PLUM PITS AS NATURAL SORBENT FOR REMOVAL OF LEAD IONS

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ABSTRACT:
Water quality is deteriorating over the years, and the main source of water pollution is industrial, agricultural and municipal wastewater. Heavy metals, organic compounds and microorganisms, present even in traces, can be very dangerous to human health, aquatic organisms and the environment. Therefore, in this study was investigate the possibility of modified and unmodified plum pits as biosorbents for Pb (II) ions removal from aqueous solution. Experimental data have shown that these bisorbents show a certain potential for application in the metal removal process. The feasibility was tested for an unmodified and modified biosorbent based on plum pits in the range of concentrations 150-200 mg/l (unmodified sample) and 100-200 mg/l (modified sample) at a contact time of 30 and 60 minutes . Adsorption parameters were determined using the Freundlich isotherm. The results showed that unmodified biosorbent based on plum pits with increasing concentration from 150 mg/L to 200 mg/L leads to a large increase in the percentage of removal of Pb (II) ions, with no significant effect on contact time. In contrast to the unmodified sample, the modified biosorbent based on plum pits % of removed Pb (II) ions significantly increases the contact time at the initial Pb (II) concentration of 100 mg/L, while at the initial concentration of 150 mg/L and longer mixing, the removal efficiency increases and amounts to 86.032 %. The calculated values of the parameters used in the Freundlich isotherm indicated the existence of high-energy sorption centers in the unmodified bisorbent based on plum pits, while the calculated values of the parameters used in the Freundlich isotherm for the modified biosorbent based on plum pits showed moderate mode adsorption.

KEYWORDS: adsorption, plum pits, modified and unmodified biosorbent, lead

INTRODUCTION

The most prized substance found in nature and an irreplaceable resource that is limited in the world is precisely water. Due to the growing population and global development, the amount of water pollution is also increasing, which is becoming an increasing problem in today's world. [1] The food industry generates large amounts of organic waste of plant origin (seeds, fruit pulp, shells, etc.). In order to minimize this type of waste, it is possible to single out many valuable components that can be further used such as pectin, fiber, antioxidants and the like. However, very often the lignocellulosic part of solid waste remains unused in large quantities. Such waste can be used for the purpose of obtaining bioethanol, as livestock, and recently such waste has been tested as an adsorbent for the removal of heavy metals from wastewater. [2] ,[3]

Heavy toxic metals such as Pb, Cu, Zn, Cd, Ni enter the water through wastewater from the metal industry and the Cd-Ni battery industry, phosphate fertilizers, mining, pigment industry, stabilizers, galvanic alloy industry, etc. they are collected in the food chain and due to the tendency of bioaccumulation they need to be removed from wastewater. [4] Pb (II) ions are able to penetrate the cell membrane and accumulate in the cell, thus causing its damage. [5] Therefore, poisoning can also be caused by quantities of lead below the maximum permitted concentrations, if the exposure to the source of poisoning is long-lasting, which is why its removal is very important.

There are many procedures and techniques of varying degrees of efficiency that are used to control and reduce water pollution caused by various pollutants, including heavy metals. However, these procedures often have various disadvantages in terms of high operating and maintenance costs, low pollutant removal efficiencies, generation of toxic waste sludge and by-products, complicated procedures and applications. On the other hand, sorption processes have proven to be a good alternative for natural and wastewater treatment given the practicality and simplicity of the process, economy and high efficiency [6]. Therefore, natural sorbents that are readily available and abundant are increasingly being used. Based on literature data, among the readily available types of biomass, there are strong natural biosorbents such as plant parts, especially those that contain cellulose: e.g. tree bark, rice peel, wheat peel, banana peel, orange peel, tea leaves, corn cob, hazelnut peel, walnuts, seaweed, microorganisms (bacteria, fungi, yeasts), activated sludge, etc. [7],[8].

The ability to remove heavy metals from water by biosorption by lignocellulosic biomaterials is enabled by the relatively porous structure and the presence of different functional groups on their surface. The advantage of lignocellulosic materials, which includes the selected biosorbent based on plum pits for wastewater treatment, is reflected in the fact that cellulose has good chemical stability and mechanical strength due to its crystal structure. [9]. In addition, in BiH this type of waste material is present in large quantities and is economically available.

