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Removal of Zn(II) and Pb (II) ions Using Rice Husk in Food Industrial Wastewater

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ABSTRACT: T he adsorption behavior of Zn^{2+} and Pb^{2+} ions on rice husk was investigated using Rice Husk to remove the metals ions in dairy wastewater. The removal of mentioned heavy metal ions from aqueous solutions was studied by batch method. The main parameters that influencing Zn^{2+} and Pb^{2+} sorption on rice husk were: amount of adsorbent, contact time and pH value of wastewater. The influences of pH (2–9), contact time (5-70min) and adsorbent amount (0.5-3 g) have been studied. The percent adsorption of Zn^{2+} and Pb^{2+} ions increased with an increase in contact time and dosage of rice husk. The binding process was strongly affected by pH and the optimum pH for Zn^{2+} and Pb^{2+} ions were 7.0 and 9.0, respectively. The experimental data were analyzed by Langmuir isotherm. The maximum adsorption capacity of the adsorbent for Zn^{2+} and Pb^{2+} ions was calculated from the Langmuir isotherm and found to be 19.617 and 0.6216 mg/g, respectively. Actually the percent of removing Zn^{2+} and Pb^{2+} ions reached maximum to 70% and 96.8%, respectively. @JASEM

Symbols:

q_e - adsorbed metal on the sorbent , (mol/Kg adsorbent)
m- weight of sorbent , (Kg)
V- volume of metal solution , (m^3)
C_o- initial metal concentration , (mol/ m^3)
C_e- metal concentration at any time , (mol/ m^3)
q_m- maximum sorption capacity
K_L- adsorption equilibrium constant , (m^3/mol)
q - weight adsorbed per unit weight of adsorbent , (mol/Kg adsorbent)
n- Freundlich constant
K_f- adsorption coefficient

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Today, with the rapidly increasing urban population, water resources becoming less and scarcer, there is a strong need to reconsider consumption patterns and the way resources used. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products (Yu, 2005). The presence of heavy metal ions is a major concern due to their toxicity to many life forms. Conventional methods for removing heavy metals from aqueous solutions include chemical precipitation, ion exchange, adsorption (Gode and Pehlivan, 2006) and membrane filtration technologies. Among them, adsorption method is simple and relatively cost-effective, thus has been widely used. Several materials are derived from natural resources, plant wastes or industrial by-products. The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as tea waste and coffee (Orhan and Buyukgungor, 1993), hazelnut straws, peanut hull, saw dusts, husk (Babarinde, 2002), corncobs, apple wastes (Maranon and Sastre, 1991), wool fibers, tea leaves, banana and orange peels, papaya wood, maize leaf, leaf powder (Hanafiah and et al., 2007), grape stalk wastes and different agricultural by-products (Pehlivanand and et al., 2006) were used and investigated . Biosorption is a promising technique for the removal of heavy metals from aqueous environments especially when adsorbents are derived from lingnocellulosic materials (Coelho and et al., 2007). Rice is the crop all over the world. Every year large amount of rice husks is produced. Structurally, rice husks consist of cellulose, hemicellulose, and lignin.

The aim of this study was to find out the effectiveness of less expensive material that could be used as sorbent for the removal of $Zn^{2+}$and Pb^{2+} ions from dairy wastewater. In this work, the adsorption behavior was studied by a set of experiments at various conditions, including pH, contact time and various biosorbent amounts.

MATERIALS AND METHODS

Adsorbent: Rice husks were washed carefully first with tap water and then deionized water to remove particulate material from their surface. After that, they were dried in an oven at 100 °C for 24 hr. The pH measurements were performed with a pH meter (Jenway 3510). An Atomic Absorption Spectrometer (AAS) (GBC –Sens AA) operating with an air–acetylene flame was used to analyze the Zn^{2+} and Pb^{2+} ion concentration in the solution. A deuterium lamp was used for background correction.

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Batch adsorption: the initial pH of the metal solution was adjusted to values in the pH range of (2–9) by the addition of 0.1M HC1 or 0.1M NaOH prior to experiment. Certain volume of waste water (30 ml) was equilibrated with varying sorbent dosage (0.5 to 3 gr), pH values (2–9), and contact time (5 to 70 min). Experiments were carried out in 100 ml beakers to study the effect of parameters (sorbent dosage, pH values and contact time).The beaker were shaken for a prescribed length of time by magnetic stirrer. After filtration thorough the filter paper, Zn^{2+} and Pb^{2+} ions remaining in wastewater, determined by AAS.
The amount of metal ion adsorbed was calculated as:

$$\% \, Adsorption: \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where C_0 and C_e are the initial and equilibrium concentration of adsorbate,respectively.
The amount of metal adsorbed per Kilogram of the biomass was calculated as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

Where q_e is the adsorbed metal on the sorbent, m is the weight of sorbent, V is the volume of metal solution, C_o is the initial metal concentration, and C_e is the metal concentration at any time. The amount of metal ion sorbed at equilibrium, q_e, is calculated using eq.2.

