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ABSTRACT: The aim of the present work was to investigate the ability of Cocopeat to remove of lead (II) from aqueous solutions. The effects of different parameters such as particle size, adsorbent dosage, pH, contact time, agitation speed and concentration on the removal process has been investigated. The maximum removal of lead ion (92.5%) took place in the pH range of 4 contact time in 30 minutes and initial concentration of 30 mg.L⁻¹. Results indicated that the Langmuir model gave a better fit to the experimental data in comparison with the Freundlich equation. The process followed pseudo-second-order kinetics.

KEY WORDS: Removal, Cocopeat, Isotherms, Kinetics.

INTRODUCTION
Aqueous heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain [1]. Lead is a toxic element which is conservative and has cumulative characteristics. Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, solder and steel products [2]. The permissible limit of lead in drinking water is 0.05 mg.L⁻¹. The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy, and hepatitis [3]. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electrodialysis. Among various treatment methods ion exchange looks like the most attractive one when effective, low-cost ion exchangers are used. Generally ion exchange and sorption are also preferred for the removal of heavy metal ions due to easy handling [1, 4].

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This paper examines the elimination of lead present in an aqueous solution using Cocopeat as a biosorbent material. Cocopeat, also known as Coir or Coir Fibre Dust, is the pithy material left after coir fibre is extracted from coconut husks. Since the Cocopeat regarded as an excellent growing medium for hydroponics or container plant growing, it was selected for studying biosorption [5]. The mostly important process parameters include concentration of metal ions and the biomass, temperature, contact time, agitation and pH. Biosorption is a quick process. The equilibrium is usually reached within few minutes. The process is usually described with either first-, second-, pseudo-first- or pseudo-second order kinetic equation [6].

EXPERIMENTAL SECTION

Cocopeat was provided from the greenhouse of Sistan and Baluchestan University, Zahedan, Iran and washed repeatedly with water to remove dust and soluble impurities. The washed materials dried in an oven to constant weight and were then ground with electronic grinder. The Cocopeat particles were sieved, and a certain size range from 150 to 420 µm was collected and finally kept in bottles. All the chemicals used in the experiments were of analytical grade. Pb(NO₃)₂ (Reidel-de-Haën, minimum assay 99%) was used as the source of Pb (II) and all the solutions were made in double-distilled water. The solutions of Pb(II) were made from a stock solution containing 1000 mg of Pb(II) in 1L. For experiments at different pH, the acidity of Pb(II) solution was adjusted by addition of drops of 0.1M HNO₃ and 0.1M NaOH solution. Removal of lead from the solution was monitored by tracing the decrease of lead concentration. Lead concentrations were measured using flame atomic absorption spectrophotometer (Philips PU9100X) equipped with Hollow Cathode Lamp and air acetylene burner. Each measurement of lead concentration was repeated three times.

RESULTS AND DISCUSSION

Effect of the sorbent particle size
The effect of particle size on uptake of Pb(II) was studied with different sizes from 150 to 420µm. The sorption of lead (II) increased by decreasing particle size up to 180µm and then it remains almost constant. This phenomenon is expected as the size of the adsorbent decreases the surface area increases [7,8]. It was revealed that the particle size of 180µm would be suitable for adsorption.

Effect of Adsorbent Dose
The effect of adsorbent dose was studied by varying the sorbent amounts from 1 to 40 g/L. For all these runs, initial concentration of lead was fixed to 30 mg/L. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites. The amount of Adsorbed lead increased from 1 to 10 g/L and decreased from 10 to 20 g/L and any further addition of the adsorbent beyond this did not cause any significant change in the adsorption. The maximum removal of lead was obtained in the adsorbent dose of 10 g/L. The results are shown in Fig. 1.

Effect of pH
PH of solution is one of the most important parameters for adsorption of heavy metals from contaminated aqueous solution. This is partly because hydrogen ions themselves are strongly competing with biosorbates [9]. The pH solution ranging from 2 to 8 was studied. As shown in Fig. 2, the uptake of lead proliferated by increasing pH from 2 to 4. The optimum pH for the maximum biosorption of lead was 4. Above pH 5.5, insoluble lead hydroxide starts precipitating therefore true adsorption study was impossible [10].

Effect of contact time
Experiments were conducted for this purpose, varying contact time from 5 to 120 min. The maximum percent
lead removal was attained after 30 min of shaking time. After this time, the amount of adsorbed lead ions was almost constant. Increase in percent removal of lead with increase in contact time can be attributed to the fact that time becomes available for metal ions to make an attraction complex with Cocopeat [11].

**Effect of agitation speed**

Biosorption studies of lead with Cocopeat was carried out in shaker working at pH = 4.0 using a lead solution of 30 mg/L by varying the agitation speeds from 50 to 500 rpm. Results showed that the high amount of adsorbed lead at equilibrium was obtained with an agitation speed of 100 rpm. The results are represented in Fig. 3.

**Effect of concentration**

The amount of a metal ion recovered from solution is affected by biomass concentration. Effect of initial Pb2+ concentration in the range of 10 to 70 mg/L on adsorption was investigated. As shown in Fig. 4, by increasing metal concentration, the percentage of removed metal decreased to 30 mg/L and constant after that. This appears to be due to the increase in the number of ions competing for the available binding sites in the biomass and also due to the Pb ions at higher concentration levels [12].