The aim of this study was to investigate the sorption capacity of removing Pb (II) ions from water using a unmodified and modified biosorbent on base plum pits, that was chemically modified with sodium hydroxide. And as the efficiency of the adsorption process is affected by the pH value, contact time, initial concentration of heavy metal and mixing rates, these parameters were examined.

MATERIAL AND METHODS

In this paper, the sorption capacity of samples of unmodified and modified biosorbent based on plum pits with 1% NaOH against Pb (II) ions at a pH higher than a certain pH point of zero charge was investigated. Also, the influence contact time and mixing rate on the sorption capacity of the selected bisorbent on the removal of Pb (II) ions from water was investigated**.**

MATERIAL

The plum pits classified as waste material were used as bisorbents. The plum pits are first washed in distilled water, then dried first in air and then in an oven to remove as much moisture as possible. The lignocellulosic part was separated from the core of the pits, and it was used in further work. Manual grinding was performed, followed by sieving through a sieve (- 0.6 mm +0.3). The samples were then dried in an oven at 60˚C to constant weight and then stored in hermetically sealed containers.

METHODS

pH point of zero charge of the modified and unmodified bisorbent based on plum pits was first determined by contacting 0.2 grams of the biosorbent with 50 ml of 0.1 M KNO_3 solution. pH values were previously precisely adjusted from 3 to 10 with 0.01 M HNO_3 and 0.01 M NaOH. (pH meter of the Mettler Toledo 220 brand). After 24 h, all samples were filtered and their pH value was measured. The pH value that did not change after 24 h corresponds to the pH point of zero charge.

For the preparation of the unmodified sample, lead solutions with a concentration of 150 mg/l and 200 mg/l (two of each concentration) were used, which were mixed with 0.2 g of the prepared sample of biosorbent. The two samples were mixed for 30 minutes, while the remaining two were 60 minutes. The Rotamix SHP-10 magnetic mixer was used for mixing. After the contact time, the separation of the biosorbent was performed by filtration, and then the concentration of lead was determined from the filtrate with the atomic absorption spectrophotometer.

The preparation of the modified sample consisted of the preparation of 3 g of the unmodified sample treated with 1 M NaOH relative to 1:15 and then stirred on a magnetic stirrer for 6 h at room temperature. The sample was then washed with distilled water to constant pH and dried at 50°C to constant weight. Four solutions of lead concentration 100 mg/l and 150 mg/l were prepared and contacted with 0.2 g of modified biosorbent. The two samples were mixed for 30 minutes, while the remaining two were 60 minutes. The separation of the biosorbent was performed by filtration, and then the concentration of lead was determined from the filtrate with the help of an atomic adsorption spectrophotometer. The adsorbed amount of lead ions on the bisorbent (bisorption capacity), qe (mg/g) was calculated according to the equation:

$$qe = \frac{(C_i - C_f) \times \mathrm{V}}{m}$$

where is:
V - the volume of sorbate solution - 50 ml;
m - mass of bisobent 0.2g / 50ml;
C_i i C_f - the concentrations at the beginning and end of the bisorption process (mg/L).
Removal efficiency is determined from the equation:

$$\% = \frac{(C_i - C_f)}{C_i} x100$$

where is:
C_i - the concentration of sorbate at the beginning of the bisorption process;
C_f - the concentration of sorbate at the end of the bisorption process.

The values of the Freundlich constants from the Freundlich adsorption isotherm were calculated [10]:

$$\log q_e = logKf + \frac{1}{n} S_e$$

where is:

q_e- amount of adsorbate adsorbed per unit weight of adsorbent (mg/g);

K_f- temperature-related parameter;

n- characteristic constant for the investigated adsorption system and are read from the diagram ($\ln q_e$) = f ($\ln C_e$).

Bisorption experiments were performed in batch mode.