RESULTS AND DISCUSSION

Effect of contact time: The effect of sorption time on sorption efficiency has been showed in Fig 1. Adsorption rate is very fast initially; about 60.0% of Pb^{2+} and 10.3% of Zn^{2+} are removed within 5 min. The adsorption capacity reaches 96% and 49% of the equilibrium adsorption capacity within 60 min for Zn^{2+} and Pb^{2+}, respectively and the sorption tends toward saturation. So the optimum agitating time for adsorption of Pb^{2+} and Zn^{2+} ion can be accepted as 60 min. The initial faster rate of metal sorption may be explained by the large number of sorption sites available for adsorption. For the initial bare surface, the sticking probability is large, and consequently adsorption proceeded with a high rate. The slower adsorption rate at the end is probably due to the saturation of active sites and attainment of equilibrium.

Effect of amount of sorbent: The effect of variation of sorbent amount on the removal of metal ions by rice husks is shown in Fig. 2. Amount of sorbent was varied from 0.5 to 3 g and equilibrated for 5 min at an initial metal ion concentration. It is apparent that the metal ion concentration in solution decreases with increasing sorbent amount for a given initial metal concentration. This result was anticipated because for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area.

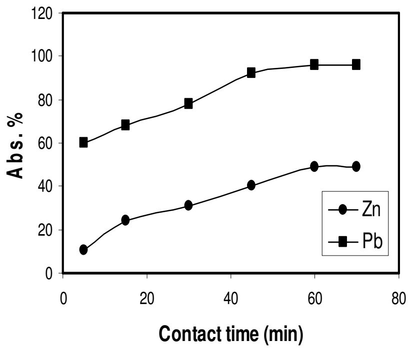

Fig. 1- Effect of contact time on the sorption of Zn^{2+} and Pb^{2+} by rice husks. Adsorption Conditions: 1g sorbent, 30mLof sample, pH 4. 4, temperature: 25±1 ◦C.

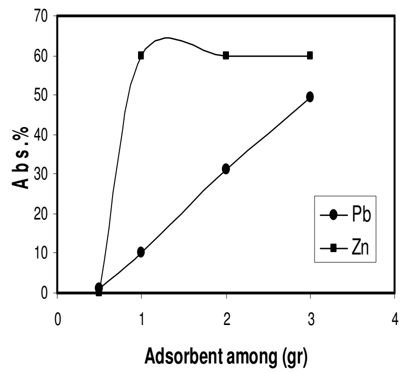

Fig. 2- Effect of sorbent dosage on the sorption of Zn^{2+} and Pb^{2+} on rice husks. Adsorption Conditions; 0.5-3g sorbent, 30mL of sample, pH 4.4, temperature: 25±1 °C.

Effect of solution pH: Changes in solution pH can alter the chemical nature of the functional groups on the rice husks and then the metal adsorption capacity of the adsorbent. Fig. 3 displayed the Zn^{2+} and Pb^{2+} ion adsorption on the rice husks as a function of solution pH. It showed that the sorption amount of Zn^{2+} and Pb^{2+} increases with the increase of solution pH, the sorption process is pH-dependent. At low solution pH, the functional groups on the rice husks are protonated and positively-charged, their adsorption capacity is lower; while at higher pH, the deprotonated groups are involved in Zn^{2+} and Pb^{2+} ion adsorption. It can be observed from Fig. 3; the percent sorption of Zn^{2+} increased with increase in pH and reached maximum 70% for at pH 7.0. The percentage Zn^{2+} removal increased from 49% to 70.0% with an increase of pH from 6.0 to 7.0. The percentage sorption of Pb^{2+} increased with increase in pH and reached maximum 98.6% at pH 9.0. The percentage Pb^{2+} removal increased from 60% to 90.0% with an increase of pH from 3.0 to 6.0. Although the binding of lead was similar at higher pH, pH 9 was used in the remaining studies. It is also known that heavy metal cations are completely released under circumstances of extreme acidic conditions. Metal biosorption is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include adsorption (chemisorption), complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption (Pehlivan and Arslan, 2007).

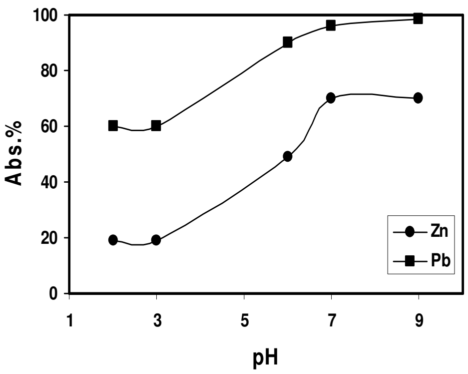

Fig.3- Effect of pH on the adsorption of Zn^{2+} and Pb^{2+} using rice husks. Adsorption conditions; 1 gr sorbent, 30mL of sample, temperature: 25±1 °C.

