

## STUDY OF ADSORPTION OF Zn<sup>2+</sup> ION ON CLAY ADSORBENTS

**Tohirbek IBRAGIMOV,**

*Independent researcher of the Tashkent Institute of Chemical Technology*

*E-mail: [tohirbekibragimov566@gmail.com](mailto:tohirbekibragimov566@gmail.com)*

*Tel: (95) 212 17 58*

**Xabiba TALIPOVA,**

*Tashkent Institute of Chemical Technology associate professor, k.f.n*

*E-mail: [talipova\\_khabiba65@gmail.com](mailto:talipova_khabiba65@gmail.com)*

*Tel: (93) 003 52 69*

**Oxunjon TANIYEV**

*Assistant teacher of the Tashkent Institute of Chemical Technology*

*E-mail: [oxunjontanitev@gmail.com](mailto:oxunjontanitev@gmail.com)*

*Tel: (99) 12127 55*

**Abstract** This paper presents the removal of Zn<sup>2+</sup> ion from polluted water by natural Angren kaolin clay (AK-clay). It was characterized using infrared spectroscopy (FTIR) method. Parameters investigated include pH, adsorbent particle size, agitation rate, metal ion concentration, and optical density. Optimal conditions were used for modified samples. Design-expert software was used to design experimental conditions using Response Surface Methodology (RSM). Mineralogical characterization showed a fraction of 63 μm treated as kaolin of the wastewater. Analysis of variance indicated that metal ion adsorption was statistically significant when p-values > 0.0001 at the 95% confidence limit. Thermodynamic analysis of adsorption data shows that the adsorption of metal ions is spontaneous, endothermic and accompanied by a positive entropy change. Compared with the unmodified natural wastewater, the adsorption capacity for Zn<sup>2+</sup> ions increased from 14.1 to 18.425 mg/g, the results indicate that it is effective for the treatment of wastewater loaded with heavy metals.

**Keywords:** Angren kaolin, zinc sulfate, diphenylcarboside, ethyl alcohol, phosphoric acid, sulfuric acid, , adsorption isotherms.

**Enter.** Due to the increasing demand for high-quality and cheap adsorbents in the chemical, food and other sectors of our developing industry today, using local raw

materials and creating new types of effective adsorbents based on them remains one of the important tasks. Kaolin deposits are known to exist in many regions of Uzbekistan, especially in Angren, and they are used for various purposes today. Angren kaolin mine is the largest kaolin mine in Uzbekistan and has been mined for more than 50 years. Kaolin is a white-brown clay, mainly composed of kaolinite. Kaolin located near the surface of the earth is mined in an open-pit method, and then enriched. Kaolin belongs to the group of silicates, and it is currently used mainly in the paper, porcelain, earthenware, chemical, rubber industries, in the production of refractory products and insulators.

As we know, kaolin is used as a suspension in oil and gas industry, as a suspension in drilling operations, in the purification of wastewater from heavy metals, as an adsorbent and raw material in the production of porcelain and a number of other industries. Scientifically and practically positive results are being achieved in our republic in obtaining selective clay adsorbents with different properties based on local kaolin and bentonites, using them in various industries, in particular in wastewater treatment. In this direction, methods of synthesis of sorbents resistant to temperature and chemical effects from modified local kaolin and bentonite minerals have been developed. Significant progress in the study of their structure, physical-colloidal properties and implementation in production industries, including the creation of organophilic nanoporous adsorbents based on bentonites and changes in their adsorption capacity due to the nature of their porosity; Researching the mechanisms of interaction between adsorbent-adsorbate is of great importance in solving theoretical and practical problems of physico-colloid chemistry.

