Treatment of textile industry wastewater with metallurgical waste

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In this paper, the possibility of purifying textile industry wastewater using metallurgical adsorbents: anode dust and waste moulding mixture was studied. The wastewater of the textile industry was simulated in such a way that a laboratory solution of copper and zinc ions was made and the competitive adsorption of the two ions was monitored. The obtained results indicated that the adsorption efficiency of both adsorbents is very high (52.3 to 94.8 %) with a slightly higher affinity towards copper ions. The experimental data were modeled by the Langmuir and Freundlich isotherm. The obtained results indicated that zinc adsorption takes place according to the Freundlich model, and copper according to the Langmuir model.

Keywords: *competitive adsorption, anode dust, waste mould mixture, wastewater of the textile industry*

1. Introduction

It is known that the main role of clothes is to protect the body from external influences. In the beginning, it was made by hand from natural materials, most often leather and fur. With the development of civilization, clothing indicates strategic affiliation, indicates status, becomes a feature of organized groups, such as the army, judiciary, etc. With the further progress of civilization, clothing becomes a "means" for beautification. All of the above leads to the improvement of clothing production procedures, including the use of special means for dyeing, bleaching, washing, etc., which to a greater or lesser extent end up in the wastewater of the textile industry. This is precisely one of the reasons why the textile industry is considered an industry that significantly burdens the environment. Various heavy metals (copper, iron, manganese, chromium, zinc, etc.), surfactants, softeners, dyes, etc., can often be found in textile industry wastewaters [1-5]. Heavy metals found in wastewater pose a significant threat to the environment. These metals have the possibility of accumulation in living organisms, especially in the human body. In addition, heavy metals often enter biochemical cycles in the human body, causing various disorders. Some of the heavy metals are carcinogenic, mutagenic and/or genotoxic [6]. Heavy metals are most often introduced into the wastewaters of the textile industry through the dyeing process. During this process, dyes are used that usually contain chromium, zinc, cadmium, copper and some other heavy metals, which depends on the type of dye used. In addition, they also enter the water from metal parts of various machines used in production, but also from various chemicals used in production. Heavy metals in textile industry wastewater can come from both natural and artificial fibers [7].

On the other hand, the metallurgical industry that does not generate large amounts of wastewaters generates large amounts of waste materials, such as slag, various dusts, blast furnace sludge, waste mould mixture, etc. The mentioned waste materials cannot be recycled. The only way is disposal in landfills. Since metallurgical production produces various waste in large quantities, the burden on the environment is also significant in this industry [8, 9]. The removal of various contaminants from water is necessary, and therefore various water purifycation procedures have been developed. Which of the procedures will be used depends primarily on the water pollution. Adsorption can be used to remove heavy metals from wastewater, including wastewater from the textile industry. Activated carbon is most often used during adsorption, as one of the adsorbents that showed the best adsorption properties. However, activated carbon has a very high price, so cheaper adsorbents are often used. Today, this is the most common application of some waste materials, especially industrial waste. In this way, in addition to the removal of heavy metals from water, the amount of waste materials at the landfill is also reduced [10, 11].

This paper studies the possibility of removing heavy metals, copper and zinc, which can be found in wastewater from the textile industry using metallurgical waste - anode dust and waste mould mixture. Anode dust (AD) is a waste produced during the production of anodes that are used in the electrolytic production of aluminium. During the production of anodes, pressing, baking and transportation are carried out, during which dust is generated. The resulting dust has the same chemical composition as the anodes, but due to the inappropriate granulometric composition, it cannot be used or returned to the anode production process. A mould mixture consisting of silica sand, bentonite as a binder, water and additives is very often used in foundries to make moulds into which the melt is poured during the production of metal castings. After cooling and solidification of the melt, the mould is broken, and the mould mixture is refreshed and used again in the casting process. The reuse of the mould mixture is limited to a certain number of casting cycles, depending on the temperature, type of melt, type of mould mixture, etc. After the mould mixture loses certain properties, it can no longer be used in the casting production process and becomes waste, i.e. waste mould mixture (WMM).

