Betel-nut Peel as an Adsorbent in the Removal of Cd, Cr and Pb from Aqueous Solutions


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Abstract

The ability of Betel-nut Peel BP, an agricultural waste material, for the removal of chromium (Cr<sup>3+</sup>), cadmium (Cd<sup>2+</sup>) and lead (Pb<sup>2+</sup>) from aqueous solution has been investigated. In the batch tests experimental parameters were studied, including solution pH, contact time, adsorbent dose, initial solution volume of metal ions and initial metal ions concentration. The adsorbent exhibited good sorption potential at pH 4.0. Maximum removal of Cr, Cd and Pb (96-98.0) % with (60 mg/mL) of sorbent was observed at 10 mg/L sorbate concentration. Removal of about 50-60% occurred in 50 min, and equilibrium was attained at around 90 min for all the three metal ions. The functional groups (C=O, S=O, −OH) present on the carbon surface of BP were responsible for the adsorption of metal ions. The adsorption parameters were analyzed using both the Freundlich and Langmuir models. The value of <i>K<sub>F</sub></i> is large and 1/<i>n</i> is 0.1-0.69, indicating that BP has high adsorption capacities for Cr<sup>3+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup>. The desorption studies were carried out using HCl. Maximum desorptions of 72% for Cd and Pb and 67% for Cr were attained with 6M HCl.

Keywords: Betel-nut Peel; Adsorbent; Removal; Chromium; Cadmium; Lead.

Introduction

The removal of heavy metal contaminants from aqueous solutions is one of the most important environmental concerns because metals are bio-refractory, and are toxic to many life forms. Various sources of chromium, cadmium and lead in water are leather tanning, textile, agrochemicals, battery manufacturing, basic steel, paper, metal-plating and fertilizer industries. Higher concentrations of heavy metals in water and soils may increase the uptake of these metals by crops and potentially affect human health via food chains [1]. Chromium, cadmium and lead are ubiquitous in the environment and are hazardous at high levels. Because of their hazardous nature, there is a necessity to remove these metals from wastewater in order to prevent contamination of natural water bodies by effluents containing toxic metals. The common methods for removing metal ions from water and wastewater include chemical precipitation, oxidation, reduction, reverse osmosis, membrane filtration and adsorption [2]. Among these, adsorption is effective and economical.

The adsorption process has been shown to be highly efficient method for the removal of inorganic pollutants from waste effluents [3]. The high cost of commercially available activated carbon limits its use as adsorbent in developing countries. Hence, there is a growing need to use locally available waste materials. Several researchers have used different agricultural wastes such as oil palm shells [4], coir pith carbon [5], peanut husks [6], olive pulp [7], rice husk [8], coconut shell [9], coffee bean husk [10], bamboo waste [11] and cassava peel [12] and jackfruit peel

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[13] for the treatment of water and wastewater. While several researchers have adopted various low-cost adsorbents, there is still a need to develop a cheaper and readily available material, which can be effective and economical for the removal of chromium, cadmium and lead from aqueous solutions.

The aim of this study was to investigate the application of BP for the removal of Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\) from aqueous solutions. The Betel-nut tree is widely available in Bangladesh. In addition, peels obtained from the BP are no economic importance and are considered as agricultural waste.

Materials and Methods

Procedure of adsorbent preparation

The adsorbents used in this study were the outer skin of BP. BP was collected from Badamtoli, Dhaka. The outer skin of BP was obtained after cutting into slivers. Thereafter the peels were washed with pure water several times to remove dust and fines and air dried for seven days. The air-dried sample was ground to fine powder using a grinding machine. It was sieved with a series of sieves of 90-460 μm meshes to obtain fine particles and stored in desiccators for further use [14]. This material was used for the removal of Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\) without further chemical treatment.

Chemicals

All the chemicals used were of analytical grade. Deionised doubly distilled water was used throughout the experimental studies. Working standards were prepared by progressive dilution of stock Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\) solution using 1000 mg/L stock solution purchased from BDH Company. ACS reagent grade, HCl, NaOH (E. Merck) was used to adjust the solution pH.

