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USING OF WASTE SORBENT FROM FOOD INDUSTRY FOR THE REMOVAL OF COPPER IONS FROM WATER

Olha Khudoiarova*, Oleg Blazhko, Alina Blazhko

Vinnytsia Mykhailo Kotsiubynskyi State Pedagogical University,
Department of Chemistry and Methods of Chemistry Teaching, 32, Ostrozhskogo str., 21100, Vinnytsia, Ukraine
**e-mail: helgakhudoyarova@gmail.com; phone +380677485922*

Abstract. The purpose of the work was to investigate the effectiveness of using a previously regenerated spent food industry sorbent modified with sulphide and hydrosulphide ions for the removal of copper(II) ions from water. A comparative analysis of the degree of removal and adsorption of copper(II) ions by the regenerated sorbent (RS) and its modified form (MS) was carried out. Insignificant adsorption of Cu^{2+} on the surface of the RS is explained both by the nature of the adsorbate and the morphology of the adsorbent after its acid-alkaline activation. Modification of the surface of the regenerated sorbent with more active sulphide and hydrosulphide ions leads to an increase in the removal of copper(II) cations from the studied solutions by 65.5 times. IR-spectroscopy and X-ray phase analysis have shown that topochemical reactions occur on the surface of the MS, leading to the formation of copper(II) sulphide CuS and elemental sulphur. The obtained results allow us to recommend the use of a RS of the food industry, modified with sulphide and hydrosulphide ions, to remove copper(II) ions from water.

Keywords: spent sorbent, reuse, regeneration, modification, copper(II) ion, removal, adsorption.

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Introduction

Pollution by sewage and solid industrial waste is a significant burden on the environment. Various physicochemical methods are used for water purification, among which the most popular is the method of adsorption with natural and synthetic sorbents [1,2], industrial waste [3,4]. To increase the sorption capacity, modification of the sorption matrix is popular [5,6]. However, even complete wastewater treatment does not guarantee environmental safety. Solid industrial waste generated as a result of cleaning is most often buried in special storage facilities or stored in landfills. The problem of accumulation of used sorbents is partially solved by restoring their sorption properties for reuse in technological processes of purification [7]. Also, spent sorbents can be used to obtain valuable technical products, for example, components of carbon and sulphur-containing plastic lubricants [8,9] and others materials [10].

During the production of sugar syrup for soft drinks, a large amount of waste sorbents is formed, which include activated carbon and kieselguhr (diatomaceous earth). One of the promising areas of research can be the use of used sorbents for removing copper(II) ions from water.

The paper presents preliminary studies of the removal of copper(II) ions from water using a regenerated sorbent modified with sulphide and hydrosulphide ions.

Experimental

Materials

Used reagents: sodium sulphide nonahydrate ($Na_2S·9H_2O$), copper(II) sulphate pentahydrate ($CuSO_4·5H_2O$), iodine (I_2), potassium iodide (KI), sodium thiosulphate pentahydrate ($Na_2S_2O_3·5H_2O$), sodium ethylenediaminetetraacetate dihydrate ($C_{10}H_{14}N_2O_8Na_2·2H_2O$), murexid ($C_8H_8N_6O_6$), starch ($(C_6H_{10}O_5)_n$), sodium hydroxide (NaOH), hydrochloric acid (HCl, 36-38%). Reagents were purchased from Sfera Sim LLC (Lviv, Ukraine) and were used without further purification.

A mixture of activated carbon of the “Decolor A” brand and kieselguhr “Bekogur 200” and “Bekogur 3500” (manufactured by E. Begerow GmbH & Co (Germany)) in a ratio of 4:6 was used as a sorbent. The spent mixture after purification of sugar syrup was collected at the “Panda” carbonated drinks enterprise (Vinnytsia, Ukraine).

Instruments

Weighing substances were taken on an analytical balance AS 220.R2 (RADWWAG, Poland). A VELP AREC high-speed magnetic stirrer (VELP Scientifica, Italy) was used for mixing.