Kaolin mineral is an aluminum silicate, which can be represented by the general formula  $(OH)_8Si_4Al_4O_{10}$ . The present composition of pure kaolin is expressed as oxides. In fact, commercial kaolins differ slightly from the above analysis, because the presence of additional minerals in the crystal lattice leads to a deterioration of the expected properties. It should be noted that up to now there have not been enough scientific studies on obtaining new types of clay adsorbents with high sorption capacity

from kaolin and bentonite, which are considered local raw materials, and researching their adsorption properties. In this scientific research, the creation of activated, organophilic, nanoporous and environmentally safe selective adsorbents based on kaolin and bentonites, which are local raw materials, the study of their sorption properties and their practical application, as well as theoretical and practical results as import substitute adsorbents. will be important to achieve. In such cases, kaolin is usually activated with predetermined properties.

**Analysis of literature on the topic.** This article aims to determine the amount of chromium in potassium bichromate. The release of heavy metal-laden industrial wastewater into the environment without proper treatment has negative effects on aquatic animals, the environment, and humans. Heavy metals are dangerous for the environment because they are toxic and do not decompose easily. Metals such as iron, lead, chromium and zinc that accumulate through the food chain are associated with health problems. For example, hypertension, lethargy, neoplasia and neurological diseases can be caused by excessive accumulation of iron. High levels of lead cause poisoning with brain damage, kidney, liver and central nervous system dysfunction. High concentrations of zinc cause health problems such as anemia, gastrointestinal upset, skin dermatitis, and nausea. In water, zinc exists in two stable oxidation states 0 and +2, which differ in their toxicity. Water-soluble  $Zn^{2+}$  is relatively nontoxic because it is less absorbed into body tissues

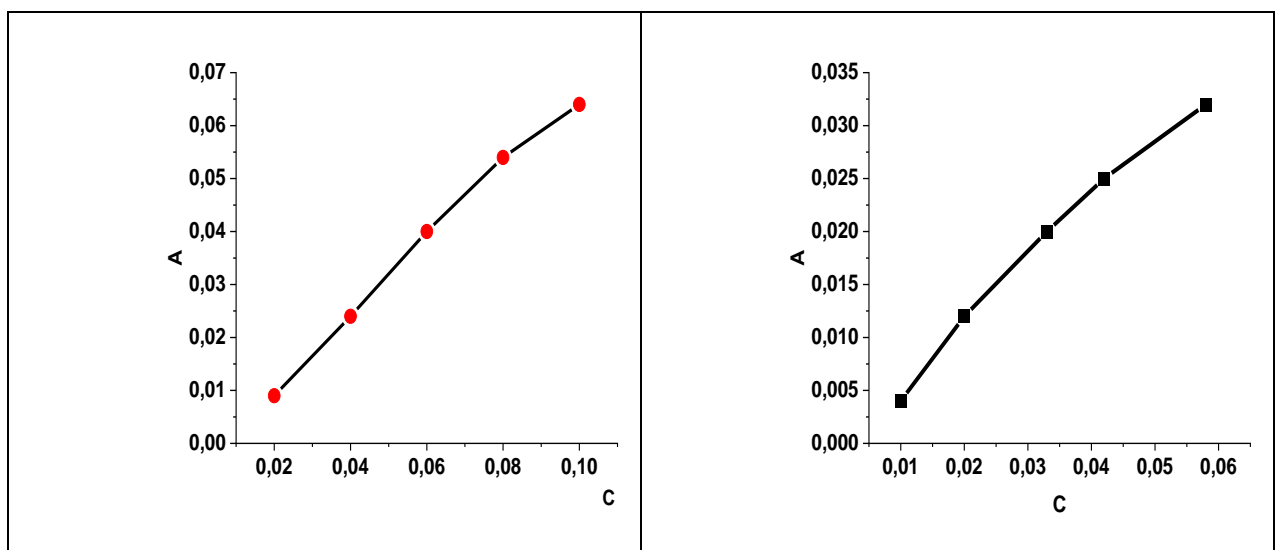
For this, 0.294 g of zinc sulfate salt was taken on an analytical scale and diluted in a 1-liter flask (a 0.006 normal solution was prepared) and adjusted to pH=4 in the presence of (HCl) hydrochloric acid. After that, zinc sulfate solution was put into 6 100 ml flasks in different volumes (in the first flask 0.5 ml, in the second flask 1 ml, in the third flask 1.8 ml, in the fourth flask 6.4 ml, in the fifth flask 12.8 ml and 25.6 mL was added to the sixth flask). During the experiment, a 0.1% solution of diphenyl carboside was prepared (0.12 g of diphenyl carboside was weighed on an analytical balance and 25 ml of a 96% solution of ethyl alcohol was used in a ratio of 0.5:1) during the experiment, a solution of 50% sulfuric acid and 50% phosphoric acid was prepared (10 ml of water and 18.3 ml of sulfuric acid were added, 10 ml of water and 17.3 ml of phosphoric acid

