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Industrial wastewater treatment from oil and petroleum products with carbonate sludge

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Abstract. In the modern world, pollution of industrial wastewater by oil and petroleum products is one of the most acute environmental problems. These pollutants have a significant negative impact on ecosystems and water quality. In this regard, there is a need to develop effective and environmentally safe methods of wastewater treatment. The aim of the study is to develop and evaluate the efficiency of using carbonate sludge as an adsorbent for removing oil and petroleum products from wastewater. The scientific and practical significance of the work lies in the proposal of an environmentally friendly treatment method that can not only improve the quality of wastewater, but also ensure the disposal of industrial waste. The use of carbonate sludge, a by-product of industry, makes the method cost-effective and reduces the environmental burden.

The main results of the study showed that carbonate sludge has a high sorption capacity for petroleum products. The adsorption isotherm belongs to type I according to the Brunauer, Deming, Deming and Teller classification, which indicates the presence of monolayer adsorption on the sludge surface. It was found that the sludge is able to remove up to 95% of pollutants from wastewater. The value of the study lies in demonstrating that carbonate sludge is an effective and affordable material for solving environmental problems associated with water pollution by petroleum products. This research contributes to the development of industrial waste recycling technologies by offering a new application for carbonate sludge. The practical significance of this work lies in the possibility of introducing this method at industrial enterprises for wastewater treatment, which can lead to a reduction in waste disposal costs and an improvement in the environmental situation. The results of the study can be useful for enterprises of the petrochemical industry and wastewater treatment plants.

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Introduction

Despite the fact that there are many reserves on the Earth's surface, most of the water reserves on Earth (approximately 0.03%) are water resources that are available for human activities. The growth of the world's population and industry generates an ever-increasing demand for water in proportion to the available sources, which remain unchanged. Thus, it is necessary to minimize its consumption, as well as return some of it to the environment with a minimal load of pollution due to the limited self-cleaning capacity, this shows the importance of the wastewater (WW) treatment process [1].

Industrial wastewater treatment from oil and petroleum products is one of the key environmental challenges facing industrial enterprises. Oil products entering aquatic ecosystems have a negative impact on living organisms, disrupt the processes of natural self-purification of water and lead to a significant decrease in water quality. One of the promising methods for solving this problem is the use of carbonate sludge for wastewater treatment.

There are various methods of wastewater treatment from oil pollution, among which physical and chemical methods (flotation, adsorption, coagulation, etc.), biological methods and membrane filtration methods are widely used. The use of carbonate sludge as an adsorbent is an effective method for removing oil and petroleum products, due to its high porosity and sorption properties.

Carbonate sludge formed as a result of water treatment at chemical industry enterprises has a high sorption activity due to the presence of hydrated oxides of calcium, magnesium and other minerals in its composition. These compounds form active centres on the surface of sludge particles that interact effectively with hydrocarbon molecules. The adsorption of petroleum products on the sludge surface occurs due to hydrophobic interactions, which contributes to wastewater treatment.

In practice, the use of carbonate sludge for wastewater treatment demonstrates high efficiency. Experimental studies have shown that carbonate sludge can remove up to 95% of petroleum products from wastewater, which makes it a promising material for use in industrial facilities. In particular, the introduction of this technology at a number of enterprises has significantly reduced the emissions of pollutants into the environment [2-5].

The aim of the study is to develop an effective method for cleaning industrial wastewater from oil and petroleum products using carbonate sludge, as well as to study its sorption properties in order to improve the environmental safety of industrial enterprises.

The relevance of the study is due to the serious environmental problem of water resources pollution by oil and petroleum products, which leads to ecosystem disruption and deterioration of water quality. Industrial enterprises, such as petrochemical plants and oil processing plants, generate significant volumes of wastewater containing petroleum products. In this regard, there is a need to develop effective and cost-effective methods for treating such waters. One of these methods is the use of carbonate sludge, which is industrial waste and has a high sorption capacity. Its use will not only improve the quality of wastewater treatment, but also solve the problem of industrial waste disposal, which makes the study particularly relevant in the context of the transition to sustainable technologies.

The object of the study is industrial wastewater contaminated with oil and petroleum products, as well as carbonate sludge used as a sorbent for cleaning these waters. Special

attention is paid to the study of the sorption characteristics of sludge and its ability to effectively remove hydrocarbons from the aquatic environment.

Materials and methods

1.1. Materials

1.1.1. Model solutions of oil-contaminated wastewater. A model solution with an Alibekmola oil field concentration of 10 mg /dm^3 is dissolved in distilled water in one step. Concentrations of oil and oil products in water were determined using the methods of Government Standards: GOST 31862-2012 and GOST R 51794-2001.