The sorbent surface was studied by physico-chemical methods: IR-spectroscopy of diffuse reflection (IR-Fourier-spectrometer NicoletiN 10FX of Thermo Fisher Scientific) and X-ray diffraction (diffractometer Dron-2 in monochromatic Co-K_α radiation (λ= 1.7902 Å).

Methods

Regeneration of the sorbent was carried out according to the method described by Ranskiy, A.P. *et al.* [7]. The sorbent was modified with a solution with a concentration of sulphide and hydrosulphide ions of 1.40 mol/L and 0.21 mol/L, respectively, which was prepared by dissolving a portion of $Na_2S{\cdot}9H_2O$ in distilled water. The residual concentration of sulphide and hydrosulphide ions in the filtrate after the sorbent modification was determined by the method of iodometric titration.

To remove copper(II) ions from water, model solutions of copper sulphate (300.0 mg/L) were used, which corresponded to the copper content in the washing waters of the electrochemical copper plating process after the use of acidic electrolytes with pH= 1.5-2.5. Solutions with the concentration of copper(II) cations of 1.5, 5.0, 30.0, 50.0, and 150 (mg/L) were obtained by diluting the initial solution (300.0 mg/L) with distilled water in appropriate proportions. The adsorption kinetics was studied on a solution with a concentration of Cu^{2+} ions of 150 mg/L. Research was conducted for different doses of regenerated sorbent (RS) (solid: liquid ratio of 2 g/100 mL; 5 g/100 mL; 10 g/100 mL; 15 g/100 mL and 20 g/100 mL).

The copper(II) ions in the solutions were determined by the complexometric titration method [11], the degree of ion removal and the amount of adsorption were calculated by Eqs.(1,2).

The degree of removal *E*, % of copper(II) ions was determined by Eq.(1).

$$E = \frac{C_0 - C_e}{C_0} \cdot 100 \qquad (1)$$

where, C_0 - initial concentration of copper(II) ions in the solution, mg/L;
C_e - residual concentration of copper(II) ions in the solution, mg/L.

The amount of adsorption *A*, mg/g of copper(II) ions was calculated by Eq.(2).

$$A = \frac{C_0 - C_e}{m} \cdot V \qquad (2)$$

where, C_0 – initial concentration of Cu^{2+} in the solution, mg/L;
C_e – concentration of Cu^{2+} after reaching adsorption equilibrium, mg/L;
m – sorbent mass, g;
V – the volume of the solution in which adsorption is carried out, L.

Results and discussion

A comparative analysis of the degree of removal and adsorption of copper(II) ions by the regenerated sorbent (RS) and its modified form (MS) was carried out. Sorption of copper(II) ions on the matrix surface of the sorbent takes place in a strongly acidic environment at pH= 1.5–2.5.

The obtained adsorption isotherm of Cu^{2+} ions on the RS belongs to the III-th type according to the classification of S. Brunauer [12], with a characteristic curve. This bend is caused by a weaker adsorbate-adsorbent interaction compared to the adsorbate-adsorbate interaction (Figure 1).

Kinetic studies were performed on a solution with a Cu^{2+} ion concentration of 150 mg/L. The studies were performed for a solution with a volume of 100 mL and for different masses of sorbent: 2; 5; 10; 15; 20 g. The mixture was stirred intensively and left for 0.5; 1.0; 1.5; 2.0; 4.0; 8.0; 24.0 h. According to the results of kinetic studies, it was found that the concentration of Cu^{2+} ions for all studied ratios decreases during the first 3 h, and at 4 h equilibrium is reached in the system “RS - copper(II) ions” (Figure 2).

