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## STUDY OF ADSORPTION CAPACITY OF ZEOLITE FOR NATURAL AND WASTE WATER PURIFICATION FROM HEAVY-METAL IONS

### Introduction

One of the most important ecological problems is the problem of natural waters contamination with heavy metals. The main causes of pollution are the content of heavy metals in waste water from municipal and industrial enterprises, inefficient wastewater treatment and discharge of such insufficiently treated wastewater into water bodies. Heavy metals delay the processes of water self-cleaning. They form quasi-equilibrium disperse systems, interact with the components of aqueous medium and form hydrated ions, oxyhydrates, and are concentrated due to the formation of complex inorganic and organic compounds [1]. There emerges a real threat to drinking and fishery water supply. By clearing wastewater from heavy metals, we will get clean rivers and wastewater sludge that can be used as fertilizers in agriculture.

In some rivers of Subcarpathia it has been found a significant concentration of cupric ions, and in the underground water – a significant content of manganese ions. Yes, in 2015 it was dropped 171 kg of copper into the Bystrytsia river, 72 kg of manganese into the Vorona river. When testing water from the well for drinking water supply, it was established that the content of manganese ions is 10 times higher than MAC (maximum allowable concentration) [2]. High level of natural and waste water pollution with heavy metals requires the improvement of the existing water purification technologies and the search for the new effective methods of their purification.

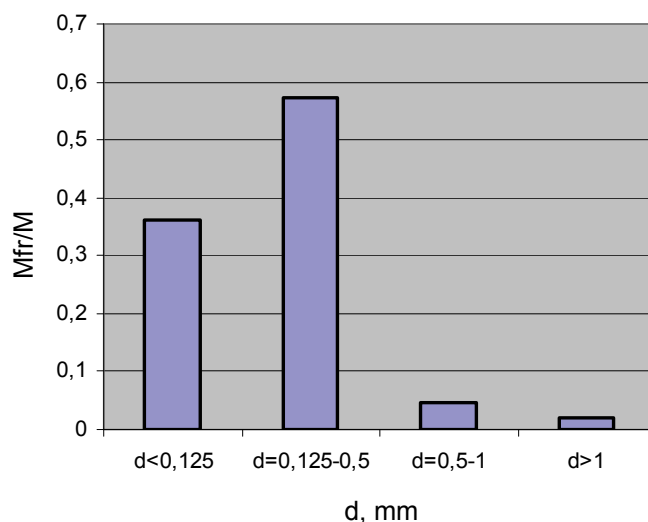
### Analysis of the last researches and publications

There are many chemical and physicochemical methods of wastewater purification from heavy metals. They are reagent, ion-exchange, electrochemical and adsorption methods [3-10]. The adsorption method is especially effective and promising among the modern methods of natural and waste water purification from heavy metals. Activated carbon, silica gel and clay are most often used for adsorption [11-17]. However, it is relevant to study natural adsorbents, one of which is zeolite. Due to its porous structure, zeolite has a high adsorption capacity conditioned by cation-exchange properties; and it is possible to achieve a high degree of purification of natural and waste water by using zeolite for heavy metals adsorption [18-24]. Despite the widespread use of natural zeolites for absorption of heavy metals of industrial waste water, literary sources have little data on the sorption of heavy-metal ions by natural zeolite in waste water of municipal enterprises.

Therefore, the **thesis objective** is the study of the possibility to use natural zeolite of Sokyryntsia deposit for purification of natural water and municipal wastewater from heavy-metal ions, in particular the determination of the effect of sorbent grains size and the concentration of cupric ions and manganese ions on the adsorption effectiveness, the establishment of optimal adsorption parameters, the study of the influence of pH environment and temperature on zeolite adsorption capacity, the determination of the specific adsorption capacity of zeolite, the construction of adsorption isotherms and calculation of their equations.

## Experimental technique

For researches we used zeolite of natural fraction with the size of grains 0.125-1 mm. The fractional composition of natural zeolite, used in experimental studies, was determined by separation on sieves with apertures of 1 mm, 0.5 mm, 0.125 mm in diameter ( $d$ ). The diagram of distribution of zeolite by fractions is presented in Figure 1. Analysis of the received data showed that the basis of zeolite is a fraction with  $d = 0.125-0.5$  mm, the portion of which in the zeolite total mass is 57.2%.