2. Experimental

A laboratory prepared solution of Zn(II) and Cu(II) ions was used as adsorbate, which simulated wastewater from the textile industry. Two types of metallurgical waste were used as adsorbents: anode dust and waste mould mixture.

Both types of waste were dried at 105 °C to a constant mass before adsorption. Their characterization was carried out using inductively coupled plasma optical emission spectroscopy (ICP-OES) to determine chemical composition (Perkin Elmer Optima 2100), Fourier transform infrared spectroscopy (FT-IR) to determine functional groups (Perkin Elmer Spectrum One) and the Brunauer-Emmett-Teller method (BET) (Micrometritics ASAP 2000) to determine specific surface area, volume and pore diameter.

Batch adsorption experiment was carried out by putting in contact 0.5 g of adsorbent and 50 cm^3 of solution (25 ml Zn(II) + 25 ml Cu(II)). The solutions were prepared by diluting the standard solution of 1000 mg/dm^3 to working solutions with concentrations of 10, 15, 20 and 30 mg/dm^3. Adsorption systems were in contact for 10, 15, 20, 30 and 40 minutes at room temperature. After the contact time had expired, filtering was carried out through a blue ribbon filter paper. The concentration of Zn(II) and Cu(II) ions after adsorption was determined in the filtrates using ICP-OES.

From the obtained results, the adsorption capacity was calculated using the following equation:

$$q_e = \frac{(c_0 - c_e)}{m} \cdot V \qquad (1)$$

Where is:
c_0 - initial adsorbate concentration, mg/dm^3,
c_e - equilibrium concentration of adsorbate, mg/dm^3,
m - adsorbent mass, g,
V - adsorbate volume, dm^3.

The following equation was used to evaluate the adsorption efficiency:

$$E = \frac{(c_0 - c_e)}{c_0} \cdot 100 \qquad (2)$$

Where is:
E - adsorption efficiency, %
c_0 - initial adsorbate concentration, mg/dm^3,
c_e - equilibrium concentration of adsorbate, mg/dm^3,

Experimental data were modeled using the two most common isotherms, the Freundlich and Langmuir isotherms, which are shown by the following equations.
Freundlich isotherm:

$$q_e = K_F \cdot c_e^{1/n} \qquad (3)$$

Where is:
q_e - adsorption capacity, mg/g,
c_e - equilibrium concentration of adsorbate, mg/dm^3,
K and n - Freundlich constants.

Langmuir isotherm:

$$q_e = \frac{q_m \cdot K_L \cdot c_e}{1 + K_L \cdot c_e} \qquad (4)$$

gdje je:
q_e - adsorption capacity, mg/g,
c_e - equilibrium concentration of adsorbate, mg/dm^3,
q_m - maximum adsorption capacity, mg/g,
K_L – Langmuir constant.

Tab.1 Chemical composition of waste mould mixture

Element	Si	Al	Na	Fe	Ca	Mg	K	P	Mn	Ba	Other elements
wt. %	89.4	1.48	0.62	0.59	0.37	0.25	0.17	0.02	0.01	0.01	7.08

Tab.2 Chemical composition of anode dust

Element	C	Al	Si	Ca	Fe	Na	Mg	Ni	Other elements
wt. %	96.8	1.27	1.27	0.22	0.19	0.13	0.07	0.02	0.03

3. Results and Discussion

Tables 1 and 2 show the chemical compositions of the tested adsorbents, waste mould mixture and anode dust.

Figures 1 and 2 show the results obtained using FTIR.
From the results obtained after the characterization of the samples, it is evident that these are two completely different adsorbents.

