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INVESTIGATION OF THE PROCESS OF ADSORPTION OF HEAVY METAL IONS BY WASTE-BASED COMPOSITE

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Sorption characteristics of the adsorbent composite synthesized on the basis of polyvinyl chloride and butadiene-nitrile rubber wastes with respect to cobalt, nickel and zinc ions from aqueous solutions were studied under static conditions. Dependences of the sorption capacity on the solution pH, composite mass, ionic strength of the solution and initial concentration of metal ions were obtained. Sorption isotherms were processed by the Langmuir and Freundlich models. It was found that the sorption of metal ions on the composite is best described by the Freundlich model.

Keywords: heavy metals, adsorption, waste-based composite

INTRODUCTION

Heavy metals are widely used in different industries. For example, cobalt is widely used in metallurgy, metal processing, chemical industry; nickel - in non-ferrous metallurgy enterprises, in production of synthetic rubber, and zinc - in mining and processing plants, electroplating plants, in production of parchment paper, mineral paints, viscose fibres, etc. As a result, they enter waste water in the form of ions with toxic properties. They are discharged into wastewater in the form of ions with toxic properties and, as a consequence, water basins are polluted with ions of these metals exceeding the Maximum Permissible Concentrations (MPC). The of these metals in water is limited: MAC_a is 0.1 mg/dm^3, MAC_{aw} is 0.01 mg/dm^3, since their increased presence in the environment leads to various types of diseases. Cobalt causes allergies, dermatitis, enlargement of the thyroid gland, damage to the heart muscle with the development of "cobalt cardiomyopathy". Nickel has a specific effect on the cardiovascular system and also leads to endemic diseases, bronchial cancer. Zinc reduces immunity, impairs the function of the pancreas, liver, causes lesions of the skin, hair and nails, and in toxic doses - cancer [1-5].

In order to ensure environmental safety, i.e., to reduce and prevent pollution of water basins, wastewater should be purified. This problem can be solved by carrying out purification measures using various adsorbents. Composite adsorbents have proven to be very effective for purifying various types of water. In particular, in number of researches [6]

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have shown that adsorbents with functional groups are promising for extracting heavy metal ions from various types of water

This work studies the process of adsorption of cobalt, nickel and zinc ions from aqueous solutions by a composite adsorbent based on polyvinyl chloride (PVC) and butadiene-nitrile rubber (BNR) wastes.

EXPERIMENTAL

The work involved PVC – waste from window frames and expired BNR (SKN-26). Before using, PVC is crushed to small sizes.

The composite was prepared as follows: 5 g of PVC was placed in a flask and 125 ml of dichloroethane was added, then mixed with heating at 50 °C for 4 hours. Then left until a homogeneous solution was formed. Then a BNR solution (5 g rubber), previously dissolved in chloroform, was added to it. The polymer mixture solution was poured into Petri dishes. It is removed after 4 days. The compositions are kept under a hot press for 10 minutes. At the next stage, it is transferred to a 20 % potassium hydroxide solution and gaseous oxygen is passed through the suspension for 4 hours. Finally, the composite was crushed, treated with alcohol, acetone, dried in air and a vacuum drying oven until constant mass.

Standard solutions of cobalt, zinc and nickel were prepared by dissolving of metal salts ($Co(NO_3)_2{\cdot}6H_2O$, $Zn(SO_4)_2{\cdot}7H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$) in the appropriate amount of distilled water. Working solutions were prepared by diluting aliquots of the initial solutions with distilled water.

The required acidity of the solution (pH=3÷9) was created using acetate-ammonia buffers. To obtain pH 1 and 2, the 0.1 N HCl solution was used. The components of the buffer solutions (HCl, CH_3COOH, NH_3) were classified as "analytical grade" or "chemically pure". pH values were monitored using the «Mettler Toledo» pH meter.

