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Research Article

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Adsorption Isotherm Studies of Pb(ll) Ions from Aqueous Solutions by Maize Stalks as a Cheap Biosorbent

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Abstract The evaluation of the ability of maize stalks to remove Pb(ll) ions from aqueous solution was carried out. Different parameters affecting Pb(ll) removal were investigated in batch experiments to optimize the removal method. These parameters include contact time, initial metal concentration, adsorbent dose, stirring rate, temperature. Langmuir and Freundlich isotherm models were applied to the equilibrium data. The developed method showed high applicability to Langmuir isotherm model (R^2>0.997) compared with Freuindlich model (R2>0.888) for the adsorption of Pb(ll) on maize stalks. Maximum saturated monolayer sorption capacity of maize stalks for Pb(ll) was 5.14 mg/g. The study showed that maize stalks can be used as a Cheap Biosorbent for the adsorption of Pb(ll) From water solution.

Keywords Pb(ll), Adsorption, Maize Stalks, Isotherms

Introduction

Contamination of water by toxic heavy metals through the discharge of industrial wastewater is a world wide environmental problem [1-3]. Rapid industrialization has seriously contributed to the release of toxic heavy metals to water streams. Mining, electroplating, metal processing, textile and battery manufacturing industry are the main sources of heavy metal ion contamination [4-5]. Metals such as lead, cadmium, copper, arsenic, nickel, chromium, zinc and mercury have been recognized as hazardous heavy metals [6-8]. Lead is a poisonous element causing several kinds of diseases. Among the health problems associated with lead include kidney damage, reproductive system and cardiovascular impairments, enzymes inhibition, anemia and death [9-11]. Lead is commonly emitted from materials such as incomplete burning of fuels, photographic materials, batteries, printing materials, pigments and paint materials [12-13].

Heavy metals are toxic and have the tendency to bio-accumulate [14, 15]. It has been consistently desired that their levels be reduced in industrial and municipal effluents before ultimate repository in the ecosystem [16-18]. In the recent years, the research for the removal of toxic metals from aqueous solution has focused on new technologies rather than conventional methods such as chemical precipitation, ion-exchange, solvent extraction and membrane processes which are generally considered not only to be expensive but are also inefficient in the removal of these toxicants from contaminated environment [19, 20]. It is therefore, essential to search agricultural by-products and to transform such materials to adsorbents. Now days, agricultural materials are receiving more and more attention as adsorbents for the removal of heavy metals from water [21-22]. Adsorbents of agricultural origin have polymeric groups like cellulose, hemi-cellulose, pectin, lignin and proteins as active centers for metal uptake [23-25].

The purpose of present study is to evaluate the efficiency of b nana peels as adsorbent for cadmium and lead, and to establish two parameter equations (Langmuir, Freundlich isotherms) to model the sorption data.

Maximum adsorption capacity of adsorbent, adsorption intensity of the adsorbate on adsorbent surface and adsorption potentials of adsorbent were estimated by Langmuir, Freundlich isotherms, respectively.

Materials and Methods

All the glass ware used were thoroughly washed with detergent and tap water then rinsed with distilled water and thereafter soaked in 10 % nitric acid for 1hour after which they were rinsed with distilled-deionised water and dried. 1000 mg/L stock solution of $Pb(NO_3)_2$ (Merck, Germany) was prepared. Working solutions of initial concentrations of 5, 10, 25, 50, 75 and 100 mg/L were then prepared from the stock solution using the dilution principle.

Biosorbent

Maize stalks were collected and used as sorbent for the biosorption of Pb(ll). The maize stalks sample was collected from research farm of Tabriz (Iran) agricultural school. Samples were washed several times using doubledistilled water to remove extraneous and dust. They were then dried in an oven at 105 ºC for 24 h. The dried biomass was chopped and filtered. The resulting powder was sieved to a particle size of 100 µm which was used for the adsorption studies.

Adsorption studies

Batch adsorption experiments were carried out at room temperature (25°C±1). Exactly 100 ml of Pb(II) solution of different concentrations (10-100 mg/L) was put in different beakers and 0.25 g of the adsorbent added to each of them and they were subsequently agitated at a stirring rate of 200 rpm with a magnetic stirrer for a period of 90 min. The pH values of the solutions were adjusted to the required value by adding either 0.1 M HCl or 1M NaOH solution. Samples were then collected, filtered and the filtrate was analysed for Pb(ll) ions contents using Buck Scientific model Shimadzu AA 6300 Atomic Absorption Spectrophotometer. Experiments were carried out in duplicate and mean values are presented. The percentage removal of Pb(II) were calculated using the following relationship [26-27]:

$$R = \frac{(Co - Ce)}{C_0} \times 100$$

Where C_0 and C_e are the initial and final (equilibrium) concentrations of the synthetic solution of solution (mg/L), respectively. Blanks containing only distilled water were used for each series of experiments as controls. The amount of the synthetic solution of adsorption per unit mass of maize stalks at equilibrium, q_e (mg/g) was calculated by the following equation [28, 29]:

$$q_e = \frac{(Co - Ce) \times V}{M}$$

where V is the volume of the synthetic solution of solution (L) and W is the weight of maize stalks (g) added to volume V.