**FIGURE 1.** Diagram of zeolite distribution by fractions, where:  $M_{fr}/M$  – ratio of fraction mass to zeolite mass,  $d$  – diameter of zeolite grains

Determination of zeolite adsorption capacity was carried out on solutions of cupric nitrate and manganese nitrate with concentrations of 0.05 mg/dm<sup>3</sup>, 0.1 mg/dm<sup>3</sup>, 1 mg/dm<sup>3</sup>, 5 mg/dm<sup>3</sup> and 10 mg/dm<sup>3</sup> prepared from standard samples. The selected concentration values are maximum permissible and most specific to natural and waste water of the region and the maximum ones out of the recorded, according to the database of the Regional Department of Environmental Protection of Ivano-Frankivsk city.

Studies of the adsorption capacity of zeolite were carried out in conical flasks, into which were placed 1 g of adsorbent and 250 cm<sup>3</sup> of solution with Cu<sup>2+</sup> and Mn<sup>2+</sup> ions. The resulting solutions were stirred and left in rest, repeating such operations every 12 hours. Forty-eight (48) hours after the experiment beginning, the solutions were filtered through an ash free "blue ribbon" filter and there were carried out measurements of residual concentration of ions by photometric method on the KFK-3-01 device (Tables 1-2).

To establish the influence of pH environment on the adsorption efficiency, we measured pH of the primary solution and the filtrates using the pH/ion meter Expert-001 (Table 3).

To determine the effect of temperature on the ability of zeolite to adsorb ions of cuprum and manganese, the glasses with the testing solutions were placed in a refrigerated heating circulator and held there for 48 hours at the temperature 275K, 283K, 293K C, 303 K, and the solutions were stirred every 12 hours (Table 4).

Ion sorption (absorption) degree  $S$  (%) was calculated by the formula:

$$S = \frac{C_0 - C_i}{C_0} \cdot 100\%$$

where:  $C_0$  – initial concentration of the determining ion in the solution, mg/dm<sup>3</sup>;  $C_i$  – residual concentration of the determining ion in the solution, mg/dm<sup>3</sup>.

Specific adsorption capacity  $a$  (mg/gr<sub>ads</sub>) was calculated by the formula:

$$a = \frac{[(C_0) - C]}{m} \times W$$

where:  $C_0$  – initial concentration of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions in the solution, mg/dm<sup>3</sup>;  $C$  – concentration of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions in the solution after contact with zeolite, mg/dm<sup>3</sup>;  $W$  – solution volume, dm<sup>3</sup>;  $m$  – quantity of zeolite, u [25].

## Results of experimental studies and discussion

Determination of the adsorption capacity of zeolite in relation to cupric ions and manganese ions was carried out using 1 g and 2 g of adsorbent. It was established that the use of 2 grams of adsorbent and zeolite fraction with grains of the diameter less than 0.125 mm is inappropriate, since in the testing solutions small dregs are formed, which prevents the determination of the residual concentration of cupric and manganese ions, and therefore all experiments were carried out using 1 g of adsorbent.

Results of the studies on determining the adsorption capacity of zeolite depending on its fractional composition in 48 hours are presented in Table 1.

TABLE 1. Zeolite adsorption of cupric and manganese ions depending of zeolite grains diameter

№	Concentration of $\text{Cu}^{2+}$ and $\text{Mn}^{2+}$ ions in initial solution, mg/dm <sup>3</sup>	Residual concentration of ions in solution, mg/dm <sup>3</sup> zeolite							
		$\text{Cu}^{2+}$	$\text{Mn}^{2+}$	$\text{Cu}^{2+}$	$\text{Mn}^{2+}$	$\text{Cu}^{2+}$	$\text{Mn}^{2+}$	$\text{Cu}^{2+}$	$\text{Mn}^{2+}$
		initial fraction, 0.125-1 mm		zeolite grains diameter 0.125-0.5 mm		zeolite grains diameter 0.5-1 mm		grains diameter more than 1 mm	
1	0.05	0	0	0	0	0	0	0	0
2	0.1	0	0	0	0	0	0	0	0
3	1	0.093	0.56	0.025	0.41	0.22	0.71	0.36	0.79
4	5	2.69	3.70	2.54	3.58	2.73	3.79	2.91	3.88
5	10	7.37	8.54	7.24	8.38	7.42	8.63	7.59	8.75