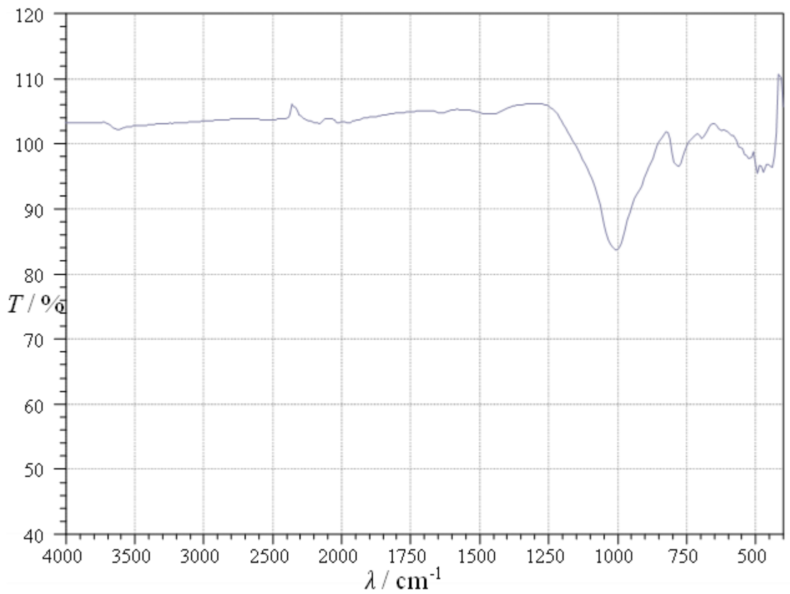

Fig.1 FTIR analysis of waste mould mixture

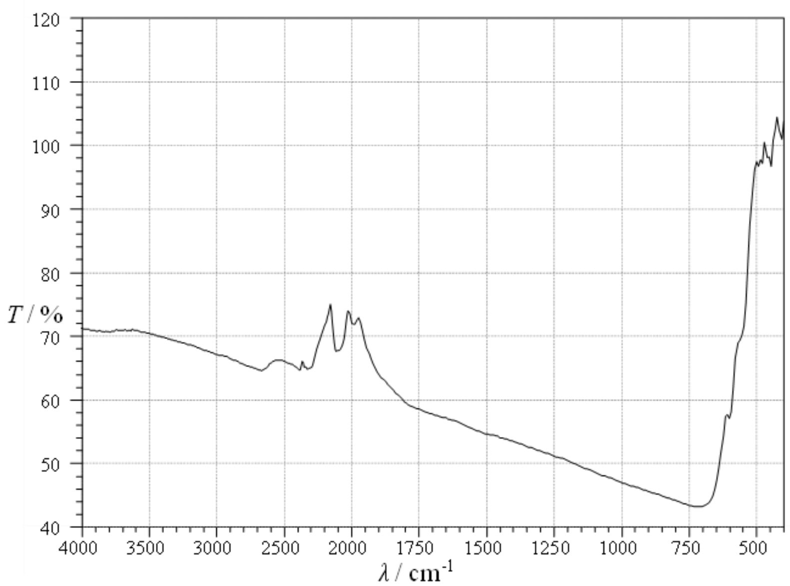

Fig.2 FTIR analysis of anode dust

The waste mould mixture has the most silicon in its composition, which comes from silica sand, which makes up most of the waste mould mixture. Carbon predominates in the anode dust, since coke is the main component in the production of anodes. Figs.1 and 2 show that there are vibrations at wavelengths correspondding to the groups Si-O, Si-OH, Si-O-Si (Fig.1) and γ(C-H) group (Fig.2). Data on the chemical composition and data obtained by FTIR analysis indicate good adsorption properties of the adsorbents used, since it is known that substances based on SiO_2 and carbon have good adsorption properties and are successfully used as adsorbents. According to literature data, adsorption on carbon materials is somewhat better than adsorption on other materials, regardless of the type of adsorbate [12, 13]. It can be expected that the investigated systems will behave in a similar way since there are differences in the specific surface area, volume and diameter of the pores between the anode dust (specific surface area 6.48 m^2/g, pore volume $2.37 \cdot 10^{-2}$ cm^3/g, pore diameter 13.22 nm) and waste mould mixture (specific surface area 4.33 m^2/g, pore volume 0.0134 cm^3/g, pore diameter 11.28 nm).
Fig.3 shows the diagram:

$$q_e = f(c_e)$$

It can be seen from Fig.3 that the adsorption capacity increases with the increase in the concentration of Cu and Zn ions. During the adsorption of copper and zinc ions on the anode dust, the adsorption takes place very quickly, which indicates a large number of free places compared to the waste mould mixture. This can be related to the larger specific surface area of the anode dust, the volume and diameter of the pores, as well as the specific functional groups.

Fig.4 shows the dependence of adsorption capacity on adsorbent-adsorbate contact time.

It can be seen from Figure 4 that copper adsorption takes place relatively quickly in the first ten minutes. After fifteen minutes of contact of copper ions with the adsorbent, there is a slight drop in adsorption, and after thirty minutes equilibrium is established. This course of adsorption indicates a large number of free sites on the adsorbent at the very beginning of adsorption. Adsorption of zinc takes place somewhat slower; equilibrium is established after fifteen minutes, and a slightly lower adsorption capacity is achieved compared to the adsorption of copper on both tested adsorbents. This phenomenon occurs probably because the tested adsorbents have a higher affinity for copper ions than for zinc ions.

In general, the adsorption of both copper and zinc is better on the anode dust than on the waste mould mixture. This theory is also supported by the results obtained by BET analysis, which indicate that anode dust has a larger specific surface area, volume and pore diameter. Furthermore, the functional groups on the anode dust are in the form of organic functional groups, which are easier to bind than Si-O and Si-O-Si groups.

In support of the above is the fact that the adsorption efficiency for an initial concentration of 10 ppm (mg/dm^3) and at the moment of establishment of equilibrium moves in the following way:

AD-Cu > WMM-Cu >
>AD-Zn > WMM-Zn.

Very high efficiency values ranging from 52.3 to 94.8 % also indicate good adsorption properties of the tested adsorbents.

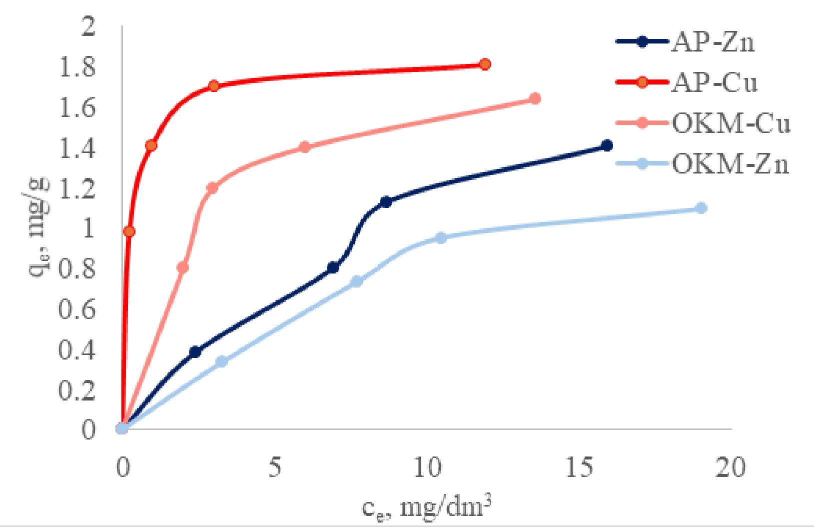

Fig.3 Dependence of adsorption capacity on the equilibrium concentration of adsorbate