Results and discussion

Effects of Contact Time and Initial Pb(II) Concentration

The effect of contact time on the efficiency of biosorption of Pb (II) ions by maize stalks is shown in Fig. 1. As seen, the efficiency of uptake of Pb (II) ions by biomass increases with the contact time. The results showed that a contact time of 90 min is enough to attain equilibrium. Above this time, there was no further appreciable adsorption of Pb (II) ions by the biomass. The adsorption process was however very rapid at the initial stage and slow down as the reaction approached the equilibrium stage. The rapid adsorption process which was observed at the initial stage may be due to the rapid accumulation of Pb (II) ions on the pore sites of the maize stalks as a result of the presence of vacant sites on its surface [30, 31]. These vacant sites become occupied by Pb (II) ions as the reaction proceeds thereby making the penetration of more Pb (II) ions into the interior of the biosorbent difficult [32-33].

The initial metal concentration is a significant factor in determining the adsorption potency of a biomass. The effect of initial concentration of the adsorbate was evaluated at different concentrations of 5, 10, 25, 50, 75 and 100 mg/L at a temperature of 25ºC, contact time of 90 min and pH of 6.0 which is shown in Fig. 2. As revealed in the figure, the amount of Pb (II) ions adsorbed increases with increase in the initial concentration of the adsorbate. But clear from Fig. 2 that the percentage removal decreases with increase in initial concentration of Pb (II) ion. The metal ion uptake were found to be 98.5%, 98.1% and 76.4% for initial metal concentrations of 5, 10 and 100 mg/L, respectively. This was due to the saturation of the adsorption sites of the adsorbent by the metal ion [34-35].

Effect of Stirring Speed

The effect of agitation speed on Pb(ll) adsorption at the adsorbent dose of 2.5 g/L and initial iron concentration of 50 mg/L at a pH 6 is shown in Fig. 3. The increase of stirring speed causes a corresponding increase in metal ion removal. As a result of increasing the stirring speed, the diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. Under these conditions, the value of the external diffusion coefficient became higher [36-37].

Adsorption isotherms

Adsorption isotherms describe qualitative information on the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. Adsorption isotherms are critical in optimizing the use of adsorbents, and the analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes. The equilibrium data were analyzed using the following Langmuir and Freundlich isotherm models [38-40]:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max}\ K_L} \times \frac{1}{C_e}$$

$$\text{Ln } q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where C_e is the equilibrium solution concentration (mg/L) and q_e is the amount of Pb(II) adsorbed onto Maize stalks at equilibrium (mg/g). q_m and K_L are the Langmuir constants related to the adsorption capacity (mg/g) and energy of adsorption (l/mg) respectively. K_F and n are the Freundlich constants related to adsorption capacity and energy of adsorption, respectively.

The equilibrium adsorption studies were conducted using various initial Pb(II) concentrations of 100 mg/L at pH 6 at three different temperatures of 25–45 ℃. Isotherm parameters of the two models obtained by using linear regression are listed in Table 1.

In order to compare the validity of each isotherm model, a normalized standard deviation Δq (%) was calculated using [41-43]:

$$\%\Delta q = 100 \sqrt{\frac{\sum((q_{exp} - q_{cal})/q_{exp})2}{n-1}}$$

Where q_{exp} and q_{cal} are experimental and calculated amount of Pb(II) adsorbed on Maize stalks, and N is the number of measurements made. It was found that the fitting to the Langmuir equation gave the higher values of correlation coefficients than those for the Freundlich equation at the temperatures investigated. Further more, The values of Δq(%) for the Langmuir equation were all lower than those for the Freundlich equation. The above results showed that the empirical Langmuir equation was better than the Freundlich equation in describing the behavior of Pb(II) adsorption onto Maize stalks, implying that the adsorption process involved monomolecular layers of coverage.