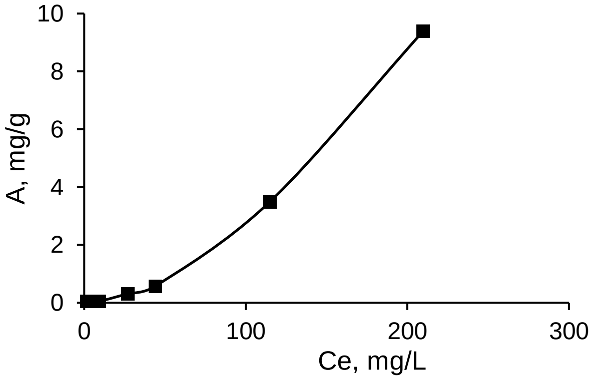

Figure 1. Adsorption isotherm of copper(II) ions on the RS.
Process conditions: V(Cu^{2+})= 100 mL, *m*(RS)= 1 g, τ= 24 h, *t*= 25 °C, pH= 1.5–2.5.

The change in the adsorption of Cu (II) ions over time for different doses of RS is shown in Figure 3.

The greatest adsorption is observed at the ratio solid: liquid of 2 g : 100 mL - 5.1 mg/g (Figure 3, curve 1), which is almost 8 times higher than for the ratio of 20 g: 100 mL - 0.6 mg/g (Figure 3, curve 5). The highest degree of removal of Cu^{2+} ions was recorded at the ratio of RS: solution 20 g: 100 mL - 85.3%, and the lowest value at the ratio of 2 g: 100 mL - 68%. At other ratios RS: solution, intermediate values of the degree of removal and adsorption are observed Cu^{2+} ions (Figure 3, curves 2-4).

The obtained experimental data do not give an unequivocal answer about the optimal amount of RS for the removal of Cu^{2+} ions. The obtained data indicate a slight adsorption of Cu^{2+} on the RS sorbent, which is explained both by the nature of the adsorbate and the morphology of the adsorbent after its acid-base activation. The results of the study showed that the degree of extraction of copper(II) ions from model solutions with a concentration of 150 mg/L on the regenerated sorbent is 23.3% and the adsorption value is about 3.5 mg/g. The studied RS sorbent exhibits cation-exchange properties. In the region of low pH values, protonation of carboxyl and phenolic groups of the sorbent occurs. Removal of copper(II) cations occurs by their binding mainly by carboxyl groups. However, there are few functional groups that provide the affinity of Cu^{2+} to this sorbent.

The degree of removal of total sulphur from aqueous solutions with a concentration of sulphide and hydrosulphide ions of 1.40 mol/L and 0.21 mol/L when modifying the regenerated sorbent is about 96%, and the adsorption value is 164 mg/g. The use of a sorbent modified with sulphide and hydrosulphide ions made it possible to increase the adsorption of copper(II) ions to 229.3 mg/g. This fact is explained by the occurrence of chemical reactions on the surface of the modified sorbent.

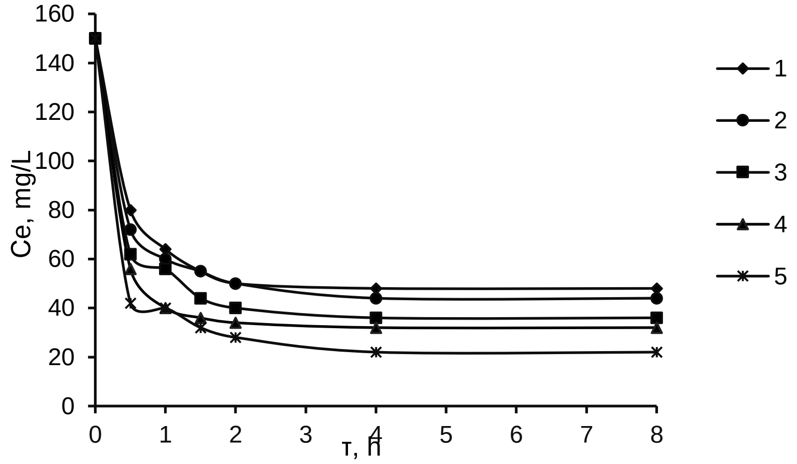

Figure 2. Kinetics curves of Cu^{2+} ions adsorption for different doses of RS (solid: liquid ratio of: 1 curve - 2 g: 100 mL; 2 curve - 5 g: 100 mL; 3 curve - 10 g: 100 mL; 4 curve - 15 g: 100 mL and 5 curve - 20 g: 100 mL), $C_0(Cu^{2+})$= 150 mg/L, $V(Cu^{2+})$= 100 mL.