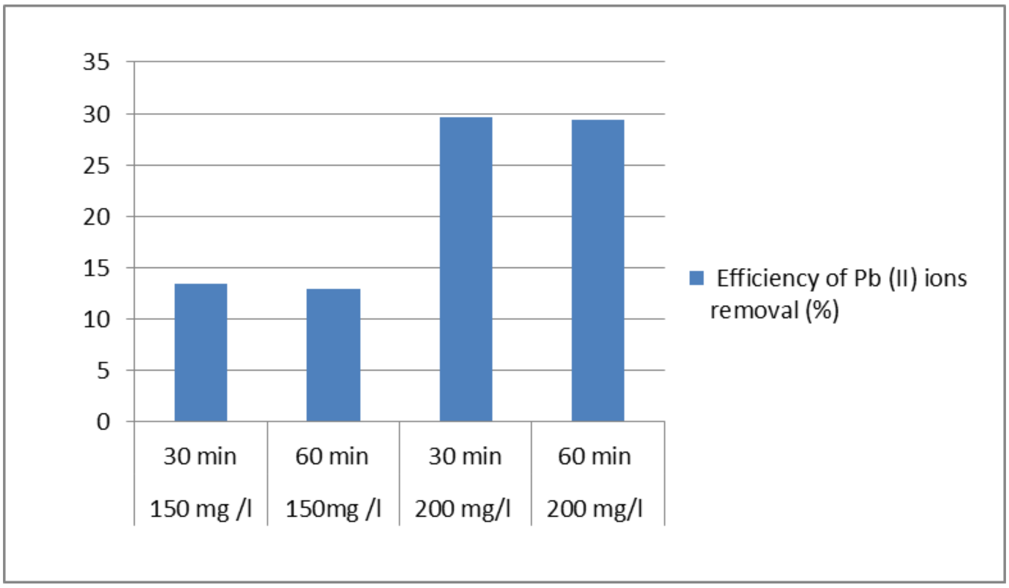
RESULTS AND DISCUSSION

The paper first determines the pH point of zero charge, a quantity that is of special importance when studying the phenomenon of adsorption in predicting the attractive or repulsive effects of the surface according to certain ionic species present in solution at a given pH value. [11]

Regarding this, the pH of the solution plays a significant role in determining both the degree of ionization of matter in solution and the dissociation of functional groups at the active sites of the adsorbent, and the chemical composition of the adsorbate particles [12].

The pH value that did not change after 24 hours was 4.5. This means that at all pH values of the aqueous solution lower than 4.5 the surface of the adsorbent will be positively charged, while at pH values above 4.5 the surface charge will be negatively charged.

The Graph 1. and Graph 2. show the values of the Pb (II) removal process for the unmodified and modified biosorbent.

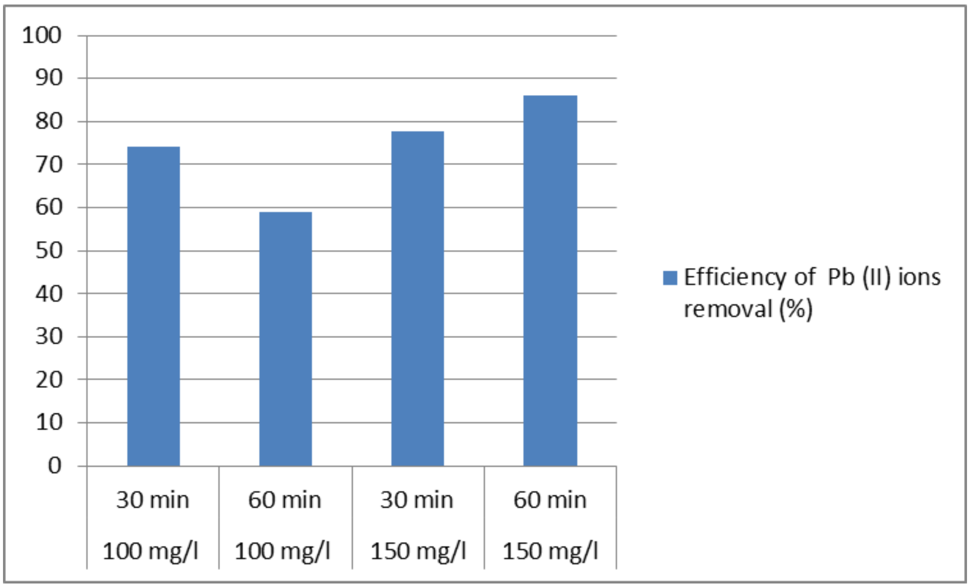


Graph 1. Removal efficieny of Pb (II) ions onto unmodified plum pits

As can be seen from the graph 1., at a contact time of 60 minutes there is a slight decrease in bisorption capacity compared to a contact time of 30 minutes. Some studies have shown that the effect of metal ion removal increases with the time of adsorption by applying almost all types of adsorbents.