Experimental studies have established that cupric and manganese ions are most effectively adsorbed by a zeolite fraction with a grain size of 0.125 mm to 0.5 mm, which was used for further researches. It was found that in the region of small concentrations (0.05-0.1 mg/dm<sup>3</sup>) in 48 hours, zeolite completely adsorbs the ions of cuprum and manganese, regardless of the sorbent grains size. Sorption efficiency decreases as the concentration of ions in the solution increases. Thus, the concentration of cupric ions of 1.0 mg/dm<sup>3</sup> in 48 hours decreased by 97.5%, the concentration of 5.0 mg/dm<sup>3</sup> – by 50.8% and the concentration of 10.0 mg/dm<sup>3</sup> – by 27.6%. In the case of manganese ions, the sorption is much lower, in particular: the concentration of manganese ions of 1.0 mg/dm<sup>3</sup> in 48 hours decreased by 59%, the concentration of 5.0 mg/dm<sup>3</sup> – by 28.4% and the concentration of 10.0 mg/dm<sup>3</sup> – by 6.2%. Comparative analysis of the data presented in Table 1 indicates that the testing zeolite shows higher adsorption selectivity to cupric ions. A rule is confirmed that the absorption of heavy-metal ions increases with the growth of the atomic weight of an ion and the decrease of its radius. Since the atomic weight of the cupric ions equals to 63,546 amu, the ion radius is 72 pm, the atomic weight of the manganese ions is 54,938,55 amu, the ion radius is 80 pm, that is, the cupric ions have larger atomic weight and smaller radius and therefore they are more easily adsorbed by zeolite [26].

In order to establish the optimal parameters of sorption of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions, there was conducted the adsorption dynamic analysis in the course of time with the cupric and manganese solutions with concentrations  $0.05 \text{ mg/dm}^3$ ,  $0.1 \text{ mg/dm}^3$  and  $1 \text{ mg/dm}^3$ . As deduced from experiments, zeolite completely adsorbs the ions of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  in one hour from solutions with concentrations of  $0.05 \text{ mg/dm}^3$  and  $0.1 \text{ mg/dm}^3$ . Reduction of the adsorption time is impossible, since the solution with zeolite, after being stirred, is illuminated in one hour and only when it can be used to determine the residual concentration of cupric and manganese ions. At the sorption of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions from the solutions of the concentration of  $1.0 \text{ mg/dm}^3$  other dependencies were established (Table 2).

TABLE 2. Dynamics of zeolite adsorption of cupric and manganese ions from a solution of the concentration of  $1 \text{ mg/dm}^3$

Study No.	$\text{Cu}^{2+}$ , $\text{Mn}^{2+}$ ions adsorption time, hr	Residual concentration of ions, $\text{mg/dm}^3$	
		$\text{Cu}^{2+}$	$\text{Mn}^{2+}$
1	1	0.310	0.990
2	2	0.290	0.990
3	4	0.275	0.980
4	6	0.260	0.802
5	24	0.200	0.650
6	48	0.025	0.410

Analyzing the dependence of the degree of sorption of cuprum and manganese ions on time (Fig. 2), it can be claimed that in the first hour the  $\text{Cu}^{2+}$  sorption is the most active when 69.0% of  $\text{Cu}^{2+}$  ions are adsorbed by zeolite. After that, the sorption speed is reduced. However, practically complete sorption of  $\text{Cu}^{2+}$  ions (97.5%) is achieved in 48 hours.