**Adsorption isotherms**

The equilibrium biosorption isotherms are most important to understand the mechanism of biosorption. The experimental data analyzed according to the linear model of the Langmuir and Freundlich isotherms. The Langmuir isotherm is valid for monolayer sorption a surface with a finite number of identical sites and is expressed in the linear form as:

$$\frac{C_e}{q} = \frac{1}{q_m b} + \frac{C_e}{q_m}$$

Where $C_e$ is the equilibrium concentration (mg/L) and $q$ the amount adsorbed at equilibrium (mg/g). The Langmuir constants $q_m$ (mg/g) represent the monolayer adsorption capacity and $b$ (1/mg) is the Langmuir bonding energy coefficient [13].

The empirical Freundlich equation based on sorption onto a heterogeneous surface and is linear form as [14]:

$$\log q = \log K_f + \frac{1}{n} \log C_e$$

Where $K_f$ (mg/g) a constant is related to the biosorption capacity and $n$ an empirical parameter related to the intensity of adsorption. The Langmuir and Freundlich
Table 1: Langmuir and Freundlich isotherm parameters for the adsorption of lead (II) by the Cocopeat.

<table>
<thead>
<tr>
<th>Langmuir parameters</th>
<th>Freundlich parameters</th>
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</thead>
<tbody>
<tr>
<td>$Q_m$ (mg/g)</td>
<td>$K_f$ (1/g)</td>
</tr>
<tr>
<td>3.918</td>
<td>0.0309</td>
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</tbody>
</table>

Fig. 5: Langmuir isotherm plot for Pb (II) adsorption onto Cocopeat.

Fig. 6: Freundlich isotherm plot for Pb (II) adsorption onto Cocopeat.

Adsorption constants evaluated from the isotherms with correlation coefficients are presented in Table 1.

Langmuir and Freundlich isotherms are shown in Figs. 5 and 6.

As shown in Table 1, Figs. 5 and 6, the Langmuir isotherm model fit equilibrium data better than Freundlich model as is evident from the $R^2$ values which suggests that lead ion are adsorbed onto the surface of Cocopeat in a monolayer pattern.

Kinetics of Adsorption

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process [15]. Sorption kinetics, expressed in terms of the rate of solute removal, that controls the residence time of the sorbate in the solid-solution interface, is one of the most important aspects of operation defining the efficiency of the process. Kinetics of sorption describes the solute uptake rate, which in turn governs the residence time of sorption reaction [16]. It is one of the important characteristics in defining of sorption. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first-order and pseudo-second-order. These models are explained as follows:

The pseudo-first-order equation

$$\ln (q_e - q_t) = \ln q_e - K_1 t$$

Where $q_e$ and $q_t$ are the amounts of metal ion sorbed (mg/g) at equilibrium and at time $t$, respectively. $K_1$ is the Lagergren rate constant of the biosorbent (1/min). Fig. 7 shows the pseudo-first-order Kinetic plot for the adsorption of lead onto Cocopeat. The pseudo-first-order rate constant $K_1$ values were calculated from the slope of Figure 7. The calculated $K_1$ values and their corresponding linear regression correlation coefficient $R_1^2$ found as 0.977 [17].

The pseudo-second-order equation

$$\frac{T}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}$$

Where $T$ is the contact time (min), $q_e$ (mg/g) is the equilibrium capacity and $q_t$ is the biosorption capacity any time $t$. $K_2$ is equilibrium rate constant of second order Kinetics model (g/mg.min).

The slopes and intercepts of plots $T/q_t$ versus $t$ were used to calculate the the pseudo-second-order rate constants $K_2$ and $q_e$. The calculated $q_e$ [15]. Fig. 8 shows the pseudo-second-order Kinetic plot for the adsorption of lead onto Cocopeat.

The pseudo-second-order rate constant $K_2$, the calculated $q_e$ value and the corresponding linear regression correlation coefficient value $R_2^2$ are given in Table. 2.
Table 2: Parameter values calculated using the pseudo-first-order and pseudo-second-order Kinetic models the adsorption of lead (II) by Cocopeat.

<table>
<thead>
<tr>
<th></th>
<th>Pseudo-first-order Kinetic model</th>
<th>Pseudo-second-order Kinetic model</th>
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<tbody>
<tr>
<td></td>
<td>$K_1$ (1/min)</td>
<td>$q_e$ (mg/g)</td>
</tr>
<tr>
<td>----------------------</td>
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<tr>
<td></td>
<td>0.0523</td>
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</table>

Fig. 7: Pseudo-first-order plot of lead (II) adsorption by Cocopeat.

CONCLUSIONS

Environmental protection requires the use of natural product instead of chemicals to minimize pollution. Cocopeat is a natural fibre made out of Coconut husks. It was evaluated as possible biosorbent for removal of lead (II) from aqueous solution. The biosorption was dependent on particle size, biosorbent dosage, pH, contact time, agitation speed and concentration. The optimum PH in this study was 4. Agitation speed studies indicated maximum lead biosorption at 100 rpm. The maximum removal of lead ion (92.5%) took place in the pH range of 4 contact time in 30 minutes and initial concentration of 30 mg.L⁻¹. The suitable time of contact is approximately 30 minutes. The Pb (II) adsorption on Cocopeat was described by the Langmuir and Freundlich isotherms. The experimental data were correlated better by the Langmuir isotherm model. Adsorption was best fitted by the pseudo-second-order model.

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REFERENCES