*Adsorption isotherm***:** The effect of pH on the sorption by the rice husks was investigated by keeping the solution volume (30 mL) and amount of the rice husks for 5 min equilibrium time. The percentage of sorption is highly dependent on the pH. The removal curves are single smooth and continuous suggesting the formation of monolayer of adsorbate on the surface of sorbent. The percent metal ion removal of rice husks increased with increasing pH. (Fig 4, 5)

Several isotherm equations have been used for the equilibrium modeling of adsorption systems. Among these, the most widely used are the Langmuir and Freundlich isotherm equations. The Langmuir equation assumes that: (1) the solid surface presents a finite number of identical sites which have uniform energy; (2) there are no interactions between adsorbed species, meaning that the amount adsorbed has no influence on the rate of adsorption; (3) a monolayer is formed when the solid surface reaches saturation (Huang and et al., 2007). Langmuir equation can be described as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \qquad (3)$$

Where K_L is the adsorption equilibrium constant including the affinity of binding sites, q_e is the amount of bound Zinc and Lead at equilibrium and q_m is the maximum sorption capacity, which represents a practical limiting adsorption capacity when the surface is fully covered with metals ion.

By plotting C_e/q_e versus C_e , K_L and q_m can be determined when a straight line is obtained. The Freundlich model is an empirical equation based on adsorption on a heterogenous surface. It is given as:

$$q = K_f C_e^n \qquad (4)$$

Where n is the Freundlich constant and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent and C_e is the equilibrium metal concentration in fluid. The values of q_m , K_L calculated from the experimental data through linear regression analysis are presented in Table 1 with the correlation coefficients (R^2). Zn^{2+} sorption capacity was 19.617mg/g and Pb^{2+} sorption capacity was 0.6216 mg/g for rice husks (Table 1).

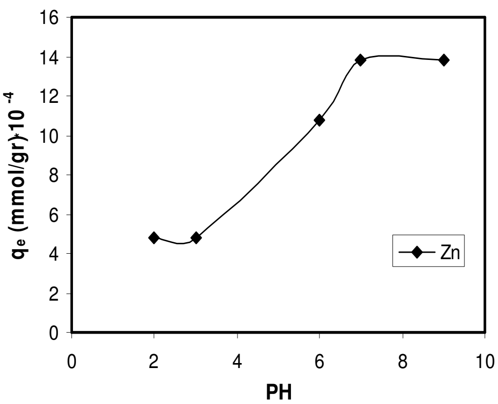

Fig. 4- Sorption isotherm of Zn^{2+} ion on rice husks as a function of pH, 1g sorbent, 30mL of sample, temperature: 25±1°C.

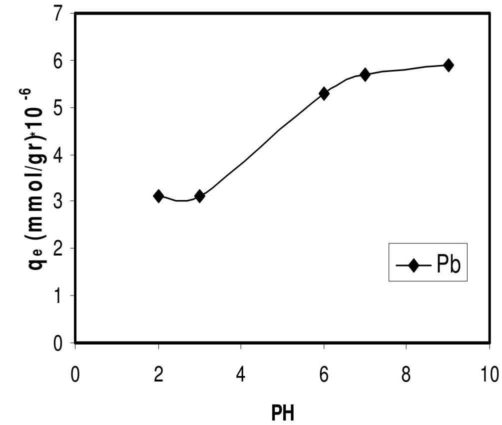

Fig. 5 - Sorption isotherm of Pb^{2+} ion on rice husks as a function of pH/ 1g sorbent, 30mL of sample, °C.1temperature: 25±

Table 1- Parameters of Langmuir isotherm model for Zinc and Lead adsorption by rice husks.

Metals	Langmuir isotherm method		
	q_m	K_L	R^2
Zn	0.3	0.066	0.9747
Pb	0.003	186.67	0.9951

Conclusions: The rice husks are an agricultural waste substance. This product exhibits very good adsorption for Zinc from wastewater, especially. Adsorption of Zinc and Lead by rice husks has been shown to depend significantly on the pH, rice husks dosage and contact time. The adsorption behavior can be well described by Langmuir isotherm model. The maximum adsorption capacity was 0.3 and 0.003 m mol/g for Zinc and Lead, respectively. The initial concentration of Zn^{2+} and Pb^{2+} has been 4.3 and 0.05 mg/l in dairy wastewater, respectively. After usage of various pH the concentration of heavy metals became to 1.3 and 0.007mg/l. Actually the percent of removing zing and lead reached maximum to 70% and 96.8%, respectively. The rice husks would be useful in treatment of wastewater containing Zinc and Lead.

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