1.1.2. Carbonate sludge. Sludge of Chemical water treatment (CWT) is a waste that is formed at the water treatment plant of thermal power plants, at the stage of preliminary treatment of natural water. The dried sludge is a fine powder from light yellow to brown in colour [6-7]. In the course of the study, a fraction with a particle size of 0.05-0.09 mm was used.

1.2. Methods

1.2.1. Determination of oil and petroleum products in water by infrared spectrometry and according to GOST 31862-2012. Water is collected in glass or metal containers that exclude contact with organic solvents and other pollutants. For analysis, carbon tetrachloride is used as a solvent. Hydrocarbon compounds are extracted from the water sample. The resulting extract is examined on an infrared spectrometer. The concentration of petroleum products is determined by the absorption of infrared radiation in the range of 2930 cm^{-1} and 2960 cm^{-1}, characteristic of C-H bonds of hydrocarbons. The method allows detecting petroleum products in concentrations from 0.05 to 10 mg/l.

1.2.2. Determination of oil and petroleum products in water by gravimetric method according to GOST R 51794-2001. Water samples are taken in the same way, without contamination by organic substances. A solvent (hexane or chloroform) is used to extract hydrocarbons from an aqueous sample. The resulting extract is evaporated to a dry residue, and then the residue is weighed to an accuracy of 0.1 mg. This residue is petroleum products. The method allows the determination of petroleum products in concentrations from 0.5 to 500 mg / l.

1.2.3. Determination of the adsorption of oil and petroleum products by carbonate sludge. Adsorption of oil and oil products by sorbents is carried out under static conditions. The adsorption capacity of the material is studied at 293 K by the constant concentration and variable weighting method. For the experiment, take 7 conical flasks with a volume of 10 cm^3 of a model phenol solution at pH = 6.5-8.5 with a different sample of sorption material: 0.01 g; 0.05 g; 0.1 g; 0.5 g; 1 g; 1.5 g; 2 g. The solutions are mixed for 24 hours. Next, the sorption material is filtered with a paper filter from the model solution, and the content of oil and petroleum products in the filtrate is determined [6].

Adsorption value:

$$A = \frac{(C_{or} - C_o)}{m} \cdot V, \quad (1)$$

where A is the amount of phenol adsorption, mg/g; V – volume of the model solution, dm^3; m is the mass of the sorbent in the volume of the model solution, g; C_{or}, C_o – initial and equilibrium concentrations of oil and petroleum products in the model solution, mg/dm^3. To determine the adsorption value of the material, an adsorption isotherm is constructed.

Results and Discussion

Modified carbonate sludge of Aktobe CHP JSC is used as a sorption material for the application of technologies for cleaning industrial WW of industrial enterprises by adsorption. X-ray qualitative and phase analysis of the sludge on P8 ADVANCE diffractometer Bruker showed the composition of the carbonate sludge, which is presented in Table 1.

Table 1. Chemical composition of carbonate sludgeof Aktobe CHP JSC

Substance	Calcite $CaCO_3$	Brucite $Mg(OH)_2$	Portlandite $Ca(OH)_2$	Quartz SiO_2	Limonite $Fe(OH)_3$	Other substances
Mass fraction, %	75	4	0.5	0.1	6	14

The composition of the CWT sludge of Aktobe CHP JSC also contains organic substances up to 9%. For their determination, the method of chromatographic analysis on a chromato-mass spectrometer (Thermo Fisher Sci.Co, USA). The analysis shows the presence of functional groups of organic substances in the sludge, including carboxylic, nitro -, aromatic compounds, alcohol and alkyl groups. The presence of these groups in the sludge composition characterizes the high hydrophilic capacity of the material. To study the properties of carbonate sludge asan adsorption material, its technological characteristics of CVP carbonate sludge were studied, which are presented in Table 2.

Table 2. Technological characteristics of carbonate sludge of Aktobe CHP JSC

Parameter	Value
Bulk density p_n, kg/ m^3	510
Humidity, %	3.3
Water capacity, %	62
Granulometric composition, % 1.4 mm 1.4-1.0 mm 0.5-1.0 mm 0.09-0.5 mm 0.09 mm	 32 7 8.1 57.2 7.4
Ash content, %	84
pH	7.3
Organic substances, %	8.4
Total pore volume,cm^3/ g	0.255

Carbonate sludge, having a high ash content, porosity and fine structure, shows good prospects as an adsorbent for wastewater treatment from petroleum products. The neutral pH value and high water capacity add additional value to the sludge for its industrial applications [7].