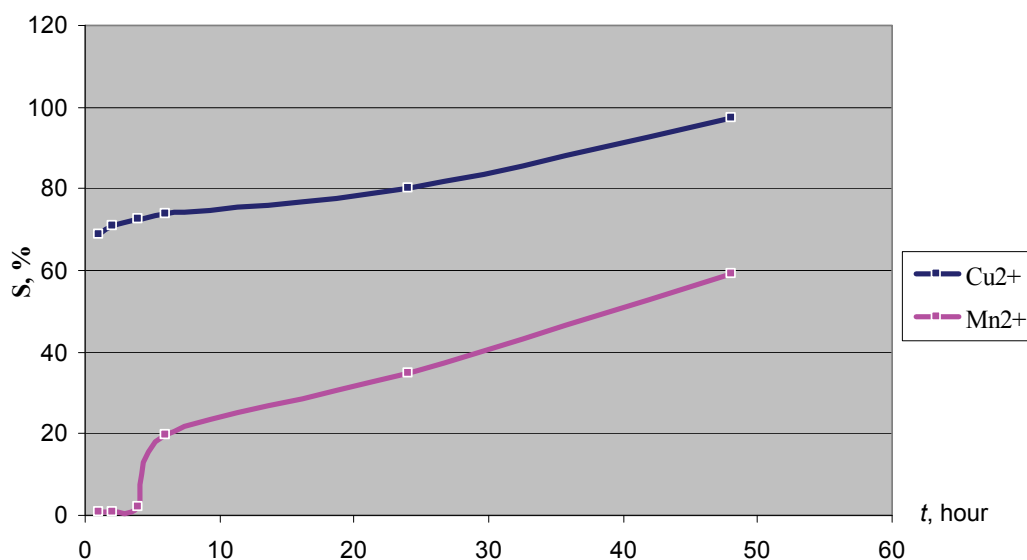


FIGURE 2. Dependence of the degree of cupric and manganese ions sorption on time

Another picture is observed in the case of  $\text{Mn}^{2+}$  ions sorption by zeolite. As can be seen from the Figure 2 the process of adsorption of manganese ions is more difficult. In the first three hours only 1-2% of  $\text{Mn}^{2+}$  is adsorbed, in three hours the degree of sorption is 19.8%, and in 48 hours only 59.0% of  $\text{Mn}^{2+}$  ions are adsorbed.

**Determination of the influence of pH environment** on zeolite ability to absorb ions of cuprum and manganese was carried out on solutions with the concentration of these ions  $1 \text{ mg/dm}^3$ . The research

was carried out at pH 3.05, 7.0 and 10.4 for cupric ions and at pH 3.0, 7.0 and 10.1 for manganese ions, using the solution NaOH to get the acidic medium 1N (Table 3).

**TABLE 3.** Influence of pH environment on zeolite adsorption of ions of cuprum and manganese from solutions with the concentration 1.0 mg/dm<sup>3</sup>

Study No.	Heavy-metal ions	Solution pH	Residual concentration of ions, mg/dm <sup>3</sup>
1	Cu <sup>2+</sup>	3.05	0.025
2		7.0	1.0
3		10.4	1.0
4	Mn <sup>2+</sup>	3.0	0.41
5		7.0	1.0
6		10.1	1.0

Table 3 data analysis shows that under static conditions natural zeolite adsorbs the Cu<sup>2+</sup> and Mn<sup>2+</sup> ions in acidic medium the most effectively. In this case, Me<sup>2+</sup> aqua ions can be effectively exchanged with mobile zeolite cations. The proportion of ionic hydroxocomplexes increases with the pH increase, metal ions in the form of Me(OH)<sup>(n-1)+</sup> have much bigger radius of hydrated ion and, as a result, do not penetrate effectively into zeolite pores. This leads to a delay of the intra-diffuse phase of the adsorption process. In the neutral and acidic media, with the appearance of hydroxyl forms, the adsorption of Cu<sup>2+</sup> and Mn<sup>2+</sup> is absent.

**In order to determine the influence of temperature** on the ability of zeolite to absorb ions of cuprum and manganese, we carried out the studies with solutions of concentrations 0.05 mg/dm<sup>3</sup>, 0.1 mg/dm<sup>3</sup> and 1 mg/dm<sup>3</sup> (Table 4).

**TABLE 4.** Influence of environmental temperature on zeolite adsorption of cupric and manganese ions

No.	Heavy-metal ions	Content of ions in input solution, C, mg/dm <sup>3</sup>	Residual concentration of ions in solution, mg/dm <sup>3</sup>			
			T = 275K	T = 283K	T = 293K	T = 303K
1	Cu <sup>2+</sup>	0.05	0.003	0.0	0.0	0.004
2		0.1	0.007	0.0	0.0	0.006
3		1.0	0.270	0.029	0.025	0.045
4	Mn <sup>2+</sup>	0.05	0.036	0.0	0.0	0.022
5		0.1	0.09	0.0	0.0	0.047
6		1.0	1.0	0.57	0.41	0.70