Instrumentation

The initial concentrations of Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\) in aqueous solutions taken in reagent bottles and concentrations of Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\) remaining in solutions after shaking with BP (adsorbent) were determinate by AAS method. The difference in concentrations was taken as the amounts of Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\) adsorbed by the BP. An Atomic absorption spectrophotometer (AA Analyst 800, Perkin Elmer, USA), with Cr, Cd and Pb hollow cathode lamp and air acetylene flame, was used for determining Cr, Cd and Pb concentrations. A pH meter (TOA, Japan) was used for pH measurements. A mechanical shaker was used for agitating the samples. Fourier transform infrared spectrometry (IR Affinity-1, Shimadju, Japan) was used to analyze the organic functional groups in the adsorbent. The transmission spectrum was acquired at 64 scans with 4 cm\(^{-1}\) resolution and the spectrum was corrected for a KBr background. Scanning electron microscope (JEOL, 5800LV, Japan) was used for surface characterization of the adsorbent.

Determination of surface area

Surface area of the adsorbent was determined by the method described by Shoemaker and Garland [15]. A 500 mg of BP (90 μm) was placed in 500 mL reagent bottles containing 50 mL of 0.05, 0.10 and 0.15 M acetic acid; a control was also prepared for each concentration without adsorbent. They were tightly closed and agitated for 1 h at 150 rpm. The samples were filtered through Whatmann No. 42 filters. The filtrate was titrated with standard NaOH solution to find out the remaining concentration of acetic acid (C). The concentration of acetic acid remaining in each case (C) was divided by the number of moles of acetic acid (N) adsorbed per gram of the adsorbent to get the ratio, C/N. The slope of the linear plot of C/N vs. C in Fig. 1(a) yielded N\(_m\) value (i. e., N\(_m\) = \(1/\)slope). Surface area, A (m\(^2\)/g) was calculated using the following equation:

\[
A = N_m \times \frac{N_0 \times \sigma \times 10^{-20}}{}\]

Where

\[
N_0 \quad \text{Avogadro number}
\]

\[
N_m \quad \text{Number of moles per gram required to form monolayer}
\]

\[
\sigma \quad \text{Molecular cross section area given in square angstrom (21 °A) for acetic acid}
\]
Batch mode adsorption studies

The removal of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ from aqueous solutions using BP by the batch method was carried out by the following experimental conditions:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration of Cr, Cd and Pb (mg/L)</td>
<td>10, 20, 30, 40, 50</td>
</tr>
<tr>
<td>Amount of BP added to each set of reagent bottle (g)</td>
<td>0.1, 0.2, 0.3, 0.4</td>
</tr>
<tr>
<td>Variation of pH</td>
<td>1.0-12.0</td>
</tr>
<tr>
<td>Variation of agitation time (min)</td>
<td>5, 15, 30, 40, 50, 60, 80, 100, 120</td>
</tr>
</tbody>
</table>

Batch adsorption experiments were carried out in a series of stopper reagent bottles. For each reagent bottle (100 mL capacity) containing 50 mL of aqueous solution with 10 to 50 mg/L of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$, a weighed amount of (0.1-0.4 g) of adsorbent was introduced. The solution pH was adjusted to the desired value by adding HCl or NaOH. The bottles were shaken at room temperature (30±1 °C) using a mechanical shaker at 150 rpm for a selected time (10-120 min) to attain equilibrium. The solutions were separated from the adsorbent by centrifugation at 2000 rpm for 20 min. The concentration of metal ions (Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$) remaining in aqueous solutions was determined by AAS method. Blank solutions were treated similarly (without adsorbent). All of the batch experiments were carried out in a duplicate and the values reported are average of two readings [1].

Desorption studies

The reversibility of adsorption was investigated by carrying out desorption experiments, which consisted of performing an adsorption experiment as already described. Once equilibrium was reached, BP (0.3 g) saturated with Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ was removed from solution and transferred into stopper reagent bottles (250 mL capacity), 100 mL of (2.0-6.0M) concentration HCl solution was added and the bottles were shaken at 150 rpm for 3 h at room temperature (30 ± 1 °C) using a mechanical shaker. Then the sorbent was removed by centrifugation. The concentration of Cr, Cd and Pb in the aqueous solutions was determined by AAS method.

