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REMOVAL OF HEAVY METALS FROM WASTEWATER WITH THE HELP OF ADSORBENT MATERIALS OBTAINED FROM SLAG PRODUCED AS A RESULT OF STEELMAKING ACTIVITIES

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Abstract

In addition to natural pollution, the environment is also affected by anthropogenic pollution, which has increased more and more with the development of industry and the excessive use of natural resources. A significant form of environmental pollution is heavy metal pollution. The most important sources of heavy metal pollution of the aquatic environment can be the discharge of domestic and industrial wastewater, agriculture and industrial processes. One way of removing heavy metals from wastewater is the application of adsorption processes using efficient adsorbents that are relatively easy to find, in large quantities and at a low price. These adsorbents can come from by-products obtained from industrial processes, such as slag resulting from the production of pig iron and steel. In this work, the use of blast furnace slag was followed to observe its ability to adsorb heavy metals from wastewater. The use of slag in the removal of heavy metals is a challenge and a way to research because there are multiple studies that provide evidence that slag can be used in wastewater treatment.

Key words: *slag, adsorbent material, wastewater.*

INTRODUCTION

A global problem is the pollution of water, surface and underground, and soil with heavy metals, which present a high toxicity and a slight biological enrichment, which makes them very dangerous for the environment and, implicitly, for human health (Ado-Ekiti et al., 2024). Heavy metals are known to be toxic and carcinogenic agents when discharged into the environment, which pose serious health problems and threaten flora and fauna in water bodies and soil (Ayesha Al Ali et al., 2021).

Chemical elements with an atomic weight between 63.5 and 200.6 and a specific gravity greater than 5 g/cm^3 are known as heavy metals (Ado-Ekiti et al., 2024). Heavy metals are ions of lead, cadmium, zinc, copper, cobalt, chromium, iron, nickel, arsenic, mercury, etc. Lead (Pb) is one of the most widespread pollutants that can accumulate quite easily in the human body, being non-biodegradable. The presence of lead in drinking water and food chains can cause neurological disorders, anemia, impairment of hemoglobin synthesis, cancer, kidney disease, nervous system damage, mental retardation, and gastrointestinal disease in the human body. Cadmium (Cd) is a dangerous heavy metal pollutant because cadmium is associated with health risks including kidney dysfunction, lung cancer, increased blood pressure, kidney failure, liver cirrhosis and bone atrophy. Zinc (Zn) is an important element for plant and animal growth, but higher content can lead to eye, nose, throat and skin irritation, stomach cramps and anemia. Copper (Cu) is a highly toxic element in drinking water, but less so than mercury. Excessive copper ingestion causes high blood pressure, anemia, liver and kidney damage, seizures, stomach and intestinal irritation (Ohidul Alam et al., 2024). Human health conditions due to long-term exposure to contact with heavy metals can be damage to nerves, muscles and physical processes, such as Alzheimer's disease, muscular dystrophy and Parkinson's disease and even lead to cancer. The high toxicity of these cationic heavy metals will cause significant damage to our lives if they are not kept under control and removed in time (Xiaofang Feng et al., 2022).

Heavy metal pollution is the result of industrial activities, improper waste disposal, and other man-made processes that release potentially toxic heavy metals into the environment. Anthropogenic activities are responsible for the significant problem of heavy metal pollution in our water resources. Water quality is significantly degraded by the presence of toxic heavy metal ions, which is a serious threat because it makes water unusable for humans and animals (Nur Azalina Suzianti Feisal et al., 2024).

Heavy metals have received a lot of attention because they can come from many sources and show substantial toxicity, long persistence, non-degradability and easy bioaccumulation. Pollution with heavy metals occurs all over the world, which causes a high contamination of water bodies (Ohidul Alam et al., 2024).