were added to a 50 ml flask) and then from sulfuric acid (1 ml in the first flask, 1 ml in the second flask, 1 ml in the third flask, 1 ml in the fourth flask, 1 ml in the fifth flask and 1 ml in the sixth flask) and phosphoric acid (0.3 ml in the first flask, 0.3 ml in the second 0.3 ml in the flask, 0.3 ml in the third flask, 0.3 ml in the fourth flask, 0.3 ml in the fifth flask and 0.3 ml in the sixth flask). We put 2 ml of the prepared 5% solution of diphenyl carboside into each flask and dilute it to the mark with distilled water and mix well and leave it for 15 minutes. (10:00 to 10:15) add 10 ml of water, 1 ml of sulfuric acid, 0.3 ml of phosphoric acid, 2 ml of diphenyl carboside and dilute to the mark in a 100 ml flask and the optical density of the first Etalon was obtained by thoroughly cleaning the flask, and then the optical density and concentrations of the solutions prepared in 6 flasks were obtained and graphs were drawn.

**Research methodology.** The concentration of the substance to be determined can be found by comparing the optical densities of the reference and test substances. For this, the optical densities of the standard and tested solutions are measured under optimal conditions, at the same wavelength. The wavelength of zinc is 540 nm, so we need to enter the wavelength of the spectrophotometer ourselves. In order to obtain accurate results, it is recommended to prepare the concentration of the standard close to that of the test substance. If the concentration values are given, the optical density of the substance under investigation is found by the formula. The concentration of the substance can also be determined based on the molar extinction coefficient of the light. For this, the optical density of the substance to be detected at a certain wavelength ( $I$ ) is measured. Knowing the molar light extinction coefficient of a substance, it is not difficult to find its concentration, that is, the molar light extinction coefficient is determined based on the measurement of the optical density of the standard solution of the substance. If it is not possible to obtain a pure sample of the substance to be determined,  $C_x$  can be obtained from the table. It should be noted that the exact value of the molar extinction coefficient is difficult to measure. It depends on such factors as the type of instrument, the width of the hole, the scattered light, the reflection, scattering and absorption of the cuvette glasses. Therefore, during the determination,

the measurement should be carried out using the same instrument. The concentration of a substance can also be found on the basis of a gradation plot.

Determination of the required amount of reagent to completely bind the ion to be detected to the colored compound. For this, several different series of solutions are prepared with the same amount of metal ion, different amount of reagent, and each time increasing amount. The optical densities of the solutions were measured, and a diagram of the dependence of the optical density on the concentration was drawn.