An experiment to study the process of adsorption of oil and petroleum products by carbonate sludge is carried out in a static mode. To obtain experimental data, 7 conical flasks were taken with a model solution of oil and petroleum products (concentration 10 mg/dm^3)

with a different weight of carbonate sludge, g: 0,01; 0,05; 0,1; 0,5; 1; 1,5; 2. Based on the results obtained, an adsorption is other is constructed (Figure 1).

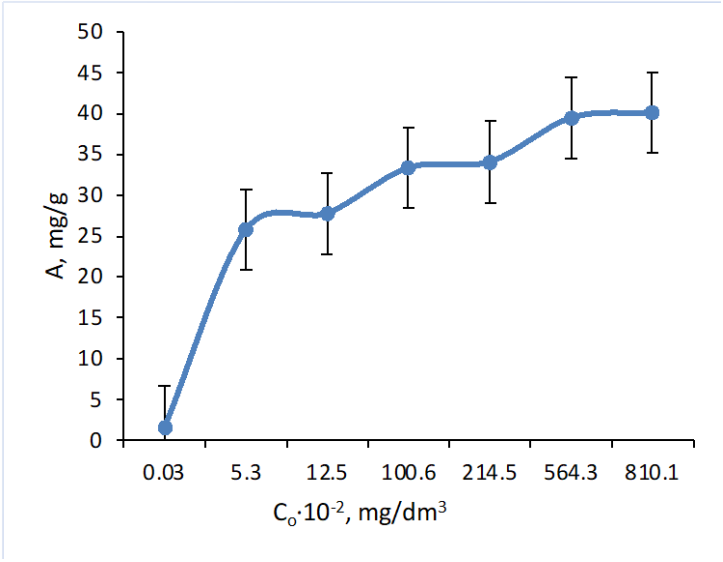

Figure 1. Isotherm of oil and oil products adsorption by carbonate sludge

The adsorption isotherm belongs to type I according to the Brunauer, Deming, Deming and Teller classification (BDDT), a similar type of isotherm characterizes adsorption on microporous materials characterizes the physical adsorption of gases or liquids on porous solids with a microporous structure. This isotherm is a classic one for adsorbents with limited pore capacity, such as activated carbon or carbonate materials.

For carbonate sludge, if its adsorption isotherm is of type I, this means that when it comes into contact with oil or petroleum products, adsorption occurs within one layer until all available pores are saturated. This also indicates that the sludge has a limited pore volume, which affects its sorption capacity. Thus, the Type I isotherm according to the BDT classification indicates that carbonate sludge is able to effectively adsorb petroleum products, but the sorption volume will be limited by the pore structure and the capacity of active centres on its surface.

Conclusion

The study confirmed that carbonate sludge is an effective sorbent for wastewater treatment from oil and petroleum products. Due to its physical and chemical characteristics, such as high ash content (84%) and a significant pore volume (0.255 cm^3/g), the sludge is able to adsorb a significant amount of hydrocarbons from the aquatic environment.

The adsorption of petroleum products on carbonate sludge occurs due to physical adsorption, which is confirmed by the type I isotherm form according to the Brunauer, Deming, Deming and Teller classification (BDDT). Adsorption is limited by the presence of micropores and active centres on the sludge surface, which makes it promising for water treatment with low and medium concentrations of pollutants.

The use of carbonate sludge, which is a by-product of industrial production, allows not only to effectively clean wastewater from petroleum products, but also to solve the problem of waste disposal. This makes the process both environmentally friendly and cost-effective, reducing the cost of producing new sorbents and reducing environmental pollution.

The use of carbonate sludge in real industrial facilities has demonstrated high efficiency of wastewater treatment, removing up to 95% of petroleum products. This allows us to recommend it for wide application in water treatment systems at oil refining enterprises and other industries related to petroleum products.

In the course of the work, it was found that further improvement of the method using carbonate sludge is possible by optimizing the adsorption parameters, such as sludge dosage, temperature and pressure conditions. It also requires research on the durability and regeneration of the sorbent for reuse, which will make the cleaning process even more efficient and cost-effective.

Thus, carbonate sludge has a significant potential as a sorbent for wastewater treatment from petroleum products and can make a significant contribution to solving environmental problems related to water pollution.

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Contributions of the authors: Beskuzov N.B.- performing chemical analyses, collecting and interpreting work results. Aikenova N.E. - writing the text, a significant contribution to the concept and design of the work.