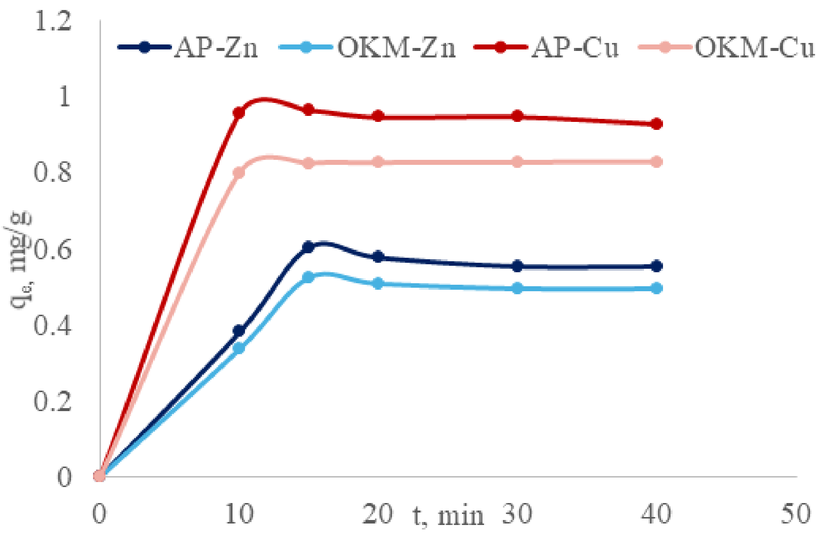

Fig.4 Dependence of adsorption capacity on adsorbent-adsorbate contact time (c_0 = 10 mg/dm^3)

Table 3 shows the parameters obtained on the basis of modelling with the Freundlich and Langmuir isotherms.

As a rule, to determine the adsorption model that best describes the adsorption process, a comparison of determination coefficients, R^2, is used. In this case, by comparing the coefficients of determination, it could be concluded that zinc adsorption takes place according to the Freundlich model, and copper adsorption according to the Langmuir model. For a more accurate definition of adsorption according to the Langmuir model, the obtained maximum adsorption capacities q_m should certainly be taken into account. By comparing the maximum adsorption capacity (q_m) and the equilibrium adsorption capacity (q_e), it is evident that the stated capacities are very similar for the AD-Cu and WMM-Cu systems, which could also indicate that in the mentioned systems adsorption takes place according to the Langmuir model. This statement is supported by the fact that the Freundlich constant 1/n is negative for the WMM-Cu system.

Tab.3 Parameters obtained on the basis of modelling with the Freundlich and Langmuir isotherm

		AP-Zn	OKM-Zn	AP-Cu	OKM-Cu
	$q_{e.}$ mg/g	0.577	0.523	0.948	0.828
Freundlich isotherm	Eq.	y=0.7117x-1.5591	y=0.6984x-1.8326	y=0.1574x+0.2782	y=-0.2314x-0.0625
	R^2	0.9722	0.9338	0.907	0.9994
	$1/n$	0.712	0.698	0.157	-0.231
	K_F	0.210	0.160	1.321	0.939
Langmuir isotherm	Eq.	y=0.3621x+5.4256	y=0.5004x+7.1444	y=0.5417x+0.1377	y=0.5188x+1.2041
	R^2	0.9072	0.9002	0.9999	0.9939
	$q_{m.}$ mg/g	2.762	1.983	1.846	1.927
	K_L	0.067	0.700	3.934	0.431

It is known from the literature [14] that the Freundlich model refers to physical adsorption, and the Langmuir model refers to chemisorption. Therefore, it can be concluded that the adsorption of zinc on both tested adsorbents takes place as physical adsorption in one layer, and the adsorption of copper as chemisorption.