Table 4 data analysis shows that the adsorption of cupric and manganese ions is maximal at the temperature 293K. The content of cupric ions with concentration of 1.0 mg/dm<sup>3</sup> at 275K decreased by 73%, at 283K the content of these ions decreased by 97.1%, and at 293K – by 97.5%, that is, with the temperature increasing from 275K to 293K, the degree of adsorption increased by 24.1%. Further increase in temperature up to 303K did not lead to the increase of the adsorption degree, but on the contrary to its decrease by 1.6% in comparison with the adsorption at 293K. As for the manganese ions, it has been experimentally established that at the concentration of 1.0 mg/dm<sup>3</sup> at 275K, manganese ions are not adsorbed by zeolite, at 283K the content of these ions decreased by 43%, and

at 293K – by 59%, that is, with a temperature rise from 283K to 293K the degree of adsorption increased by 16%. With the temperature increase up to 303K, the adsorption degree was 30% and, as compared to the adsorption at 293K, decreased by 29%.

Comparing the data on adsorption of ions at different temperatures, an ambiguous effect of temperature on the adsorption process was established. It is known that adsorption is the exothermic process and temperature reduction would contribute to its behavior, because with the temperature increase such processes deteriorate. However, at adsorption of ions, the sizes of which are close to the effective sizes of sorbent pores, the penetration of these ions into the pores depends on their kinetic energy [27]. In addition, for each temperature, there is a state of equilibrium between adsorption and desorption. In our case, it was established that under static conditions,  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions are most effectively adsorbed at the temperature of 293K. Obviously, the kinetic energy of sorbate at the temperature of 293K increases, the viscosity decreases, which provides more effective penetration of the ions into the adsorbent pores.

**In order to determine the specific adsorption capacity of zeolite** and to calculate adsorption equations according to experimental data from the Table 1, isotherms for  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions have been constructed by zeolite fraction with grain sizes from 0.125 mm to 0.5 mm (Fig. 3).

The adsorption isotherms, both for  $\text{Cu}^{2+}$  and for  $\text{Mn}^{2+}$ , have quite a steep shape, and this indicates that zeolite has a developed system of micropores and ultramicropores. The so-called "sieve" effect is observed in microporous adsorbents, which consists in the fact that only the molecules the size of which is smaller or equal to the radius of pores can be adsorbed into micropores [28].

The adsorption isotherm obtained by the form refers to the type I isotherm and is described by the Langmuir monomolecular adsorption theory [29, 30].

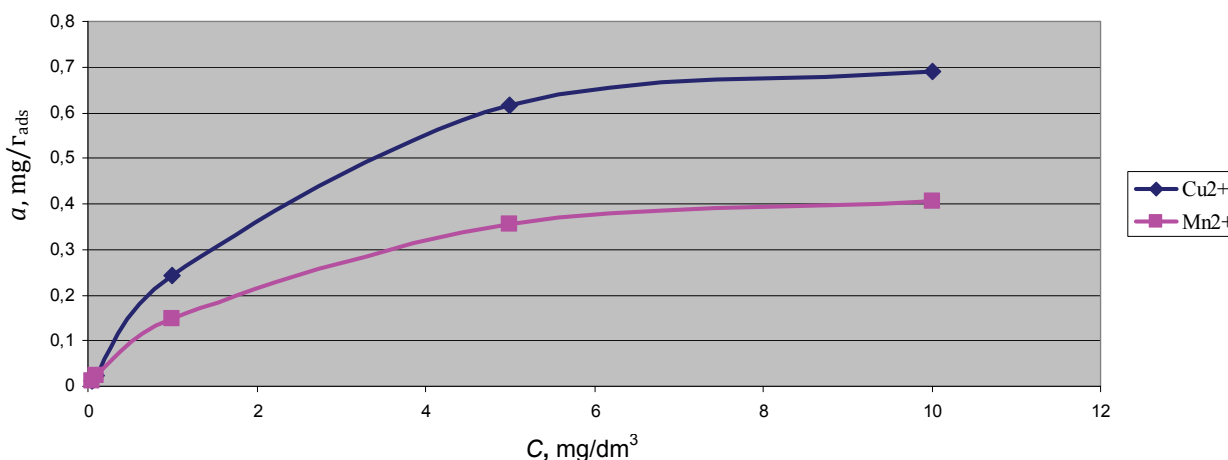


FIGURE 3. Zeolite adsorption isotherm of cupric and manganese ions

Absorption isotherms of  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  ions indicate that the process of redistribution of system components between the surface layer and the bulk phase takes place. In this case, the concentration of the dissolved substance at the interface of the phase separation occurs. The motive force of the components between a volume and a surface layer is to equalize their chemical potentials in the volume and in the surface layer [31, 32].