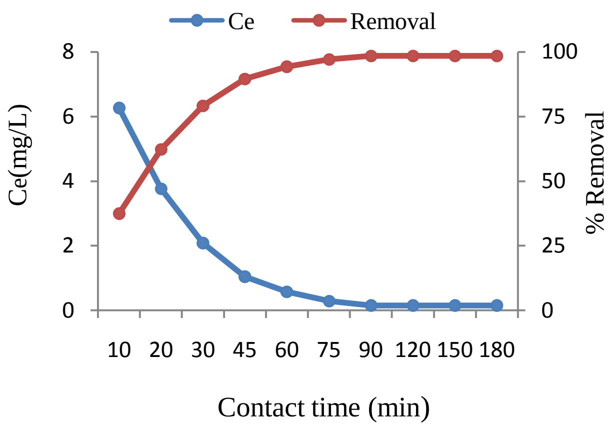

Figure 1: Effect of contact time on the removal of Pb(II) by maize stalks (Dose = 2.5 g/L, Pb(II) concentration = 10 mg/L, pH = 6, Stirring speed 200 rpm and Temp= 25 °C)

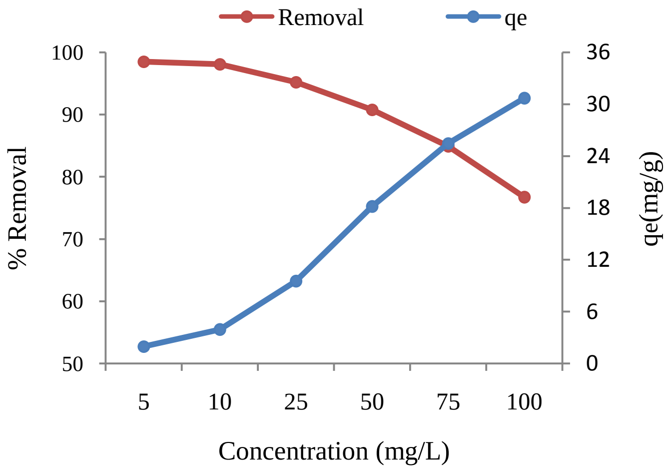

Figure 2: Effect of contact time and initial metal concentration on the removal of Fe(II) by maize stalks (Dose = 2.5 g/L, Contact time 90 min, pH = 6, Stirring speed 200 rpm and Temp= 25 °C)

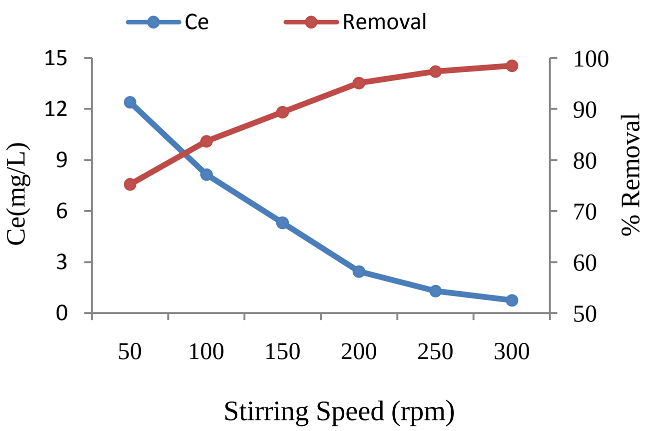

Figure 3: Effect of stirring speed on the removal of Pb(II) by maize stalks (Dose = 2.5 g/L, Pb(II) concentration = 50 mg/L, pH = 6, Contact time 90 min and Temp= 25 °C)

Table 1: Isotherm parameters for Pb(II) adsorption onto Maize stalks at different temperatures

Isotherms	Parameters	25 ℃	35 ℃	45 ℃
Langmuir	q_m (mg/g)	28.48	29.11	29.86
	K_L (l/mg)	0.224	0.195	0.181
	R^2	0.998	0.999	0.997
	Δq(%)	1.85	2.18	2.76
Freundlich	K_F(l/mg)	28.24	31.45	32.79
	1/n	0.244	0.281	0.325
	R^2	0.884	0.902	0.928
	Δq(%)	11.28	10.98	14.35

Conclusion

The efficiency of Maize stalks to remove Pb (II) ions from aqueous solution was investigated. In batch studies, the optimum Initial Pb(II) Concentration, Stirring Speed and contact time were optimized. As a result, Initial Pb(II) Concentration of 5 and 10 mg/L, Stirring Speed of 200 rpm and contact time of 90 min were found to be optimized condition for the removal of Pb(II) by Maize stalks**.** Langmuir adsorption model can be applied successfully to the adsorption of Pb (II) ions compared to Freundlich. The adsorption capacity corresponding to monolayer coverage is 28.48 mg/g according to Langmuir model at room temperature (25 ℃). Thus, it can be concluded that Maize stalks is a good agricultural residues for the removal of Pb (II) ions from aqueous solution.

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