The adsorption of metal ions was studied in a static mode using the limited volume method according to the following procedure: a certain volume of a solution (0.015 dm^3) with the appropriate acidity and containing the metal ion was added to the composite (0.010-0.10 g) placed in a flask. The phases were kept in contact for a certain time (~24 h), and then solid and liquid parts separated by filtration, and the content of the metal ion in the solution was determined. The experimental results on the study of sorption were expressed as the value of the sorption capacity of a given ion (SC, mmol/g) and the degree of sorption (R, %) according to formulas (1) and (2):

$$\mathrm{SC} = \frac{(C_0 - C_{eq}) \cdot V}{g}, \qquad (1)$$

$$R = \frac{C_0 - C_{eq}}{C_0} \cdot 100 \qquad (2).$$

where SC is the amount of sorbed ion per gram of adsorbent, mmol/g; Co, Ceq are the initial and equilibrium concentrations of ions in the solution, respectively, mmol/dm^3; V is the volume of the solution; g is the mass of the composite.

The determination of metal ions was carried out by a spectrophotometric method using analytical reagents [7].

RESULTS AND DISCUSSION

The studied composite is a small light-brown film, insoluble in water, acids, alkalis and organic solvents.

The presence of carboxyl groups and chlorine-containing fragments is assumed as functional groups in the composite structure.

An important role when working with adsorbents containing acid groups of this type is played by the acidity of the medium, which determines the state and reactivity of the functional groups of the adsorbent. The forms of metal ions in the solution also depends on the acidity of the medium, changing which it is possible to control the adsorption process [8].

Therefore, for determination the adsorption properties of the composite, firstly influence of pH medium to the degree of sorption was investigated. It was revealed that the maximum sorption of metal ions is observed at a pH value of 6. Based on this, all further studies were carried out at this pH value.

As is known [8], the ionic strength of the solution has a great influence on the sorption processes, which changes the conformation of the polymer macromolecules and the ionic environment of the functional groups of the adsorbent. As a result of the studies, it was established that (Figure 1) an increase in the concentration of NaCl in the solution significantly reduced the sorption capacity. The negative effect of sodium chloride on sorption can be explained by the transformation of some acid groups to the Na - form and a decrease in the total concentration of hydrogen ions in the composite phase. On the other hand, as a result of hydration of the added salt, the activity of water decreases, leading to a decrease in the degree of swelling of the composite and deterioration of its sorption properties.

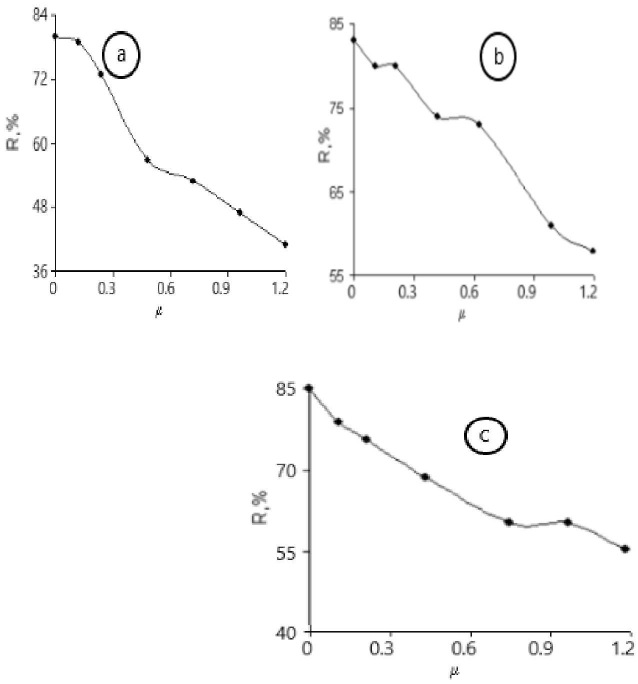

Figure 1. Dependence of the degree of sorption of metal ions on the ionic strength of the aqueous phase: a-Ni^{2+}, b-Co^{2+}, c-Zn^{2+}; Process conditions: C_0= 1 mmol/dm^3; V=0,015 dm^3, g=0,05 g, pH=6.