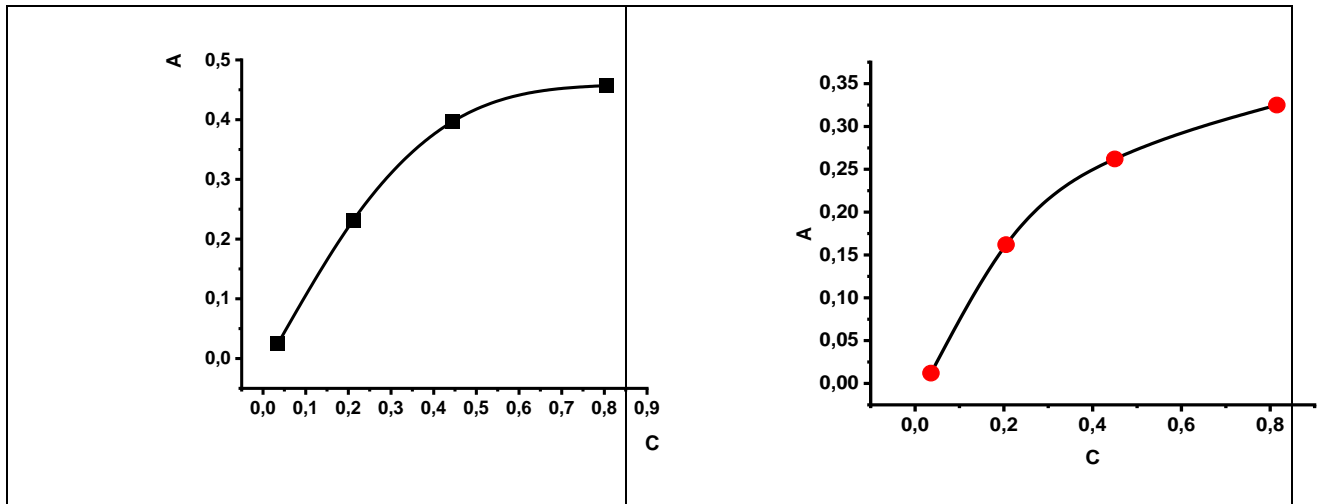


**Based on the results of the experiment, the graph of the concentration dependence values of the kaolin from the "Angren" mine is presented in Figure 1 below.**

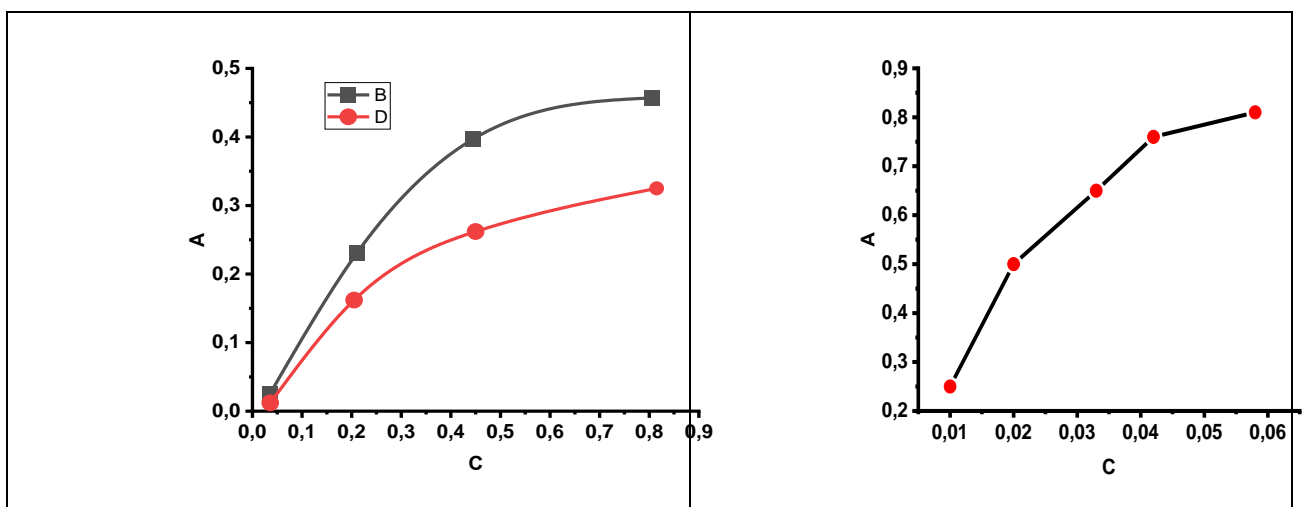
The optical density of the solution depends on the following factors. 1) The wave depends on the length and concentration. Usually, this relationship is called a graded graph. The amount of the unknown substance is found using this graph. The graded graph depends on the absorption thickness (f.). The absorption thickness should be chosen in such a way that the measured optical densities are in the range of 0.1-1.0. In this range, the error is minimal, so we took our solutions from 0.02 mg/l to 0.8 mg/l.