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Өнеркәсіптік ағынды суларды мұнай мен мұнай өнімдерінен карбонатты шламмен тазарту

Аңдатпа. Қазіргі әлемде өнеркәсіптік ағынды сулардың мұнаймен және мұнай өнімдерімен ластануы экологиялық проблемалардың бірі болып табылады. Бұл ластаушы заттар экожүйелер мен су ресурстарының сапасына айтарлықтай теріс әсер етеді. Осыған байланысты ағынды суларды тазартудың тиімді және экологиялық таза әдістерін жасау қажеттілігі туындайды. Зерттеудің мақсаты-карбонатты шламды ағынды сулардан мұнай мен мұнай өнімдерін кетіру үшін адсорбент ретінде пайдалану тиімділігін әзірлеу және бағалау. Жұмыстың ғылыми және практикалық маңыздылығы ағынды сулардың сапасын жақсартып қана қоймай, сонымен қатар өндірістік қалдықтарды жоюды қамтамасыз ететін экологиялық таза тазарту әдісін ұсыну болып табылады. Өнеркәсіптің жанама өнімі болып табылатын карбонатты шламды пайдалану әдісті үнемді етеді және экологиялық жүктемені азайтады. Зерттеудің негізгі нәтижелері карбонатты шламның мұнай өнімдеріне жоғары сорбциялық қабілеті бар екенін көрсетті. Адсорбция изотермасы Брунауэр, Деминг, Деминг және Теллер классификациясы бойынша I типке жатады, бұл шлам бетінде моноқабатты адсорбцияның болуын көрсетеді. Шлам ағынды сулардан ластанудың 95% - на дейін кетіруге қабілетті екендігі анықталды. Зерттеудің құндылығы карбонатты шлам судың мұнай өнімдерімен ластануына байланысты экологиялық мәселелерді шешу үшін тиімді және қолжетімді материал екенін көрсету болып табылады. Бұл зерттеу карбонатты шламға жаңа қолдануды ұсына отырып, өнеркәсіптік қалдықтарды қайта өңдеу технологияларын дамытуға ықпал етеді. Жұмыстың практикалық маңыздылығы ағынды суларды тазарту үшін өнеркәсіптік кәсіпорындарда осы әдісті енгізу мүмкіндігі болып табылады, бұл қалдықтарды кәдеге жарату шығындарының төмендеуіне және экологиялық жағдайдың жақсаруына әкелуі мүмкін. Зерттеу нәтижелері мұнай-химия өнеркәсібі кәсіпорындары мен ағынды суларды тазарту қондырғылары үшін пайдалы болуы мүмкін.

Түйін сөздер: адсорбция, ағынды сулар, адсорбенттер, карбонатты шлам, суды тазарту, мұнай және мұнай өнімдері.

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Очистка промышленных сточных вод от нефти и нефтепродуктов карбонатным шламом

Аннотация. В современном мире загрязнение промышленных сточных вод нефтью и нефтепродуктами является одной из наиболее острых экологических проблем. Эти загрязнители оказывают значительное негативное воздействие на экосистемы и качество водных ресурсов. В связи с этим возникает необходимость разработки эффективных и экологически безопасных методов очистки сточных вод. Целью исследования является разработка и оценка эффективности использования карбонатного шлама как адсорбента для удаления нефти и нефтепродуктов из сточных вод. Научная и практическая значимость работы заключается в предложении экологически безопасного метода очистки, который может не только улучшить качество сточных вод, но и обеспечить утилизацию промышленных отходов. Использование карбонатного шлама, побочного продукта промышленности, делает метод экономически выгодным и снижает экологическую нагрузку.

Основные результаты исследования показали, что карбонатный шлам обладает высокой сорбционной способностью к нефтепродуктам. Изотерма адсорбции относится к I типу по

классификации Брунауэра, Деминга, Деминга и Теллера, что свидетельствует о наличии монослойной адсорбции на поверхности шлама. Было установлено, что шлам способен удалять до 95% загрязнений из сточных вод. Ценность исследования заключается в демонстрации того, что карбонатный шлам является эффективным и доступным материалом для решения экологических проблем, связанных с загрязнением вод нефтепродуктами. Это исследование вносит вклад в развитие технологий вторичного использования промышленных отходов, предлагая новое применение для карбонатного шлама. Практическое значение работы

заключается в возможности внедрения данного метода на промышленных предприятиях для очистки сточных вод, что может привести к снижению затрат на утилизацию отходов и улучшению экологической обстановки. Результаты исследования могут быть полезны для предприятий нефтехимической отрасли и очистных сооружений.

Ключевые слова: адсорбция, сточные воды, адсорбенты, карбонатный шлам, очистка вод, нефть и нефтепродукты.

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