The mass of the composite is an important parameter, changing which it is possible to obtain valuable characteristics of the sorption process under study. Below is a series displaying the dependence of the degree of extraction on the adsorbent weight under other equal conditions (pH=6; initial concentration of metal ions 1 mmol/dm3; solution volume 0.015

Table 1. Dependence of sorption of metal ions on the mass of the composite

Co^{2+}	g, mass	0.01	0.02	0.03	0.04	0.05	0.07	0.10

	R, %	59.3	68.3	79.6	83.8	88	89	89.5
Ni^{2+}	g, mass	0.01	0.02	0.03	0.04	0.05	0.07	0.10
	R, %	20.6	31.2	59.8	68.5	77.6	78.5	78.8
Zn^{2+}	g, mass	0.01	0.02	0.03	0.04	0.05	0.07	0.10
	R, %	29.6	43,9	63,5	71,3	79.6	81.8	82

It is evident that the mass of the composite for complete extraction of metal ions is 0.05 g. When studying other parameters, the mass of the composite corresponded to this value.

The sorption isotherm is the main characteristic of the sorption capacity of any adsorbent and reflects the functional relationship of the equilibrium concentration (Ceq) with the equilibrium amount of the sorbed substance. Analysis of sorption isotherms allows us to draw certain conclusions about the nature of the sorbent surface, the nature of the ions-adsorbent interaction, etc. [9].

To construct sorption isotherms, the effect of the initial concentration of metal ions in the solution on the sorption capacity of the composite was first studied. It was found that with an increase in the initial concentration of ions, the sorption capacity of the composite increases. Based on these studies, a sorption isotherm was constructed (Figure 2).

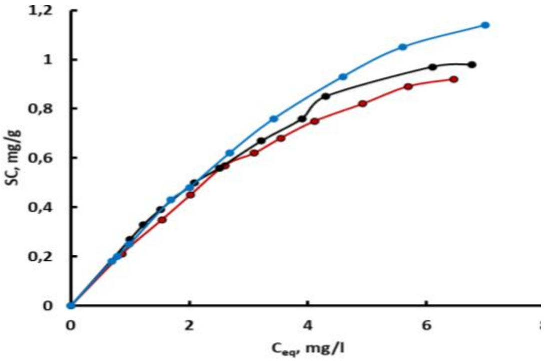

Figure 2. Sorption isotherm of metal ions: black line – cobalt, red line – nickel, blue line – zinc.

Three parts can be distinguished on the isotherms. The initial, steeply rising, almost linear part of the curve shows that at low concentrations, sorption is practically proportional to this value (Henry part). In this case, a monolayer of ions is formed on the surface of the composite. The almost horizontal part, corresponding to high concentrations, corresponds to the surface of the composite completely saturated with metal ions. Under these conditions, if only a monomolecular layer of ions can form on the surface of the composite, the amount of sorbed substance practically ceases to depend on the concentration. The middle part of the curve corresponds to intermediate degrees of surface filling.

For the mathematical description of the static equilibrium established during the sorption process, the Langmuir [10] and Freundlich [11] models were used. The equations of the models in linear forms are given in equations (3) and (4), respectively:

$$\frac{C_{eq}}{SC} = \frac{1}{K_L \cdot SC_{max}} + \frac{1}{SC_{max}} \cdot C_{eq}, \tag{3}$$

$$lgSC = lgK_F + \frac{1}{n} \cdot lgC_{eq}. \tag{4}$$

Here are the experimental values of the SC adsorbent sorption for metal ions (mmol/g); C_{eq} is the equilibrium concentration of metal ions in the solution (mmol/l). In equations (3), K_L and SC_{max} are the parameters of the Langmuir model; K_F, 1/n are the parameters of the Freundlich model;

In Figure 3, the sorption isotherm is presented in linear form.