Spectrophotometric instruments have two cuvettes, 282 g of the tested solution is placed in one, and solvent in the other (zero solution equals zero absorption). It allows measuring the optical density of the test or standard solution relative to the solvent.

The same volume of solutions is placed in both cuvettes. In the spectrophotometry method, instead of the solvent, a standard solution of the substance to be determined is placed in the cuvette.

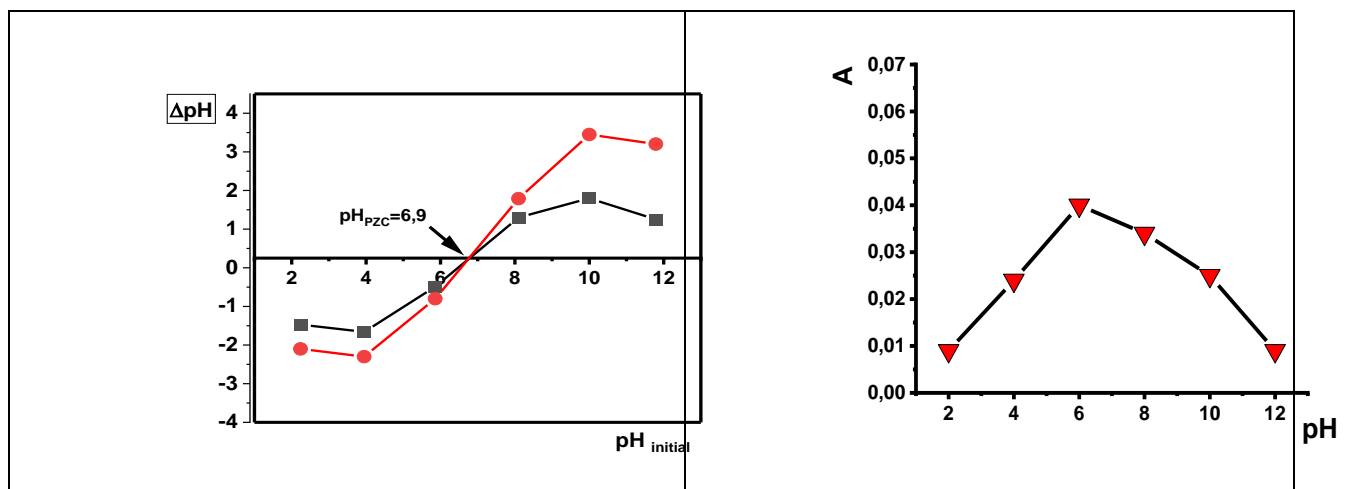


Based on the results of the experiment, the graph of the optical density of "Angren" mine kaolin as a function of concentration is shown in Figure 2 below. **keltirilgan.** 50 ml of the prepared potassium bichromate solution was added to 6 flasks, and 50 ml of Angren's activated kaolin, i.e. 0.05 g, was added and mixed for 1 hour using a shaker at 150 ppm. After the obtained suspension was filtered, the concentration dependence values of the optical density (SHIMADZU) were determined in a spectrophotometer.



**Based on the results of the experiment, the graph of optical density of Angren kaolin and Dehkhanabad bentonites as a function of concentration is presented in Figure 3 below.**

To determine the optimal pH range for the formation of a light-absorbing compound, the optical density of the solution at different pH values is measured and the  $A(C)=f(\text{pH})$  graph is drawn. From the graph, the limit of optimal values of  $\text{pH } \Delta\text{pH} = \text{pH}(\text{solution}) - \text{pH}(\text{NaCl solution})$  was found.