Sorption isotherm models

Adsorption capacities ($q$), the amount (mg) of adsorbed metal per weight (g) of biomaterials, were determined from Equation 2 [16].

$$q = (C_0 - C) \times \frac{V}{W} \quad (2)$$

Where $C_0$ and $C$ are the initial and the final metal concentrations of the solution (mg/L), respectively, V is the volume of the solution in L and W is the amount of biomaterial (g).

The sorption equilibrium data of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ onto BP were analyzed in terms of Langmuir and Freundlich isotherm models for the purpose of interpolation and limited extrapolation of the data. The relative coefficients of these models were calculated using linear least-squares fitting.

The linear form of Langmuir sorption isotherm equation becomes [17].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \quad (3)$$

A plot of $C_e/q_e$ versus $C_e$ should indicate a straight line of slope $1/q_m$ and an intercept of $1/(q_m K_a)$ where $C_e$ is the equilibrium concentration.
(mg/dm³), qₑ, the amount of metal sorbed (mg/g), qₑ₀ for a complete monolayer (mg/g), and Kₑ is the sorption equilibrium constant (dm³/mg). The essential characteristics of Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, Rₑ, which is defined as [1].

\[ Rₑ = \frac{1}{1 + \frac{Kₑ}{C₀}} \]

(4)

Where Kₑ is the Langmuir constant and C₀ is the initial concentration of Cr³⁺, Cd²⁺ and Pb²⁺. The Rₑ values indicate the shape of the isotherm.

<table>
<thead>
<tr>
<th>Rₑ</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt; 1</td>
<td>Unfavorable</td>
</tr>
<tr>
<td>1</td>
<td>Linear</td>
</tr>
<tr>
<td>0 &lt; Rₑ &lt; 1</td>
<td>Favorable</td>
</tr>
<tr>
<td>0</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

According to Mckay et al. [18], Rₑ values between 0 and 1 indicate favorable adsorption.

The Freundlich isotherm equation

\[ qₑ = Kₑ Cₑ^n \]

can be written in the linear form as given below [17].

\[ \log(qₑ) = 1/n \log(Cₑ) + \log(Kₑ) \]

(5)

Where qₑ and Cₑ are the equilibrium concentrations of Cr or Cd or Pb in the adsorbed and liquid phases in mmol/g and mmol/L, respectively; Kₑ and n are the Freundlich constants that are related to the sorption capacity and intensity, respectively. The Freundlich constant Kₑ and n can be calculated from the slope and intercept of the linear plot, with log (qₑ) vs. log (Cₑ).

**Kinetic models**

The sorption kinetic data of Cr³⁺, Cd²⁺ and Pb²⁺ measured on BP was analyzed in terms of pseudo-first-order and pseudo-second-order sorption equations [1, 19]. The simplified pseudo-first-order equation is shown below:

\[ \log(qₑ - qₜ) = \log qₑ - \frac{K₁}{2.303} t \]

(6)

The sorption rate constant, K₂ can be calculated by plotting \( \log(qₑ - qₜ) \) vs. t.

Where \( K₁ \) (min⁻¹) is the rate constant of the pseudo-first order sorption, qₑ (mg/g) denotes the amount of sorption at t (min), qₑ (mg/g) is the amount of sorption at equilibrium. The second-order equation can be obtained on into a linear form [1]:

\[ \frac{t}{qₚ} = \frac{1}{K₂ qₑ^2} + \frac{1}{qₑ} \]

(7)

K₂ and qₑ can be obtained from the intercept and slope of plotting t/qₑ vs. t.