For this reason, at the beginning of the treatment, the rate of removal of metal ions increases with the increase of the initial concentration, due to the large concentration of free binding sites on the surface. On the other hand, with the increase of the initial metal concentration, the active binding sites on the surface are saturated, so saturation appears as another important factor. [13]

However, the increase in the amount of adsorbed ions is proportional to the time to a certain maximum adsorption capacity, ie. the phase in which all available adsorption, active sites are filled under certain conditions, after which time is almost no longer affected. The results show that the equilibrium state in these tests is within 30 minutes during which most of the lead ions are adsorbed. By increasing the initial concentration of the pollutant of interest, it was found that the amount of adsorbed pollutant per unit mass of biosorbent usually increases. In this study, it was found that increasing the initial concentration of Pb (II) ions by 50 mg/L increases the sorption capacity more than twice.



Graph 2. Removal efficieny of Pb (II) ions onto modified plum pits

From Graph 2. it can be concluded that the removal efficiency of Pb (II) with the used modified plum pits sample % of removed Pb ions decreases significantly with increasing contact time at the initial Pb (II) concentration of 100 mg/L, while at the initial concentration of 150 mg/L and prolonged mixing, the removal efficiency increased to 86.032 %.

One of the most well-known isotherms often used by adsorption-desorption analyzes is the Freundlich isotherm [14], which was also used in this paper, and its values for the modified and unmodified biosorbent based on plum pits are shown in Tables 1. and 2.

Table 1. Freundlich adsorption isotherm constants for unmodified bisorbent base on plum pits

Number	The contact time (min)	The values of the Freundlich constants			
		lnK_f	K_f	1/n	R^2
1.	30	0,5387	1,71377	1,0782	1
2.	60	0,4698	1,59967	1,109	1

Table 2. Freundlich adsorption isotherm constants for modified bisorbent base on plum pits

Number	The contact time (min)	The values of the Freundlich constants			
		lnK_f	K_f	1/n	R^2
1.	30	2,4662	11,777	0,4526	1
2.	60	2,4516	11,606	0,5111	1

The value of the Freundlich constant indicates the relative adsorption capacity of the adsorbent, while the value of 1/n is an indicator of the strength of adsorption. If the value of 1/n is less than one, the adsorption process is considered to be of high intensity (Babaeivelni et al., 2013). A value of constant n greater than 1 indicates favored adsorption [15]. Some authors state the parameter 1/n as a heterogeneity factor, and the lower its value the greater the heterogeneity [16]. K_f is a parameter related to the binding capacity of the adsorbate, while the value of the constant n shows the affinity of the adsorbent for the adsorbate.

The calculated values for the biosorbent based on the unmodified biosorbent based on plum pits are presented in Table 1. As can be seen from the table, the value of the coefficients 1/n for the tested bisorbent is 1.0782 during a contact of 30 minutes and 1.109

during a contact of 60 minutes, which indicate the existence of high - energy absorption centers, while adsorption is more pronounced at lower concentrations.

From Table 2. it can be seen that the calculated values of the coefficients 1/n for the tested modified bisorbent based on plum pits indicate a moderate adsorption intensity, where at a contact time of 30 minutes the value of 1/n is 0.4526 and at a contact time of 60 minutes , 1/n is 0.5111.

CONCLUSION

The results of the examination of the possibility of application and sorption capacity of biosorbents based on modified and unmodified plum pits showed that the mentioned biosorbents can be used to remove Pb (II) ions, and that the pH point of zero charge is 4.5. The test results showed that there is an increase in the % removal with increasing concentration from 150 mg/L to 200 mg/L in the unmodified biosorbent where most of the lead ions are adsorbed within 30 minutes. It was found that increasing the initial concentration of Pb (II) ions by 50 mg/L increases the sorption capacity more than twice.

It has also been shown that the removal efficiency of Pb (II) with the modified biosorbent on based plum pits used % of removed Pb (II) ions decreases significantly with increasing contact time at an initial Pb (II) concentration of 100 mg/L, while at an initial concentration of 150 mg / L and prolonged mixing, the removal efficiency increases to 86.032 %.

The values of the coefficients 1/n from the Freundlich isotherm for unmodified biosorbent based plum pits are 1.0782 during a contact of 30 minutes and 1.109 during a contact of 60 minutes, indicating the existence of high-energy absorption centers, while adsorption is more pronounced at lower concentrations, while the values of the coefficients 1/n for the tested modified bisorbent based on plum pits indicate a moderate adsorption intensity, where at a contact time of 30 minutes the value of 1 / n is 0.4526 and at a contact time of 60 minutes, 1/n is 0.5111.

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