**The graph of the values of optical density of the solution as a function of pH based on the experimental results is presented in Figure 4 below.**

Methods for determining the concentration of a substance in a solution (absorption methods) Standard series method. According to the method, the color intensity of the analyzed substance solution is compared with the color intensities of several standard solutions, and as a result, the concentration of the analyzed substance is determined. For this, solutions are prepared in the same colorimetric test tubes. In the same way and conditions, the analyzed substance is converted into a colored compound. The color intensities of the analyzed solution and the standard solution are compared visually and the concentration is determined. Subjective cases can be allowed. The pH value of the sample was determined by taking 100 ml of a 0.1 M solution of NaCl in the range from 2.0 to 12.0. In this case, pH values of 0.1 M HCl and 0.1 M NaOH solutions were used. 1.0 g of Angren kaolin was added to the prepared solutions and stirred for 24 hours using a shaker at 150 ppm. The resulting suspension was filtered

and pH values were determined (METTLER TOLEDO). As a result of the experiment,  $\Delta$ pH values were determined by the following formula:  $\Delta$ pH = pH(solution) - pH(NaCl solution).

The results are presented in Table 1.

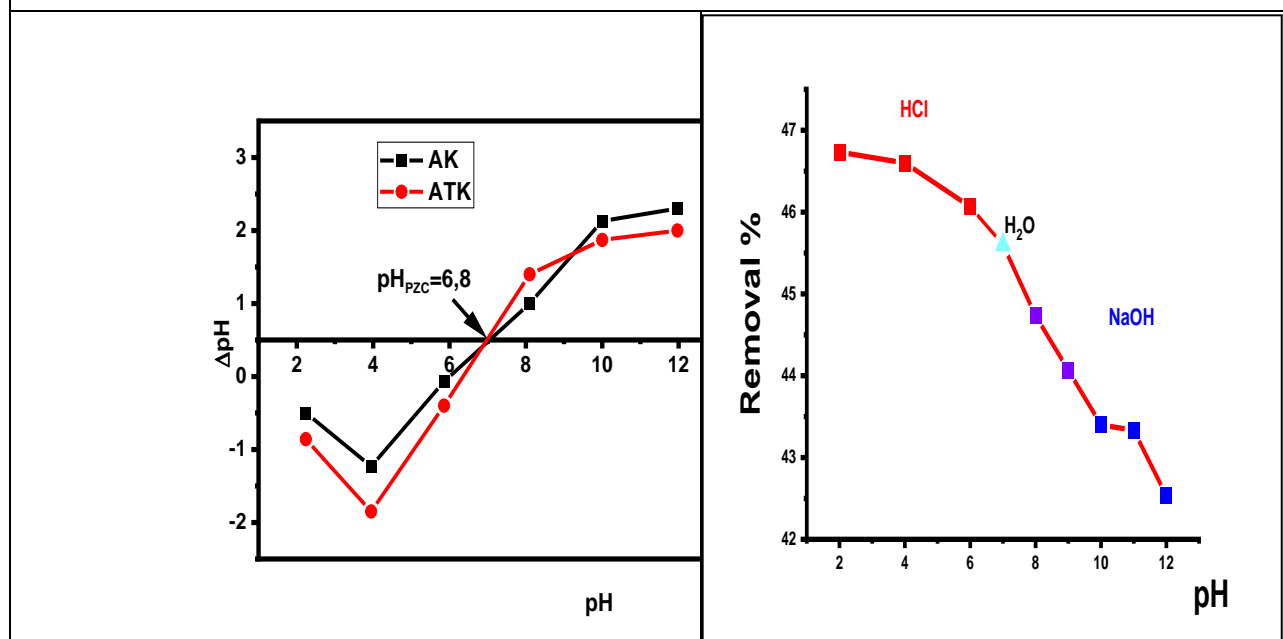
<b>Angren kaolin</b>	<b>H</b> nitial	,0	,0	,0	,0	,0	,0	,0	0	1	2
	<b>H</b> fter adsorp tion	,1	,45	,3	,4	,55	,78	,18	,2	,4	,2
	<b>pH</b>	0,1	0,45	1,3	1,4	0,55	,22	,82	,8	,6	,8