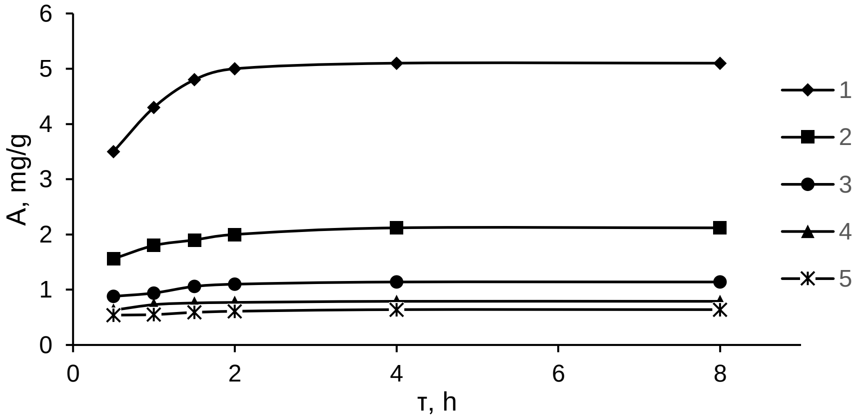

Figure 3. Change in adsorption of Cu (II) ions over time for different doses of RS (solid: liquid ratio of: 1 curve - 2 g: 100 mL; 2 curve - 5 g: 100 mL; 3 curve - 10 g: 100 mL; 4 curve - 15 g: 100 mL and 5 curve - 20 g: 100 mL).

Surface modification with more active sulphide and hydrosulphide ions leads to a significant increase in its adsorption relative to copper(II) ions. Adsorption begins with the formation of a sorption complex between the sorbate (Cu^{2+}) and the initially activated centre of the sorbent. The modified sorbent surface contains a large number of sulphide and hydrosulphide ligands, which ensure rapid adsorption of Cu^{2+} ions. The type of interaction and the formed products depend on the chemical structure of the sorbent surface, as well as on the objects of purification, the pH of the medium and some other factors [13]. The possible catalytic effect of activated carbon on the passage of topochemical transformations on the sorbent surface was taken into account. In this case, copper(II) sulphide and elemental sulphur are formed on the sorbent surface which was confirmed by X-ray studies (Figure 4). Modification of the RS surface with sulphur-containing ions (S^{2-}, HS^{-}) allowed to increase the removal of copper(II) cations by 65.5 times.

The possibility of undergoing topochemical transformations was established by IR-spectral and X-ray phase studies. In the studied samples, characteristic valence vibrations of organic functional groups were observed: –OH, –C(=O)OH, –C(=O)O– and valence vibrations of chemical bonds Si–O, C–S, Cu–S (Table 1). Associated, blurred valence vibrations of the –OH group were observed in the spectra of all studied samples in the interval 3410–3110 cm^{-1}.

There are no strong valence vibrations of the carboxyl group in the spectra –C(=O)OH in the interval 1725–1700 cm^{-1}. Instead, fluctuations in the average intensity of the carboxylate anion COO^{-} were observed in the range 1550–1510 cm^{-1}. This fact logically corresponds to the activated surface of the regenerated sorbent after its treatment with NaOH solution. In the IR spectra, there is a very strong and constant absorption at 1045 cm^{-1}. This corresponds to the fluctuations of the Si–O bond and indicates the inertness of the Bekogur brand regenerated sorbent during topochemical transformations. In many works, it is noted that activated carbon acts as an active catalyst of topochemical reactions on a solid surface [14,15]. The modofied sorbent (MS) and MS + Cu^{2+} samples in the IR spectra have weakly intense valence vibrations of the bonds *ν*(C–S) and *ν*(Cu–S), respectively, at 770–744 cm^{-1} and 590 cm^{-1}.

Table 1

Characteristic fluctuations of functional groups of IR-Fourier diffuse reflectance spectra.