According to zeolite structure there may form complex salts  $\text{M}_2(\text{Cu}(\text{SO}_4)_2) \cdot 6\text{H}_2\text{O}$  and  $\text{M}_2(\text{Mn}(\text{SO}_4)_2) \cdot 6\text{H}_2\text{O}$ , where  $\text{M}_2$  – alkali metals (Na, K) [25]. The obtained adsorption isotherms are described by the Langmuir equation:

$$a^* = a_{\infty} \times \frac{bC}{1 + bC}$$

where:  $a_{\infty}$  – maximum amount of substance absorbed by adsorbent, mg/g<sub>ads</sub>;  $a$  – amount of substance absorbed by adsorbent, mg/g<sub>ads</sub>;  $b$  – constant;  $C$  – pollutant concentration, mg/dm<sup>3</sup>.

To find the constant  $b$  the linear form of Langmuir equation is used:

$$\frac{1}{a^*} = \frac{1}{a_\infty \times b} \times \frac{1}{c} + \frac{1}{a_\infty}$$

Characteristic curves in coordinates  $\frac{1}{a} = f\left(\frac{1}{c}\right)$  were plotted for cupric and manganese ions, that will allow finding  $a_\infty$  and describing adsorption isotherm with the Langmuir equation (Fig. 4).

**Linear form of Langmuir adsorption isotherm for cupric and manganese ions**

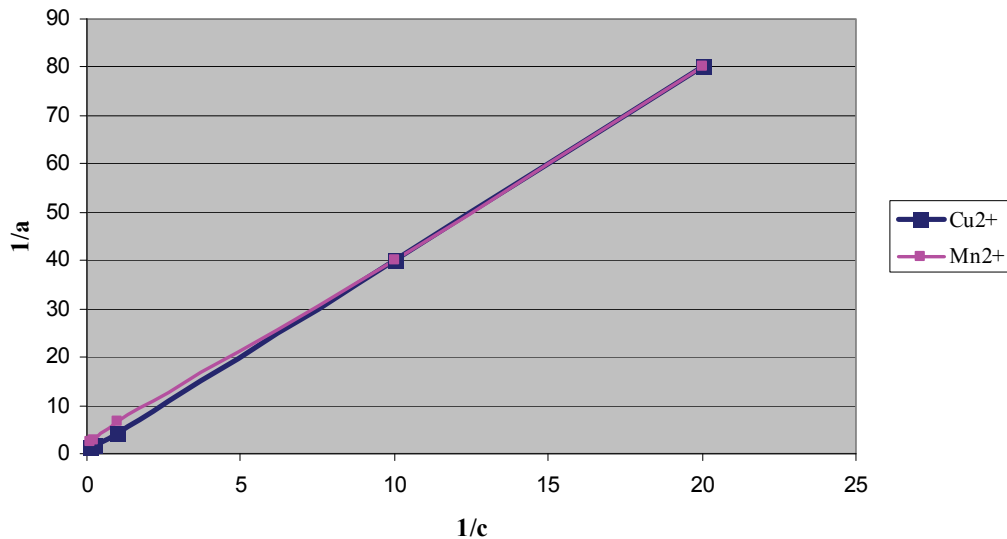


FIGURE 4. Dependence of  $\frac{1}{a} = f\left(\frac{1}{c}\right)$  for cupric and manganese ions

From the adsorption isotherm  $\text{Cu}^{2+}$  we find  $a_\infty$

$$\frac{1}{a_\infty} = \frac{1}{0.690} = 1.4492, \quad a_\infty = 0.690 \text{ mg/g}_{\text{ads}}$$

$$\text{tgc} = 0.3793$$

$$b = \frac{1}{0.690} \times 0.3793 = 0.5497$$

Adsorption isotherm equation for ions of  $\text{Cu}^{2+}$ :

$$a = 0.690 \times \frac{0.5497c}{1 + 0.5497c}$$

From the adsorption isotherm  $\text{Mn}^{2+}$  we find  $a_\infty$ :

$$\frac{1}{a_\infty} = \frac{1}{0.405} = 2.47, \quad a_\infty = 0.405 \text{ mg/g}_{\text{ads}}$$

$$\text{tgc} = 0.3214$$

$$b = \frac{1}{0.405} \times 0.3214 = 0.7935$$

Adsorption isotherm equation for ions of  $\text{Mn}^{2+}$ :