4. Conclusion

From the obtained results, it can be concluded that both tested adsorbents, anode dust and waste mould mixture can be used for the purification of wastewaters from textile industry that contain Cu(II) and Zn(II) ions in its composition. These conclusions are indicated by the results obtained after the characterization of the samples, but also based on the adsorption experiment. The results of the determination of the chemical composition indicate that there is carbon in the anode dust, and silicon in the waste mould mixture, which are otherwise good adsorbents. Furthermore, the results of the FTIR analysis show the presence of SiO, Si-O-Si and Si-OH, or C-H groups that contribute to the adsorption properties. Since it is a competitive adsorption in which copper and zinc ions compete with each other, the results showed that both adsorbents have a greater affinity for copper ions. Despite this, the adsorption experiment showed that both adsorbents simultaneously show high removal efficiency for both ions. Adsorption of zinc on both adsorbents takes place according to the Freundlich model, and adsorption of copper according to the Langmuir model.

References:

[1] Azanaw, A., B. Birlie, B. Teshome, M. Jemberie: Textile effluent treatment methods and eco-friendly resolution of textile waste-water, Case Studies in Chemical and Environmental Engineering, 6 (2022), 1-13.
[2] Halepoto, H., T. Gong, H. Memon, Current status and research trends of textile wastewater treatments - A bibliometric-based study, Frontiers in Environmental Science, 10 (2022), 1-18.
[3] Pavunc, M., E. Vujasinović, I. Matijević, Tekstil u kontekstu održivog razvoja, Tekstil 63 (2014.) 5-6; 195-203.
[4] Jurac, J., E. Felić, V. Jurac, Otpadne vode u Pamučnoj industriji Duga resa, Sigurnost, 50 (2008) 2, 129 – 138.
[5] Pušić, T., B. Vojnović, N. Dimitrov, M. Čurlin, K. Višić, Generiranje i otpu-štanje fibrila i funkcionalnih čestica u procesu pranja, Book of Proceedings 2nd International Conference The Holistic Approach to Environment, ur. A. Štrkalj, Z. Glavaš, Sisak: Udruga za promicanje cjelovitog pri-stupa okolišu, 2021., 512-520.
[6] Nordberg, G. F., B. A. Fowler, M. Nordberg, L. Friberg, Handbook of Toxi-cology of Metals, European Environment Agency, Copenhagen, 2005.
[7] Bisschops, I., H. Spanjers, Literature review on textile wastewater characterisation, Environmental Technology, 24 (2003), 1399-1411
[8] Rađenović, A. A. Štrkalj, J. Malina, Svojstva kemijski aktivirane ugljične anodne prašine, Enginering Review, 29 (2009) 2, 13-20.
[9] Štrkalj, A., Z. Glavaš, Lj. Slokar, Microstructural and equilibrium adsorption study of the system of waste foundry molding sand/Cu (II) ions, Archives of Metallurgy and Materials, 61(2016)4, 1805–1812.
[10] Basar, C. A., Applicability of the various adsorption mo-dels of three dyes adsorption onto activated carbon pre-pared waste apricot, Journal of Hazardous Materials, 135 (2006) 1–3, 232-241.
[11] Maguana, Y. E., N. Elhadiri, M. Benchanaa, R. Chikri, Activated Carbon for Dyes Removal: Modeling and Understanding the Adsorp-

tion Process Journal of Chemistry, 1 (2020) 1-9.

[12] Shawabkeh, A., N. M. Faqir, K. M. Rawajfeh, I. A. Hussein, A. Hamza, Adsorption of CO_2 on Cu/SiO_2 nano-catalyst: Experimental and theoretical study, Applied Surface Science, 586 (2022), 152726.

[13] Sabzehmeidani, M. M., S. Mahnaee, M. Ghaedi, H. Heidari, V. A. L. Roy, Carbon based materials: a review of adsorbents for inorganic and organic compounds, Materials Advances, 2 (2021), 598-627.

[14] Fouad, M. R., Physical characteristics and Freundlich model of adsorption and desorption isotherm for fipronil in six types of Egyptian soil, Current Chemistry Letters 12 (2023), 207-216.