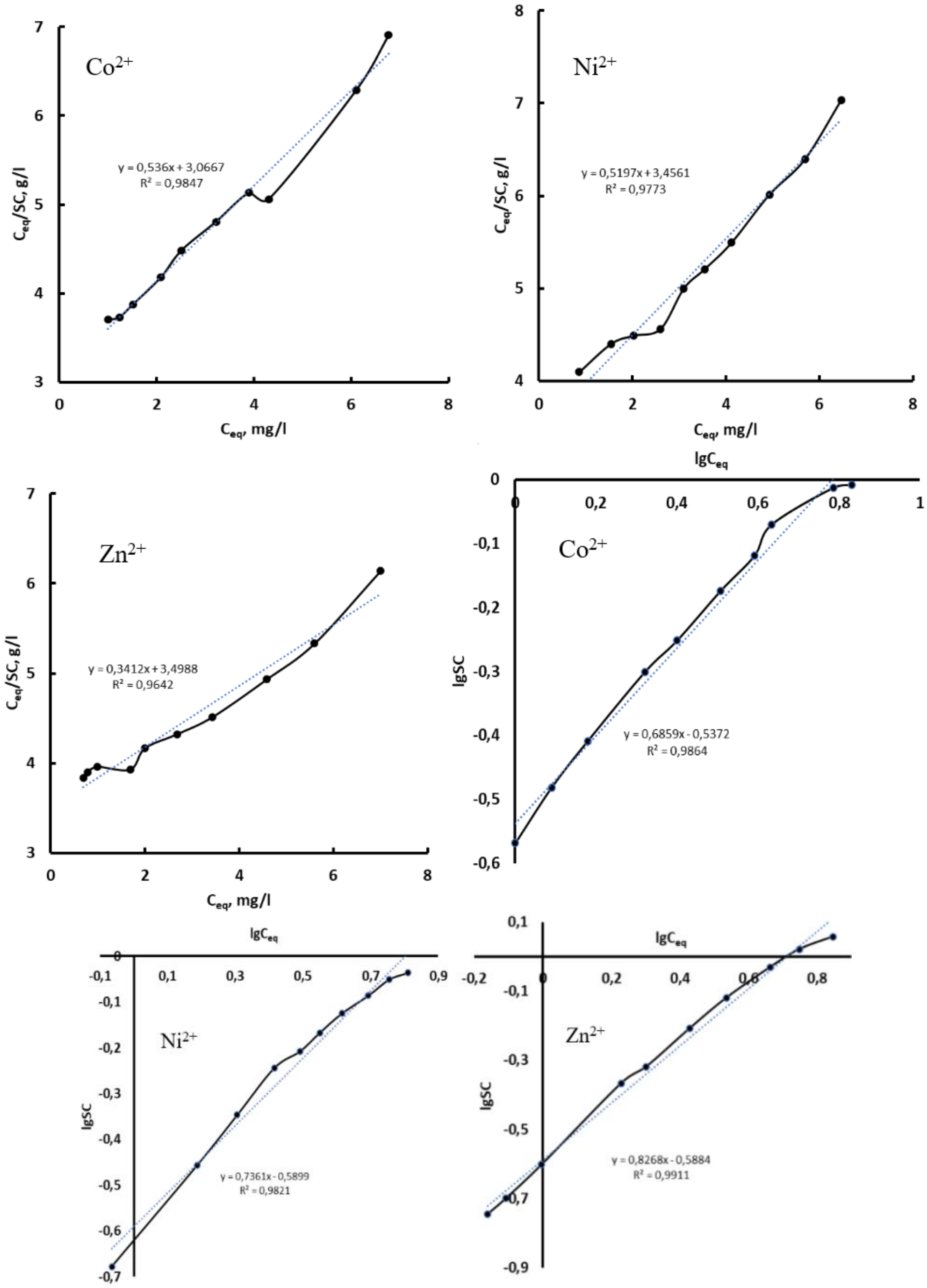

Figure 3. Sorption isotherm of metal ions in linear form according to Langmuir and Freundlich

The obtained constants and correlation coefficients are summarized in Table 2.

Table 2. Sorption isotherm constants of metal ions

Parameters of the Langmuir model			Parameters of the Freundlich model		
CE$_{max}$, mmol/g	K$_L$, /mmol	R^2	K$_F$, (mmol/g)·(l/mmol)$^{1/n}$	1/n	R^2
			Co^{2+}		

1.866	0.175	0.9847	0.290	0.686	0.9864
Ni^{2+}					
1.924	0.150	0.9773	0.258	0.736	0.9821
Zn^{2+}					
2.931	0,098	0.9642	0.258	0,826	0.9911

As can be seen from Table 2, the Freundlich equation describes the sorption isotherm better. This indicates that the sorption of metal ions occurs on active centers of various natures. Such active centers can be functional groups of various natures, located both in the pores and on the surface. In the general case, a monomolecular layer of metal ions is formed on the surface of the composite during the sorption process.