**Results and Discussion**

**Characteristics of the adsorbent**

The physical characteristics in the Be BP are presented in (Table 1). The FT-IR spectrum of the BP is shown in (Fig. 1b). The absorption at 3370 cm⁻¹ indicates the presence of OH group, which was probably attributed to adsorbed water on the carbon [21]. The band appearing at 1590 cm⁻¹ is ascribed to the formation of oxygen functional groups like a highly conjugated C=O stretching in carboxylic groups, and carboxylate moieties [22]. The additional peak at 1116 cm⁻¹ indicate the presence of S=O group [23]. These carbon containing polar functional groups (C=O, S=O, -OH) could be involved in chemical bonding and may be responsible for the adsorption of metals [16, 24].

**Table 1. Characteristics of the BP**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesh size</td>
<td>90 μm</td>
</tr>
<tr>
<td>Specific surface area (m²/g)</td>
<td>420.0</td>
</tr>
<tr>
<td>pHₚₚ</td>
<td>3.7</td>
</tr>
<tr>
<td>Moisture</td>
<td>12.0%</td>
</tr>
</tbody>
</table>

The SEM picture of the porous texture betel-nut peel before and after adsorption of Cr³⁺, Cd²⁺ and Pb²⁺ is shown in (Fig. 1c). From the SEM images of BP, there are uniform and well developed pore structure on the surface of the BP. Physically and chemically BP show tremendous, perfect and constructed pore structures on the
surface. High surface area and pore structure are the basic parameters for an effective adsorbent. When the porosity increases the surface area also increases. Therefore, Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\) significantly adsorbed on this adsorbent.

![Figure 1(b). FT-IR spectra of BP](image)

Chromium adsorbed on BP

![BP](image)

Lead adsorbed on BP

Cadmium adsorbed on BP

**Adsorption isotherm**

The adsorption studies were conducted at a fixed adsorbent dosage by changing initial metal ion concentrations of Cr\(^{3+}\), Cd\(^{2+}\) and Pb\(^{2+}\). The equilibrium data were analyzed using Langmuir and Freundlich equilibrium models (equations 3 and 5) in order to obtain best fit isotherm. The Freundlich and Langmuir isotherms are shown graphically in (Fig. 2 and Fig. 3).

The fitted constants for two models along with regression coefficients and few related works are summarized in Table 2 and Table 2(a) respectively. Typically, the sorption data were analyzed according to the linear form of the Langmuir isotherm (Eq. 3). Plots of the specific sorption, \(C_e/q_e\) against the equilibrium concentration, \(C_e\) for Cd, Cr and Pb are shown in (Fig. 2), and the linear isotherm constants \(q_m\) and
$K_a$ and the coefficient of determination, $r^2$ are presented in (Table 2).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Langmuir (Eq. 2)</th>
<th>Freundlich (Eq. 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r^2$</td>
<td>$q_m$ (mg/g)</td>
</tr>
<tr>
<td>Cd</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>99</td>
<td>34</td>
</tr>
<tr>
<td>Cr</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>86</td>
<td>43</td>
</tr>
<tr>
<td>Pb</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>99</td>
<td>43</td>
</tr>
</tbody>
</table>

These isotherms were found to be linear over the entire concentration range studied with high $r^2$ values. The $r^2$ values suggest that the Langmuir isotherm provides a good model of the sorption system. The sorption constant, $K_a$ and the saturated monolayer sorption capacity, $q_m$ onto BP were satisfactory.

Examination of the Freundlich isotherm plot suggests that a good model for the sorption of heavy metals (Cr$^{3+}$, Cd$^{2+}$) has been achieved. Cd$^{2+}$ and Pb$^{2+}$ are moderately fitted. Table 2 shows the linear Freundlich sorption isotherm constants, $K_F$ and $1/n$, and the coefficients of determination, $r^2$. The value of $K_F$ is large, and $1/n$ is 0.1-0.69, indicating that the adsorbents employed have a high adsorptive capability.