Heavy metals, unlike organic pollutants, do not break down naturally and tend to accumulate in living organisms once they are introduced into the environment, so it is important that industrial effluents containing heavy metals are properly treated before they are released in the environment, to minimize their pollution and to protect both our natural environment and human health (Jonas Bayuo et al., 2024). The removal of harmful heavy metal ions from wastewater is crucial for protecting human health and the environment. By removing heavy metals from water, we can significantly reduce their harmful effects on the environment (Nur Azalina Suzianti Feisal et al., 2024).

Heavy metals in wastewater are strictly regulated by environmental protection authorities because of their harmful impact on health and toxicological properties. Useful technologies and materials must be developed for the removal of heavy metals from effluent waterways. The most widespread method of reducing and removing heavy metals from wastewater is adsorption (Niraj S. Topare, 2023).

Adsorption represents the retention of a matter or a substance at an interface, where the process takes place between a solid adsorbent and polluted water. It is a mass transfer progression that plays an important role in effluent treatment. The substance (pollutant) that is adsorbed is the adsorbate, and the adsorbing material is called the adsorbent. Adsorption is a surface phenomenon and occurs due to the weak Van der Waal's forces between the adsorbent and the adsorbate, resulting in a physical adsorption or due to the strong covalent bonds between the adsorbent and the adsorbate expressing chemical adsorption (Dawn S., Vinita V., 2021). Adsorption is a physico-chemical method that can be used to remove heavy metals from wastewater. Adsorption is flexible in design and operation, and cost and removal efficiency depend on the choice of adsorbent [Ayesha Al Ali et al., 2021].

Effective adsorbents should exhibit many beneficial properties, including high selectivity for rapid separation, thermal, chemical and mechanical stability, ability to be regenerated, low solubility in the contact liquid, large surface area, high efficiency, adequate pore size and volume, accessibility and low costs (Niraj S.T., Vinayak S.W., 2023).

Various parameters influence the adsorption process: contact time, pH of the solution, temperature of the solution, dosage of adsorbent, specific surface area of the adsorbent. Contact time has a significant effect on the adsorption, as the contact time increases, the adsorption rate also increases, after reaching the equilibrium, the removal rate is constant, as the time further increased, the adsorption rate is slowed due to the reduction of available active sites filled with heavy metal ions. Adsorbent dosage is a critical factor in controlling adsorption rates, it has been demonstrated that a small amount of adsorbent is sufficient to remove a reasonable concentration of heavy metals from contaminated media. When the pH of a negatively charged adsorptive surface is reduced, the surface is neutralized by the H^+ ions that are present in high numbers, enhancing the rate of adsorption. As the temperature increases, the rate of adsorbate diffusion across the external boundary layer also increases in the internal pores of the adsorbate. The adsorption rate directly depends on the surface area of the adsorbent: that is, the larger the surface area of the adsorbent, the high efficiency of adsorption. (Yared Daniel Retaa et al., 2023).

The removal of heavy metals using commercial adsorbent materials such as activated carbon is an expensive process, which has led researchers to find alternatives to commercial adsorbents. The adsorption mechanism, due to its simplicity, covers all types of adsorbents (Dawn S. and Vinita V., 2021). Including those obtained from waste and industrial by-products, such as blast furnace slag.

There are many studies and researches on the development of new and low cost adsorbents to remove heavy metals from wastewater by converting solid waste into good adsorption materials (Mengyu Ma et al., 2023), an example would be blast furnace slag that was used to remove heavy metals, as well as other pollutants, from wastewater: heavy metals: Hg^{2+}, Cr^{6+}, Pb^{2+}, Cu^{2+} (Alsulaili A. et al., 2023); heavy metals, phosphate and dyes (Abdelbasir M. et al., 2022); heavy metals like nickel, zinc, lead, chromium, copper, cadmium (Anjali M.S. et al., 2019); Pb(II), Cu(II), Zn(II), Cd(II), Ni(II) (Blahova L. et al., 2018); dyes, heavy metals like copper, nickel (De Gisi S. et al., 2016) etc.

