Environmentally friendly waste for wastewater treatment

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In this paper, the adsorption properties of two wastes from the metallurgical industry were studied: waste after shot blasting of the castings and waste moulding mixture, and waste from the wood industry, i.e. oak sawdust. A solution of Cu(II) ions was used as the adsorbate. Experimental data have shown that the waste from the metallurgical industry can be used as an adsorbent for removal of Cu(II) ions from wastewater. For oak sawdust, it could not be confirmed with certainty whether it had adequate adsorption properties due to the release of substances that lead to the coloration of the adsorbates. Lagergren's and Ho's model was used to describe the adsorption kinetics of the system waste moulding mixture/Cu(II) ions and waste after shot blasting of the castings/Cu(II) ions. It was concluded that both systems are better described by Ho's model, i.e. that the adsorption kinetics in both systems take place according to pseudo-second order reactions.

Keywords: *environmentally friendly waste, wastewater, Cu(II) ions, adsorption kinetics*

1. Introduction

Preservation of the environment includes, among other things, human activities in terms of rational use of resources, but also the production of as little waste as possible. European Union policies aim to reduce the impact of waste on the environment. Nevertheless, in 2018, 5.2 tonnes of waste per inhabitant were produced in the countries of the European Union alone, of which only 38.1% was recycled [1]. Therefore, the longterm plan of this policy is to reduce waste generation and, in cases where it is not possible to avoid waste generation, to recycle or safely dispose of waste [1]. Recently, there has been a lot of research on how to use industrial waste for wastewater treatment [2-5].

Contamination of wastewater with heavy metals is very common. Heavy metals are elements that, in very small amounts, are essential for human health because they are involved in almost all biochemical reactions in the body. However, elevated concentrations of heavy metals in the body are toxic, sometimes carcinogenic, and even deadly. Copper is one of the heavy metals that is needed in small amounts for the normal functioning of the body. Its deficiency in the body leads to serious health problems such as mineral loss in the bones, anemia, increased cholesterol, etc. On the other hand, people who are exposed to higher concentrations of copper through occupational exposure to copper, but also through the environment (water, air, soil), also have significant health problems that manifest themselves in behavioural disorders, learning difficulties, tremors, mental disorders, etc. [6]. For these reasons, it is very important to reduce the concentration of heavy metals in the environment. The removal of heavy metals from water is particularly important, but it also

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*Paper presented at the 2nd International Conference “The Holistic Approach to Environment”, May 28, 2021, Sisak, Croatia attracts the attention of researchers because it allows the use of waste materials as a means of binding heavy metals. Biological wastes are most commonly used, such as various biomasses of microorganisms, wastes from food, oil and metallurgical industries, but also some natural materials (clay, zeolites, soil, etc.). The most suitable method for this purpose is adsorption. By using the above materials it is possible to adsorb almost 80-99.9% of the pollution in the wastewater [7].

Apart from the fact that the use of waste materials as adsorbents ensures high efficiency in the removal of pollution, these adsorbents are also very cheap. Moreover, their use reduces the amount of waste sent to landfills or disposed of, which undoubtedly contributes to the protection of the environment [8].

In this research, the adsorption properties of wastes from metallurgical industry were studied: waste moulding mixture and waste after shot blasting of castings, and waste from the wood industry, i.e. oak sawdust. Adsorption of copper ions from an aqueous solution onto the above adsorbents was performed. In addition, the kinetics of the adsorption systems waste moulding mixture/Cu(II) ions, waste after shot blasting/Cu(II) ions and oak sawdust/Cu(II) ions were studied.

2. Experimental

The adsorption characteristics of three types of waste were studied: waste moulding mixture, waste after shot blasting and oak sawdust, as well as the kinetics of adsorption of Cu(II) ions on the studied wastes. The waste moulding mixture represents the waste produced in the foundry after multiple castings of molten metal into moulds made from green sand. Most of this waste consists of quartz sand (SiO_2).

Waste after shot blasting is produced during cleaning of castings after casting. The base of this waste is steel shot and scale particles, as well as particles of the moulding mixture. Sawdust is the waste produced during sawing and processing of oak wood.

