materials and methods

The natural mineral diatomite from the Aktobe deposit was chosen as the objects of study. The efficiency of mineral sorption was determined by passing solutions of tap water from the city of Uralsk through filters with modified and natural diatomite. Organoleptic and physicochemical indicators such as hardness, permanganate oxidation, pH, color, turbidity, odor, taste, as well as mass concentrations of copper and iron were determined in the original water and water passed through diatomite filters. Organoleptic indicators were determined according to the generally accepted method (Drinking water. Methods for determining taste, smell, color and turbidity. GOST 3351-74). Water hardness was determined by the complexometric method (Drinking water. Methods for determining hardness. ST RK 1514-2006). pH was determined by the potentiometric method (Water quality. Methods for determining pH. ST RK ISO 10523 - 2013). The permanganate number was determined by the titrometric method (Water quality. Determination of permanganate number. ST RK 1498-2006). The content of copper and iron ions in the studied water samples was determined by atomic spectrometry (Drinking water. Determination of element content by atomic spectrometry methods. ST RK GOST R 51309-2003). Copper ions were chosen as model heavy metals. Model copper solutions were prepared by adding 1 molar solution of copper sulfate to distilled water to obtain the corresponding concentrations: 0.5; 1.0; 5. The natural sorbent was pre-crushed on inertial cone crushers. Sorbents of the required fraction were obtained by sifting out mineral particles on screens. The resulting consistency of diatomite was placed in a column with polypropylene spacers. This column was subsequently used to pass the test water. Modification of diatomite with hydrochloric acid was carried out by heating in a water bath for 4 hours. After chemical activation, the adsorbent was thoroughly washed with distilled water to neutral pH and dried at a temperature of 1000 C. The physicochemical characteristics of the resulting sorbent were studied by electron microscopy and X-ray fluorescence analysis (XRF, FOCUS-M2).

3 Results and Discussion

At the first stages of work, modification of diatomite was carried out. As a result of the process of activation of diatomite with hydrochloric acid, the chemical composition of diatomite changes, the porous structure and physicochemical properties improve (Table 1).

Table 1. Structural indicators of natural and activated diatomite.

Reagent	Specific surface area, m^2/g	Pore volume, cm^3/g
Natural diatomite	32.699	0.017
Modified diatomaceous earth	85.157	0.055

In the process of activation of natural diatomite with hydrochloric acid, the specific surface area of diatomite increases by 2.5 times: from 32.699 to 85.157 m^2/g, while the pore volume also increases significantly. Thus, by activating diatomite with an acidic reagent, we double its sorption characteristics.

X-ray fluorescence analysis of the chemical composition of diatomite showed a decrease in iron and an increase in silicon content (Table 2).

Table 2. Elemental composition of diatomite.

Element	Concentration		Radiation intensity	
	natural	activated	natural	activated
Fe	31.144	14.549	344.41	131.56
Si	26.002	48.042	1.01	1.35
Ca	0.337	0.433	4.57	5.55
Ti	0.925	2.427	5.85	11.24
Mn	0.232	0.067	2.26	0.55
K	17.360	6.247	25.52	5.61
Al	22.881	27.799	0.33	0.41
Sr	1.119	0.107	8.20	0.78

Analysis data show that natural diatomite contains predominant concentrations of iron, silicon and aluminum. The results of X-ray fluorescence analysis before and after modification of natural diatomite (Table 2.) showed an increase in silicon and aluminum from 26 mg/l and 22 mg/l to 48 mg/l and 27 mg/l, and a decrease in Fe concentration, from 31 mg/l to 14 mg/l. For both elements, the emission intensity increased after modification. This indicates an increase in the purity of the samples after modification. A decrease in the amount of certain elements as a result of the processes of their movement and dissolution in acid apparently increases the content of Si and Al.

Modification with hydrochloric acid can cause a chemical reaction with the mineral components of diatomite, changing its chemical composition and structure.

Organoleptic indicators, pH and hardness of tap water are signs of its suitability for consumption (Table 3).

Table 3. Organoleptic characteristics, pH and hardness of tap water.