Blast furnace slag is a by-product of pig iron production, it has a bulk density between 1200 and 1300 kg/m^3 and a specific gravity of about 2.90, having a complex chemical composition, showing, in particular, oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO Due to the crystalline structure that develops during the solidification process, blast furnace slag has the ability to adsorb pollutants.

Some research found that leaching from blast furnace slag was in the same range compared to leaching from untreated gravel, thus noting that neither the environment nor human health were adversely affected by this process.

Blast furnace slag presents a number of metal oxides with high porosity, specific surface area and strong adsorption characteristics, which can be successfully used as adsorbent material in wastewater treatment (J.N. Sahu et al., 2023).

MATERIALS AND METHODS

In this work, powdered blast furnace slag was used. The slag was passed through a set of sieves obtaining a granulometric distribution of 1 mm, 500 µm, 250 µm, 125 µm, 90 µm, 45 µm and a fraction below 45 µm. The slag fraction with the granulometry of 45 µm was collected, which is 16.15% of the slag taken into account.

An atomic absorption spectrometer contrAA 800 was used to perform the quantitative analysis of the slag sample. The solution of the sample to be analyzed is sprayed into the flame, taking place a series of processes through which free atoms are obtained. Atomic absorption spectrometry is a method based on the measurement of the absorption of electromagnetic radiation of a certain wavelength, by free atoms of the sample, in vapor state.

Previously, 3 solutions of different concentrations of 1 mg/L, 5 mg/L, 10 mg/L were prepared using 0.5% HNO_3 solution and multi-element solution of heavy metals to obtain the wastewater samples. A control sample was as well prepared, 0.5% HNO_3 solution, without pollutant. Also, 3 blast furnace slag samples were prepared, of 10 mg, 25 mg and 50 mg. The working times were 15 minutes, respectively 30 and 60 minutes.

The slag samples, in amounts of 10 mg, 25 mg and 50 mg, were immersed in 30 mL of heavy metal solution with a concentration of 5 mg/L. Magnetic stirring plates were used, at about 60 rpm, at room temperature, for 15 min, 30 min and 60 min. To remove the slag from the solution with heavy metals, the samples were centrifuged at 6 x 100 rpm for 10 min. For this work, the presence of heavy metals lead, cadmium, zinc and copper was monitored.

RESULTS AND DISCUSSIONS

The adsorption process is influenced by some important properties, such as pH, temperature, electrical conductivity (Table 1). The analysis of the amount of lead, cadmium, copper and zinc was carried out by atomic absorption spectrometry in flame. The analytical characteristics of the determination of the heavy metals analyzed in this work by atomic absorption spectrometry in the flame are shown in Table 2. Following the examination of the 10 mg, 25 mg and 50 mg samples with a flame atomic absorption spectrophotometer, the amounts of lead, cadmium, copper and zinc presented in Table 3 were found.

Table 1. The properties of the blast furnace slag sample

	pH, at 25°C	Electrical conductivity, µS/cm, at 25°C	Total dissolved solids content, mg/L
The sample of slag in water, 10%	8.9-10.3	72.4	39.7
The slag sample in the solution mixture containing pollutants	4.8-4.9	1000	531

Table 2. Analytical characteristics of the determination of heavy metals

Analytical characteristic / Heavy Metals	Wavelength [nm]	Linearity of the curve, R^2	Limit of detection [mg/L]	Sensitivity of the method [mg/L/1% A]	Type of flame
Pb	217.0005	0.947614	2.081	0.059125	acetylene - air
Cd	228.8018	0.998584	0.3392	0.121037	
Cu	324.7540	0.994043	0.6963	0.023723	
Zn	213.8570	0.852891	3.545	0.027533	

Table 3. The amounts of heavy metals found in the analyzed samples

Heavy metals / Sample		S1 [mg]	S2 [mg]	S3 [mg]
Pb	15′	5.305	3.584	2.709
	30′	5.374	4.346	2.799
	60′	5.085	4.754	2.932
Cd	15′	6.827	6.844	6.945
	30′	6.805	6.960	6.902
	60′	6.678	7.109	7.234
Cu	15′	4.789	3.496	2.563
	30′	5.047	3.858	2.450
	60′	5.063	3.994	2.633
Zn	15′	7.102	7.032	7.075
	30′	7.119	6.999	6.890
	60′	7.100	7.182	6.983

The 10 mg sample was marked with S1, the 25 mg sample with S2, and the 50 mg sample with S3.
The contact time for each sample was 15 minutes (15'), 30 minutes (30') and 60 minutes (60').