$$a = 0.405 \times \frac{0.7935c}{1 + 0.7935c}$$

## Conclusions

1. The possibility to use zeolite of Sokyrnytsia deposit for purification of natural water and municipal wastewater from cupric and manganese ions was established.
2. It was found that in the region of small concentrations (0.05-0.1 mg/dm<sup>3</sup>) in 48 hours, zeolite completely adsorbs the ions of cuprum and manganese, regardless of the sorbent grains size. Sorption efficiency decreases as the concentration of ions in the solution increases.
3. It was experimentally established that the efficiency of sorption by zeolite of cupric ions is much higher as compared to manganese ions.
4. The influence of pH environment on the effectiveness of adsorption of cupric and manganese ions by zeolite of Sokyrnytsia deposit was studied. It was also established that cupric and manganese ions are most effectively adsorbed by zeolite in acidic medium.
5. The influence of temperature on the effectiveness of adsorption of cupric and manganese ions was studied. It was also established that cupric and manganese ions are most effectively adsorbed by zeolite at the temperature of 20°C.
6. The equation for adsorption isotherm of cupric ions and manganese ions was derived, which makes it possible to calculate the specific adsorption capacity of zeolite for any concentration.

## References

- [1] Тимофеева С.С., *Состояние и перспективы развития методов очищения сточных вод красильно-отделочного производства* / С.С. Тимофеева, Химия и технология воды, 1991, Т.13, No 6, С. 555-569.
- [2] Водні ресурси Івано-Франківської області. Звіт Івано-Франківського обласного управління водних ресурсів, 2016
- [3] Зинатулина Н.М., *Физико-химические методы обезвреживания сточных вод* / Н.М. Зинатулина, Г.И. Ханина, О.А. Коваленко, Н.В. Гудзь, Хімічна промисловість України, No 1-2, 2000, С. 93-98.
- [4] Жуков А.И., *Методы очистки производственных сточных вод* / А.И. Жуков, И.Л. Монгайт, И.Д. Родзилер; Справочное пособие.- М. : Стройиздат, 1977, С. 173-201.
- [5] Ожередова М.А., *Установка обезвреживания никельсодержащих промывных вод* / М.А. Ожередова, А.В. Суворин, А.Д. Тюлбпинов, Экотехнологии и ресурсосбережение, 2006, No 5, С. 72-75.
- [6] Максин В.И., *Оценка взаимного влияния ионов на реагентную очистку сточных вод гальванических производств*, ХиТВ, 1997, Т. 19, No 6, С. 579-587.
- [7] Кочетов Г.М., *Комплексная очистка сточных вод промышленных предприятий с регенерацией тяжелых металлов* / Г.М. Кочетов, Экотехнологии и ресурсосбережение, 2000, No 4, С.41-43.
- [8] Запольский А.К., *Комплексная переработка сточных вод гальванического производства* / Запольский А.К., Образцов В.В., К: Техника, 1989, С. 167.
- [9] Гребенюк В.Д., *Состояние и перспективы развития метод очистки сточных вод гальванических производств* / Гребенюк В.Д., Соболевская Т.Т., Махно А.Г., ХиТВ, 1989, Т. 11, No 5, С. 407-421.
- [10] Криворучко А.П., Пономарев М.И., Корнилович Б.Ю., *Очистка медьсодержащих сточных вод электролизом*, ХиТВ, 1997, Т. 19, No 6, С. 622-625.
- [11] Мальований М.С., *Адсорбційні технології забезпечення техногенної безпеки шляхом використання природних дисперсних сорбентів* / [ М.С. Мальований, З.С. Одноріг, М.І. Санніков, І.М. Петрушка та інші], Проблеми економії енергії: III міжнар. наук-прак. конф, 10-14 жовтня 2001р.: зб. мат., 2001, С. 246-247.
- [12] Третинник В.Ю., *Природные дисперсные минералы Украины и перспективы их использования в технологии водоочистки* / В.Ю., Химия и технология воды, 1998, Т. 20, No 2, С. 183-191.
- [13] Дрий В.А., *Глинистые минералы* / Дрий В.А., Косовская А.Г., М.: Мир, 1980, С. 204.
- [14] Мальований М.С., *Очищення стічних вод природними дисперсними сорбентами: монографія* / М.С. Мальований, І.М. Петрушка, Львів: Вид-во Львівської політехніки, 2012, С. 80.