<b>pH</b>	<b>Absorban ce BL</b>	<b>C O</b>	<b>Ce BL</b>	<b>%R BL</b>	<b>Q e</b>
2	0,049	50	3,2	46,7	4 6,5
4	0,051	50	3,4	46,6	4 6
6	0,059	50	3,9	46	4 5,8



7	0,066	50	4,4	45	4 5,6
8	0,079	50	5,2	44	4 4,7
9	0,089	50	5,9	43	4 4
10	0,099	50	6,6	42	4 3
11	0,1	50	6,7	41	4 2
12	0,112	50	7,4	39	4 0

The obtained results are presented in Table 2.



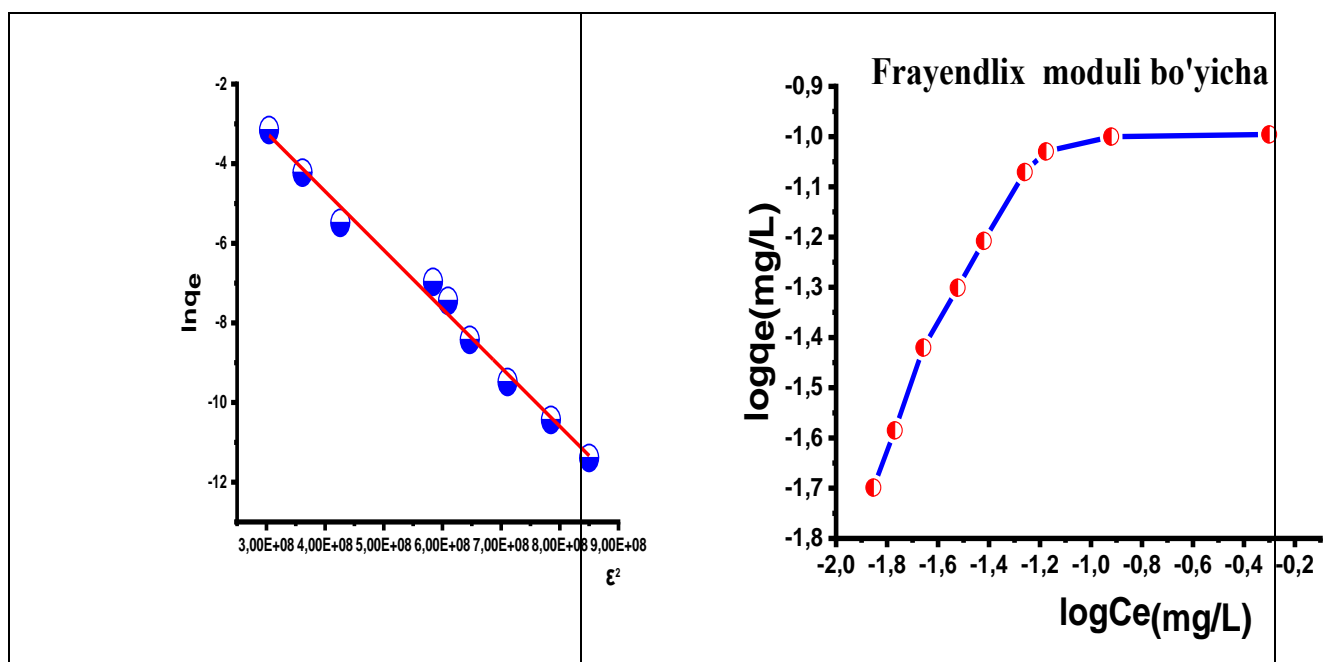
The graph of the absorbed amount of adsorbent (%) depending on the pH based on the experimental results is presented in Figure 5 below.