Since sawdust is a waste of organic origin, the basis of this waste is carbon.

The experiment was carried out in such a way that 0.5 g of waste was weighed and contacted with 25 ml of a solution of Cu(II) ions with an initial concentration of 1000 mg/L, which was used as adsorbate. In this way, three adsorption systems were created: waste moulding mixture/Cu(II) ions, waste after shot blasting/Cu(II) ions and oak sawdust/Cu(II) ions. The contact time between adsorbent and adsorbate was 1, 3, 5, 15, 30 and 60 minutes. After the tested times, filtration was performed and the concentration of Cu(II) ions in the filtrate after adsorption was determined using the method UV-VIS according to the standard procedure [9].

From the results obtained, the adsorption capacity was calculated according to the following eq. (1).

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

where is:
q_e – adsorption capacity, mg/g,
c_0 - initial adsorbate concentration, mg/L,
c_e – equilibrium concentration of adsorbate, mg/L,
m – mass of adsorbent, g,
V – volume of adsorbate, L.

To describe the adsorption rate, the measurement results were processed using two kinetic models: Lagergren and Ho, eq. (2) and (3).

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \qquad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

where is:
q_t – adsorption capacity in time t, mg/g,
q_e – equilibrium adsorption capacity, mg/g,
t – contact time, min,
k_1 - first-order reaction rate constant, min,
k_2 - second-order reaction rate constant, g/mg·min.

3. Results and discussion

Fig.1 shows the dependence of the adsorption capacity on the contact time between adsorbent and adsorbate.

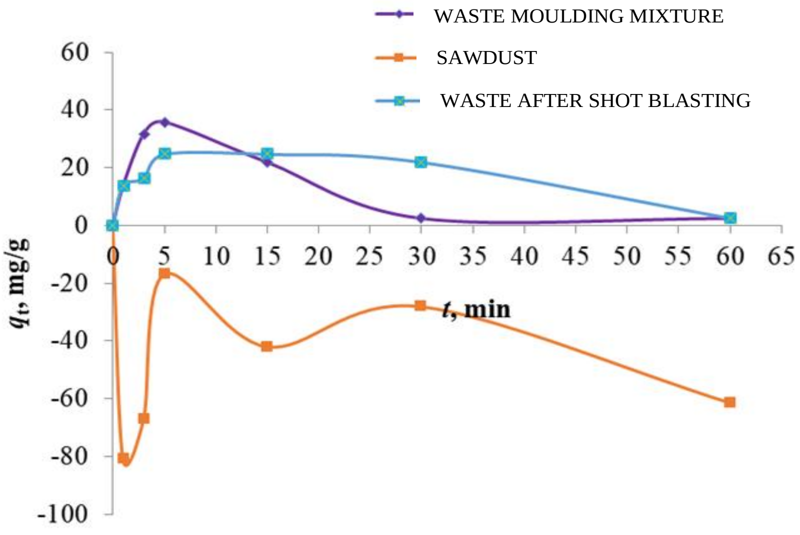

Fig.1. Dependence of adsorption capacity on contact time adsorbent/adsorbate

From Fig.1 it can be seen that the adsorption capacity of Cu(II)ions on waste moulding mixture and waste after shot blasting increases with time. The maximum capacity is reached in 15 minutes in the system waste after shot blasting/ Cu(II)ions, ie. in 5 minutes in the system waste moulding mixture Cu(II)ions. The obtained data indicate that the dynamic equilibrium is reached in 15 or 5 minutes (depending on the tested system). After that, the adsorption capacity decreases in both systems. This could indicate that all available sites on the adsorbent are occupied and there is no possibility to bind additional Cu(II) ions. There is also the possibility that both adsorption and desorption occur simultaneously, and after equilibrium has been reached, desorption is more dominant [10].