Sample	*Fluctuations of functional groups in IR-Fourier spectra, cm^{-1}*					
	ν(OH)	*ν*(COOH)	*ν*(–C(=O)O)	*ν*(Si–O)	*ν*(C–S)	*ν*(Cu–S)
RS	3410 3196	–	1510	1045	–	–
MS	3390	–	1550	1045	744	–
MS + Cu^{2+}	3110	–	1550	1045	770	590

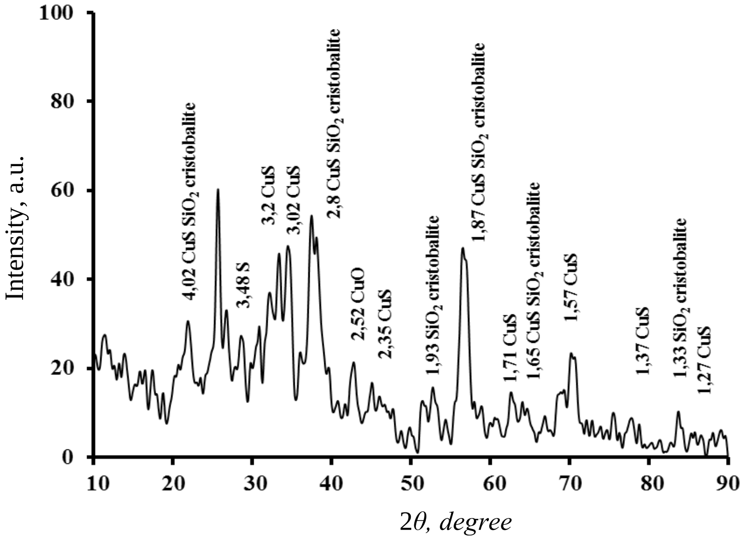

Figure 4. X-ray diffraction pattern of CuS and S compounds on the surface of the MS after removal of Cu(II) ions.

The obtained sorbent with sulphur and copper(II) sulphide sorbed on its surface can be used as a component of special purpose plastic lubricants [8,9,16]. There is a high probability of CuS_2 formation during the operation of various friction pairs [16]. CuS_2 is considered as a possible analogue of MoS_2 in plastic lubricants.

Conclusions

In the case of removal of copper(II) cations by a regenerated sorbent, their sorption is carried out mainly by carboxyl groups, the degree of removal is 23.3%. When using a modified sorbent, the removal of copper(II) cations occurs due to sulphide-hydrosulphide sorbed fragments. The use of a sorbent modified with sulphide and hydrosulphide ions increases the degree of removal of copper(II) cations from the studied solutions by 65.5 times compared to the unmodified regenerated sorbent. The feasibility of using a regenerated sorbent based on activated carbon and kieselguhr modified with sulphide and hydrosulphide ions to remove copper(II) ions from water was established.