CONCLUSION

The adsorption properties of a composite obtained by thermal processing of a film made from PVC waste and expired BNR and its treatment in a sodium hydroxide solution were studied. As sorbates ions were taken. The influence of various factors to the sorption process have been investigated. Sorption isotherms were plotted and the experimental results were verified for compliance with the corresponding models. It was established that the chemical affinity of metal ions to the adsorbent changes in the following order: $Co^{2+} > Ni^{2+} = Zn^{2+}$

REFERENCES

1. Sarker, A.; Al Masud, M.A.; Deepo, D.M.; Das, K.; Nandi, R.; Ansary, M.W.; Islam, A.R.; Islam, T. Biological and Green Remediation of Heavy Metal Contaminated Water and Soils: A State-of-the-Art Review. *Chemosphere* **2023**, *332*, pp. 138861, https://doi.org/10.1016/j.chemosphere.2023.138861
2. Wu, C.; Li, F.; Yi, S.; Ge, F. Genetically Engineered Microbial Remediation of Soils Co-Contaminated by Heavy Metals and Polycyclic Aromatic Hydrocarbons: Advances and Ecolo-gical Risk Assessment. *J. Environ. Manag.* **2021**, *296*, pp. 113185, https://doi.org/10.1016/j.jenvman.2021.113185
3. Chen, S.-Y.; Wu, J.-Q.; Sung, S. Effects of Sulfur Dosage on Continuous Bioleaching of Heavy Metals from Contaminated Sediment. *J. Hazard. Mater.* **2022**, *424*, pp. 127257, https://doi.org/10.1016/j.jhazmat.2021.127257
4. Ali, S.S.; Abdelkarim, E.A.; Elsamahy, T.; Al-Tohamy, R.; Li, F.; Kornaros, M.; Zuorro, A.; Zhu, D.; Sun, J. Bioplastic Production in Terms of Life Cycle Assessment: A State-of-the-Art Review. *Environ. Sci. Ecotechnol.* **2023**, *15*, pp. 100254, https://doi.org/10.1016/j.ese.2023.100254
5. Abdelfattah, A.; Ali, S.S.; Ramadan, H.; El-Aswar, E.I.; Eltawab, R.; Ho, S.-H.; Elsamahy, T.; Li, S.; El-Sheekh, M.M.; Schagerl, M. Microalgae-Based Wastewater Treatment: Mechanisms, Challenges, Recent Advances, and Future Prospects. *Environ. Sci. Ecotechnol.* **2022**, *13*, pp. 100205, https://doi.org/10.1016/j.ese.2022.100205
6. Qasem, N.A.A.; Mohammed, R.H.; Lawal, D.U. Removal of heavy metal ions from wastewater: a comprehensive and critical review. *Clean Water* **2021**, *4*, pp. 36, https://doi.org/10.1016/j.jenvman.2010.11.011
7. Das, S.; Blomberg von der Geest, K.; Mäkinen, Ar.; Roos, A.; Ikonen, E.; Laurila, T. Sensitive Detection of Metal Concentrations in Aqueous Solution Using Real-Time Micro-Plasma Emission Spectroscopy. **2024,** *Anal. Lett. 57*, pp. 2376-2387, https://doi.org/10.1080/00032719.2023.2294358
8. Altin, O.; Önder Özbelge, H.; Dogu, T. Effect Of Ph In An Aqueous Medium On The Surface Area, Pore Size Distribution, Density, And Porosity Of Montmorillonite, J. Colloid

Sci. **1999**, *217*, 1, pp. 19-27, https://doi.org/10.1006/jcis.1999.6271

9. Wang, J.; Guo, X. Adsorption isotherm models: classification, physical meaning, application and solving method. *Chemosphere* **2020**, *258*, pp. 12727, https://doi.org/10.1016/j.chemosphere.2020.127279
10. Swenson, H.; Stadie, N.P. Langmuir's Theory of Adsorption: A Centennial Review. *Langmuir* **2019**, *35*, pp. 5409–5426, https://doi.org/10.1021/acs.langmuir.9b00154
11. Vigdorowitsch, M.; Pchelintsev, A.; Tsygankova, L.; Tanygina, E. Freundlich isotherm: an adsorption model complete framework. *Appl. Sci.* **2021**, *11*, pp. 8078, https://doi.org/10.3390/app11178078