The adsorption capacity of Cu(II) ions on sawdust shows a trend of alternating increase and decrease, which is possible but not common for adsorption. This would also imply that both adsorption and desorption occur simultaneously. However, during the contact of sawdust/Cu(II) ions, the formation of a coloration of the solution was observed, which ultimately led to a problem in the formation of complexes and the development of a colour during the spectrometric measurements. Precisely for this reason, it was not possible to accurately determine the concentration of Cu(II) ions in the solution after adsorption. Therefore, the data presented in Fig.1 cannot be considered meaningful, i.e., based on the obtained results it is not possible to conclude whether adsorption takes place, according to which model and what is the adsorption capacity. In any case, it is necessary to repeat the measurements with a different instrument and/or method. It is assumed that the coloration of the adsorbate is due to the release of tannins from the sawdust, which everyone should check with appropriate methods. In the event that tannins are released, tannin removal should be performed before determining the concentration of Cu(II) ions after adsorption.

From the comparison of adsorption capacities, it can be seen that the waste moulding mixture has the best adsorption properties. At the moment of equilibrium, the adsorption capacity for the waste moulding mixture/Cu(II) ions system is 35.8 mg/g and for the waste after shot blasting/Cu(II) ions system is 24.7 mg/g. It can be concluded that both wastes can be used to remove Cu(II) ions from wastewater. The use of sawdust in wastewater treatment processes by adsorption is questionable precisely because of the formation of coloration. The coloration certainly indicates the release of undesirable substances into the water, which requires the removal of these substances from the treated water before discharge into natural recipients. This step would certainly have a negative impact on the economics of using sawdust as an adsorbent.

The experimental data for the systems waste moulding mixture/ Cu(II) ions and waste after shot blasting/Cu(II) ions were processed with kinetic equations (2) and (3), and the obtained results are shown in Tab.1.

The selection of the kinetic model that best describes the adsorption systems is done by comparing the correlation coefficients [10]. The obtained data (Tab.1) suggest that the adsorption kinetics of the two studied systems is better described by the Lagergren model, ie. adsorption proceeds according to the pseudo-first order model. However, a comparison of the actual (experimental) adsorption capacity, eq. (1), and the theoretical adsorption capacity, Tab.1, eq. (2) and (3) shows significant discrepancies. Comparison of the above parameters for Ho's model shows better agreement between the experimental and theoretical adsorption capacities, indicating that the adsorption kinetics of both tested systems proceed according to Ho's model, ie. pseudo-second-order reaction kinetics. This is supported by the fact that the correlation coefficients for both systems are greater than 0.64, indicating a strong correlation [11].

Tab.1. Kinetic parameters for the systems waste moulding mixture/Cu(II) ions and waste after shot blasting/Cu(II) ions

	ADSORPTION SYSTEM					
KINETIC MODEL	**waste moulding mixture/Cu(II) ions**			**waste after shot blasting/Cu(II) ions**		
Lagergren's model	Linear eq.	q_e. mg/g	k_1. min	Linear eq.	q_e. mg/g	k_1. min
	y=13.873x+1.4397 r^2=1	4.21	13.873	y=-2.7778x+25 r^2=1	$72 \cdot 10^9$	-2.778
Ho's model	Linear eq.	q_e. mg/g	k_2. g/mg·min	Linear eq.	q_e. mg/g	k_2. g/mg·min
	y=0.0165x+0.053 r^2=0.9594	60.61	0.56	y=0.0383x+0.0113 r^2=0.9211	26.10	0.54

4. Conclusion

From the results of this study, the waste after shot blasting and waste moulding mixture can be used to remove Cu(II) ions from wastewater. When Cu(II) ions are adsorbed on oak sawdust, substances are released that cause the coloration of the wastewater. For this reason, it was not possible to accurately determine the concentration of Cu(II) ions in the solution after adsorption, and it could not be determined whether adsorption had occurred. In addition, the release of substances that cause coloration of the wastewater limits the application of the adsorbent, even if it has good adsorption properties, because it requires additional treatment of the wastewater before discharge into natural recipients. Studies on the kinetics of adsorption show that in the systems waste moulding mixture/Cu(II) ions and waste after shot blasting/Cu(II) ions, equilibrium is reached relatively quickly, after 5 and 15 minutes, respectively. Both systems investigated follow pseudo-second order reaction kinetics.

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