In order to highlight the amounts of heavy metals (Pb, Cd, Cu, Zn) found in the analyzed samples, we made the graphs below (Figure 1). In the case of the amount of Pb found in samples S2 and S3, an increase in the amount of Pb can be observed as the contact time increases, and in the case of sample S1, there is a decrease in the upward trend for a contact time of 60 minutes. Regarding the amount of Cd in the analyzed samples, in sample S1 a slight decrease is observed with the increase in contact time, in S2 there is an increase, and in S3 it goes through a slight decrease, as then at the time of 60 minutes to increase as the contact time increases. In the determination of the amount of Cu, an increase is observed in the case of samples S1 and S2, and in S3 there is a slight decrease and then an increase with the increase of the contact time. And in the case of the amount of Zn, there are changes for each sample like this, in S1 there is an increase and then a decrease, in S2 and S3 there is a decrease and then an increase with the increase in contact time. Thus, the influence of the amount of adsorbent and the contact time on the adsorption process can be observed.

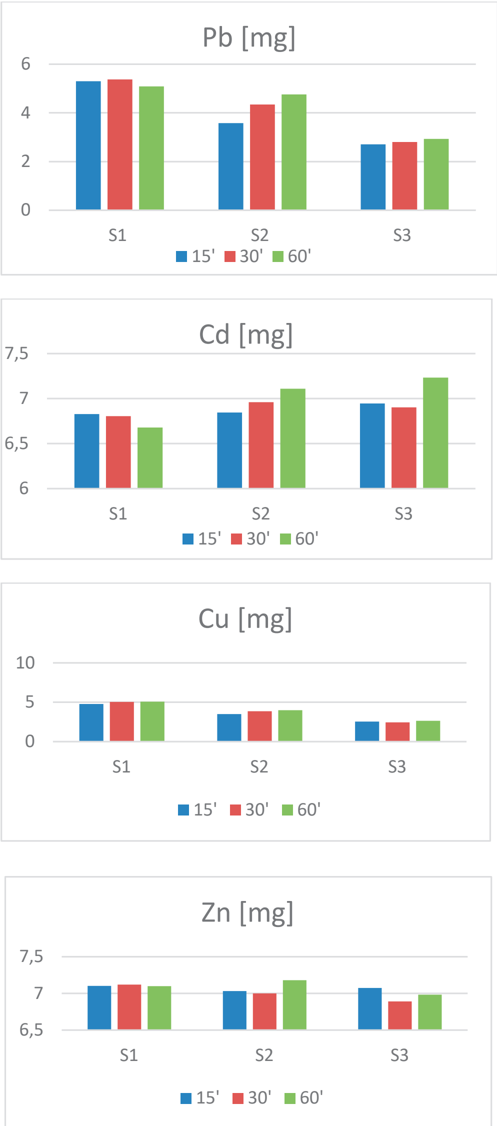

Figure1. The amounts of heavy metals found in the samples (a) lead, (b) cadmium, (c) copper, (d) zinc

CONCLUSIONS

In numerous researches, it is observed that blast furnace slag can be used in wastewater treatment as an adsorbent material for the removal of many pollutants, including heavy metals.

In this work, blast furnace slag, with a diameter of 45 µm, was used to observe its capacity to adsorb heavy metals from wastewater. The influence of the amount of adsorbent and the contact time on the adsorption process was also observed.

Blast furnace slag is an industrial by-product that can be used as an adsorbent in the removal of heavy metals, such as lead, cadmium, copper, zinc, from waste water.

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