Indicators	**Source water**	**Filter with natural diatomaceous earth**	**Activated diatomaceous earth filter**
Taste, score	3	1	0
Smell, score	3	0	0
Color,°	15	5	0
Turbidity, EM	3	1	0
pH	6.8	7.2	7.25
Water hardness (mg-eq/l)	5.34	3.48	2.28

According to the approved hygienic standards for safety indicators of household, drinking and cultural water use of the Republic of Kazakhstan, water turbidity should be within 3.5 mg/l, color in degrees should be 20, and taste and odor indicators should correspond to 2 points. Analysis of the organoleptic properties of water revealed the unsatisfactory condition of tap water in the city of Uralsk. In the water treatment facilities of the city of Uralsk, outdated treatment devices and reagent methods are used. This technology purifies water only from dispersed particles. Molecules and ions of many toxic substances are not captured by the system and remain in the water. In addition, existing treatment schemes are dangerous due to such water disinfection processes as the use of chlorine gas. When organic pollutants are present in water, highly toxic compounds appear. After passing tap water through a filter column with diatomaceous earth (flow rate 2-3 ml per minute), the organoleptic properties of water in all experimental variants improved significantly. Indicators of color and turbidity moved within normal limits, and the chlorine smell ceased to be felt. The pH of water when passed through a mineral sorbent increased slightly from 6.8 to 7.2. The water hardness in water treated with diatomite decreased from 5.34 to 2.28. The increase in OH groups in water is apparently due to the influence of oxygen on the dispersed surface of silicon. Modification of the natural mineral diatomite makes it possible to improve not only sorption characteristics, but also to adjust the salt composition of drinking water. It is known that silicon is involved in lipid metabolism, phosphorus metabolism, and also affects the calcium content in the body. With a lack of silicon, diseases such as rickets and malignant neoplasms can develop [16].

The excess of iron ions in tap water is a consequence of secondary pollution caused by wear and tear of distribution networks (Table 4).

Table 4. Content of iron ions in water (mg/l).

Source water	**Filter with natural diatomaceous earth**	**Activated diatomaceous earth filter**
0.7	0.25	0.11

Tap water was characterized by a high content of iron ions. The maximum permissible concentration of iron is 0.3 mg/m^3. A significant decrease in the concentration of iron ions was observed in water treated with the sorbent.

The maximum permissible concentration for copper ions is 1 mg/l, which makes it possible to select this heavy metal as a model toxicant (Table 5). It should be assumed that the effective sorption of copper is similar to the sorption of other heavy metals.

Table 5. Content of copper ions in model water (mg/l).

Source water	Filter with natural diatomaceous earth	Activated diatomaceous earth filter
0.48	0.10	0.05
0.92	0.28	0.12
4.65	0.78	0.72

Based on the data in Table 5, we see that the natural mineral sorbent diatomite effectively removes copper ions from water. The sorption values in the case of activated diatomaceous earth show greater purification efficiency values. In both values, it was possible to reduce the concentration of copper ions to an acceptable value. Changes in the content of metals in water treated with a natural mineral sorbent can be caused by structural changes in water molecules under the influence of silicon [17].

The permanganate oxidation indicator is used as one of the methods for determining organic water pollution. The permanganate number is an indicator of the presence of easily oxidized organic substances in water.

Table 6. Permanganate oxidation of tap water (mg O_2 /l).

Source water	Filter with natural diatomaceous earth	Activated diatomaceous earth filter
4.8	3.2	1.8

Treatment of water with natural and activated sorbent made it possible to significantly reduce the permanganate oxidation of water.

4 Conclusion

- The use of diatomite allows you to purify water from excess iron content. Acid-activated diatomaceous earth was superior in efficiency to the natural sorbent.
- Treatment with diatomaceous earth sorbent can improve the organoleptic characteristics of tap water: color, taste, aftertaste, turbidity.
- It should be noted that there is an increase in pH, a decrease in hardness and permanganate oxidation in tap water treated with diatomite.
- Modification with hydrochloric acid can cause a chemical reaction with the mineral components of diatomite, changing its chemical composition and structure.
- Modified diatomaceous earth can be successfully used not only in water treatment systems, but also in water conditioning.

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