References

1. Malovanyy, M.; Palamarchuk, O.; Trach, I.; Petruk, H.; Sakalova, H.; Soloviy, K.; Vasylinych, T.; Tymchuk, I.; Vronska, N. Adsorption extraction of chromium ions (III) with the help of bentonite clays. Journal of Ecological Engineering, 2020, 21(7), pp. 178–185. DOI: https://doi.org/10.12911/22998993/125545
2. El Sayed, E.E. Natural diatomite as an effective adsorbent for heavy metals in water and wastewater treatment (a batch study). Water Science, 2018, 32(1), pp. 32–43. DOI: https://doi.org/10.1016/j.wsj.2018.02.001
3. Chouchane, T.; Boukari, A.; Khireddine, O.; Chibani, S.; Chouchane, S. Cu (II) removal from aqueous medium using blast furnace slag (BFS) as an effective adsorbent. Eurasian Journal of Chemistry, 2023, 28(2), pp. 115–130. DOI: https://doi.org/10.31489/2959-0663/2-23-3
4. Tsai, W.-T.; Hsu, H.-C.; Su, T.-Y.; Lin, K.-Y.; Lin, C.-M. Removal of basic dye (methylene blue) from wastewaters utilizing beer brewery waste. Journal of Hazardous Materials, 2008, 154(1-3), pp. 73–78. DOI: http://doi.org/10.1016/j.jhazmat.2007.09.107
5. Khokhotva, A.P. Extraction of heavy metal ions from water using the phosphorylated carbon sorbent based on natural raw materials. Journal of Water Chemistry and Technology, 2019, 41, pp. 242–247. DOI: https://doi.org/10.3103/S1063455X19040064
6. Yantasec, W.; Lin, Y.; Fryxell, G.E.; Alford, K.L.; Busche, B.J.; Johnson, C.D. Selective removal of copper(II) from aqueous solution using fine – grained activated carbon functionalized with amine. Industrial & Engineering Chemistry Research, 2004, 43(11), pp. 2759–2764. DOI: https://doi.org/10.1021/ie030182g
7. Ranskiy, A.P.; Khudoyarova, O.S.; Gordienko, O.A.; Titov, T.S.; Kryklyvyi, R.D. Regeneration of sorbents mixture after the purification of recycled water in production of soft drinks. Journal of Water Chemistry and Technology, 2019, 41, pp. 318–321. DOI: https://doi.org/10.3103/S1063455X19050084
8. Khudoiarova, O.; Blazhko, O.; Blazhko, A. Receiving of new carbon-sulfur-containing plastic lubricants based on regenerated products and used sorbents. Key Engineering Materials, 2023, 944, pp. 51–58. DOI: https://doi.org/10.4028/p-8hu326
9. Khudoyarova, O.; Gordienko, O.; Blazhko, A.; Sydoruk, T.; Ranskiy, A. Desulfurization of industrial water-alkaline solutions and receiving new plastic oils. Journal of Ecological Engineering, 2020, 21(6), pp. 61–66. DOI: https://doi.org/10.12911/22998993/123254
10. Russ, W.; Mortel, H.; Meyer-Pittroff, R.; Babeck, A. Kieselguhr sludge from the deep bed filtration of beverages as a source for silicon in the production of calcium silicate bricks. Journal of the European Ceramic Society, 2006, 26(13), pp. 2547–2559. DOI: https://doi.org/10.1016/j.jeurceramsoc.2005.04.023
11. Schwarzenbach, G.; Flashka, G. Complexometric titration. Helvetica Chimica Acta, 1968, 51(8), pp. 1833.
12. Donohue, M.D.; Aranovich, G.L. Classification of Gibbs adsorption isotherms. Advances in Colloid and Interface Science, 1998, 76–77, pp. 137–152. DOI: https://doi.org/10.1016/S0001-8686(98)00044-X
13. Montoya, A.; Mondragon, F.; Truong, T.N. Adsorption on carbonaceous surfaces: cost-effective computational strategies for quantum chemistry studies of aromatic systems. Carbon, 2002, 40(11), pp. 1863–1872. DOI: https://doi.org/10.1016/S0008-6223(02)00035-0
14. Xue, Y; Guo, Y; Zhang, Z; Guo, Y; Wang, Y; Lu, G. The role of surface properties of activated carbon in the catalytic reduction of NO by carbon. Applied Surface Science, 2008, 255(5), part 2, pp. 2591–2595. DOI: https://doi.org/10.1016/j.apsusc.2008.07.167
15. Li, B.; Yu, D.; Cao, Z.; He, T.; Chen, X.; Zheng, W. Effect of acid-treatment on the activated carbon of Ru/AC catalysts for catalytic decomposition of hydroxylamine nitrate and hydrazine nitrate. Applied Catalysis A: General, 2024, 681, pp. 119801. DOI: https://doi.org/10.1016/j.apcata.2024.119801
16. Khudoyarova, O.; Ranskiy, A.; Korinenko, B.; Gordienko, O.; Sydoruk, T.; Didenko, N.; Kryklyvyi, R. Integration of technological cycles of industrial waste processing. Journal of Ecological Engineering, 2021, 22(6), pp. 209–214. DOI: https://doi.org/10.12911/22998993/137821