- [15] Круглицкий Н.Н., *Физико-химические основы регулирования свойств дисперсий глинистых минералов* / Н.Н. Круглицкий, Киев 1968, С. 456.
- [16] Степова К.В., *Хемосорбція гідроген сульфідом модифікованими природними сорбентами: автореф. на здобуття наук. ступеня канд. техн. наук : спец. 05.07.08 – «Процеси та обладнання хімічної технології»* / К.В. Степова, Львів. 2011, С. 20.
- [17] Петрушка І.М., *Теорія локальної ізотропної турбулентності при адсорбції барвенника активного алого 4ЖТ на глауконіті* / Петрушка І.М., *Восточно-европейский журнал передовых технологий*, 2011, No 6/6, С. 39-42.
- [18] Цицишвили Г.В., *Природные цеолиты* / Г.В. Цицишвили, Т.Г. Андроникашвили, Г.Н.Киров, Л.Д. Фелизова, М.: Химия 1985, 224с.
- [19] Соболев Н.В., *Физико-химические и медико-биологические свойства природных цеолитов* / Соболев Н.В., Белицкий И.А., Панин Л.Е. и др., Новосибирск: Изд-во АН СССР, Сиб. Отд., 1990, С. 286.
- [20] Тарасевич Ю.И., *Природные сорбенты в процессах очистки воды*. К.: Наукова думка, 1981, С. 302.
- [21] Маслякевич Я.В., *Звіт про пошукові роботи на цеоліти, проведених Закарпатською геологічною експертизою в 1973-1974 рр. в Солотвинській впадині Закарпатської області УРСР, м. Берегово* / Я.В. Маслякевич, В.В. Висотський, 1974, Т. 1, С. 117.
- [22] Брек Д., *Цеолитовые молекулярные сита*. М. : Мир, 1976, С. 778.
- [23] Горшкова Н.В., *Возможность использования клиноптилолита в качестве адсорбента диоксида углерода, водяных паров, модификатора карбамида* / Н.В. Горшкова, Т.И. Нефедова, В.Н. Мельникова, *Использование природных цеолитов Сокирницкого месторождения в народном хозяйстве: Республиканская научно-практическая конференция, 23-24 октября 1990г.: сообщения*, 1991, С. 30-31.
- [24] Scott M., Kathleen A., Prabir K., *Handbook of zeolite science and technology*, eds. CRC Press, 2003, p. 16.
- [25] Гомонай В.І., *Фізична та колоїдна хімія: Підручник*/ Гомонай В.І., Вінниця: Нова книга, 2007, С. 496.
- [26] Некрасов Б.В., *Основы общей химии*. Т.2. М., Химия, 1973, С. 668.
- [27] Чубур В.С., *Вплив температури на швидкість процесу адсорбції з водних розчинів на твердих сорбентах* / В.С. Чубур, І.В. Умнік, С.Б. Большанина // *Сучасні технології у промисловому виробництві: матеріали науково-технічної конференції викладачів, співробітників, аспірантів і студ. фак-ту технічних систем та енергоефективних технологій (м. Суми, 14-17 квітня 2015 р.)* – Суми: СумДУ, 2015, Ч.1, С.103.
- [28] Дубинин М.М., *Молекулярно-ситовые эффекты как следствие активированного характера физической адсорбции* / М.М. Дубинин, К.М. Николаев, Н.С. Поляков, *Труды III Всесоюзной конференции по теоретическим вопросам адсорбции*, 1973, С. 26-31.
- [29] Akyil S., *Preparation of composite adsorbents and their characteristics* / S. Akyil, M. Eral, *Journal of Radioanalytical and Nuclear Chemistry*, 2005, pp. 33-37.
- [30] Toth J., *Calculation of the BET-compatible surface area from any type I isotherms measured above the critical temperature*. *Colloid Interface Sci*, 2000, No 225, P. 378-383.
- [31] Фролов Ю.Г., *Курс коллоидной химии. Поверхностные явления и дисперсные системы* / Ю.Г. Фролов – М.: Химия, 1989, С. 462.
- [32] Киселев А.В., *Поверхностные явления и адсорбция* / А.В.Киселев, Я.И.Герасимов, *Курс физической химии*, М.:Госхимиздат, 1963, Т. 1, С. 624.