The experiment to study the effect of pH on the adsorption of metal ions on Angren kaolin was carried out in the range of 2, 3.59, 6.14, 7.1, 7.51, 10, 12 for Zn<sup>2+</sup> ion, respectively. (amount of adsorbed metal ions) ions used to calculate the specified pH range is to avoid the precipitation of metal hydroxides above the pH range noted

above. 60 Other parameters kept constant include particle size 63  $\mu\text{m}$ , adsorbent concentration 0.04 mg/g, temperature 293 K, and stirring speed. 250 rpm and an initial metal ion concentration of 100 mg/g.

From the zero charge point graph of "Angren" kaolin, it was determined that  $\text{pH}_{\text{pzc}}=6.7$ . The chemical composition of Bausch bentonite shows that a relatively large amount of  $\text{Na}_2\text{O}$  oxides was found in its composition. This shows that an adsorbent with high sorption properties can be obtained from it.

The following factors are important in the adsorption processes in solution: firstly, the nature of adsorbents, secondly, the nature of solvents, and thirdly, the nature of the adsorbate, the nature of intermolecular interactions in the "adsorbent-solvent-adsorbate" system, in the cumulative concentration of organic molecules on the surface area of the adsorbent. is important. According to the scientific literature, there is competition between solvent and adsorptive molecules in solutions In this process, physical adsorption of adsorptive molecules to adsorbents is determined. In addition, it was noted that the polarity, size and configuration of the adsorbate molecule play a major role in adsorption processes. The purpose of this scientific work is to study the mechanisms of zinc sulfate salt adsorption in static conditions on aminated adsorbents.



Based on the results of the experiment, the graph of the values of the zero charge point of "Angren" mine kaolin is presented in Figure 7 below.

Isotherm models	Indicators	Adsorbents		
		293	303	313
Freundlich module	$q_{max}$ (mg/g)	1,3422 82	0,0060 4	1,3422 82
	$K_L$ (L/mg)	1,5481 91	0,1062 61	1,4481 91
	$R_L$	0,0127 54	- 0,21607	0,0227 54
	$R^2$	0,963	0,986	0,963
	$R^2$	0,999	0,988	0,999
	$\beta$ (g <sup>2</sup> /L·mg <sup>-3</sup> )	10,00	0,978	9,00
	$R^2$	0,958	0,938	0,858

**Table 3. Indicators of Langmuir models based on adsorption of Zn<sup>2+</sup> ions**

### Conclusions and suggestions

In the study of objects of this research, it was shown that the ability of kaolin clay to adsorb heavy metal ions can be realized by treatment with sulfuric acid. The formation of Angren kaolin improved the adsorption capacity. The optimal conditions of experimental parameters studied as functions of contact time for Zn<sup>2+</sup> ion adsorption on natural Angren kaolin were determined as follows. pH (7.5 for Zn<sup>2+</sup>), adsorbent concentration (4.0 g for Zn<sup>2+</sup>, stirring rate (250) 293 K for Zn<sup>2+</sup> at an initial metal ion concentration of 100 mg L<sup>-1</sup>). The effect of contact time for all parameters showed that the rapid adsorption of metal ions mainly occurs during the first 60 to 90 min and then after 120 or 150 increases continuously up to the minute. Above these contacts, time led to adsorption equilibrium with increased uptake of metal ions. Applying the optimum conditions of the parameters to sulfate-treated Angren kaolin

recorded an increase in the adsorption of  $Zn^{2+}$  ions and a decrease in the adsorption of  $Zn^{2+}$  ions.

During the adsorption of Angren kaolin with zinc cations, it forms the best polymolecular layers, which is explained by the high adsorbent-adsorbate interaction of the adsorption active centers of the adsorbent. It led to a slight decrease in the strength of interaction of the adsorbent with zinc cations.

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