**Adsorption Kinetics**

The sorption kinetics were investigated with a constant concentration of Cr, Cd and Pb : 20 mg/L at 0.3g/50 mL sorbent dose in the contact time of 0 to 120 min. The results are summarized in Table 3. The equilibrium sorption capacities $q_e$ (cal) determined using pseudo-first-order model do not agree with the experimental $q_e$ (exp) values. However, the equilibrium sorption capacities $q_e$ (cal) determined using pseudo-second-order plots in (Fig. 4) by the method of Ho Wang [25] is in good agreement with the experimental $q_e$ (exp) values.
Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The binding of metal ions by surface functional groups is strongly pH dependent [26]. The adsorption of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ ions as a function of pH (2 to 12) for BP is shown in (Fig. 5) The analysis of the results of adsorption of Cr, Cd and Zn at equilibrium (pH 4.0) indicates that Pb has a slightly higher affinity towards adsorbent than Cr and Cd. This phenomenon depends on the metal hydrolysis constants of the three metal ions [27].

The correlation between metal acidic property and its affinity towards adsorbent is more important than the functional groups present on the adsorbent surface. Hence the aliphatic (C-H) functional groups that are present on the adsorbent do not have much effect on the adsorption of Cr, Cd and Pb. At low pH, the surface of the adsorbent was surrounded by hydronium ions that compete with metal ions, which prevented the metal ions approaching the binding sites on the adsorbent. The increase in metal removal as pH increase can be explained on the basis of a decrease in competition between hydronium ions and metal species for the surface sites and also by the decrease in positive surface charge on the adsorbent, which results in a lower electrostatic repulsion between the surface and the metal ions and hence uptake of metal ions increases. The effect of pH can also be explained in terms of pH$_{pzc}$ of the adsorbent; at pH$_{pzc}$ the number of positive and negative groups are equal and thus total surface charges becomes zero. The PZC of the adsorbent (pH$_{pzc}$) was 3.7, which was determined by the method described by Kinnidurgh et al [28]. The surface charge of the adsorbent was positive when the solution pH was below the pH$_{pzc}$ value while it was negative at a pH was above the pH$_{pzc}$; thus below pH of 3.7, the surface charge of the BP was also positive and uptake of metals was low. When the solution pH was increased above 3.7, the surface of BP was negatively charged. The adsorption increases as long as the metal species are positively charged. Furthermore, cations adsorption will be favorable at pH value higher than pH$_{pzc}$ and anion adsorption at pH values lower than pH$_{pzc}$. At pH >4.1 all the three metal ions precipitate as Cr(OH)$_3$, Cd(OH)$_2$ and Pb(OH)$_2$, preventing further adsorption of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$. Hence pH 4.0 was selected as optimum pH in the adsorption studies of Cr, Cd and Pb.

Table 3. First and second-order adsorption rate constants and calculated and experimental $q_e$ values for Cr, Cd and Pb

<table>
<thead>
<tr>
<th>Metal Conc. (20 mg/L)</th>
<th>$q_{e(exp)}$ mg/g</th>
<th>First order kinetics</th>
<th>$R^2$</th>
<th>Second order kinetics</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_1$ min$^{-1}$</td>
<td>$q_e$(cal) mg/g</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>12.010</td>
<td>0.048</td>
<td>11.09</td>
<td>0.962</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.98</td>
<td>0.996</td>
</tr>
<tr>
<td>Cd</td>
<td>12.121</td>
<td>0.051</td>
<td>11.191</td>
<td>0.944</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.412</td>
<td>0.997</td>
</tr>
<tr>
<td>Pb</td>
<td>12.324</td>
<td>0.049</td>
<td>11.332</td>
<td>0.943</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.662</td>
<td>0.996</td>
</tr>
</tbody>
</table>

log $K_{Pb} > log K_{Cr} > K_{Cd}$

HO–H + M$^{n+}$ → M(OH)$^{(n+)}$ + H$^+$  

(11)

The correlation between metal acidic property and its affinity towards adsorbent is more important than the functional groups present on the adsorbent surface.
Effect of BP dosage

The effect of adsorbent dosage on the removal of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ has been presented in (Fig. 6). The amount of BP required for the removal of Cr, Cd and Pb from 50 mL (20 mg/L) of solution was 0.3 g. The percentage of removal increased to (96-98.0)% with an adsorbent dose of 0.3 g/50 mL (6 mg/mL) in the case of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ and then remains almost constant. It is apparent that by increasing the adsorbent dose, the removal efficiency increased (69% to 96% for Cr, 80% to 98% for Cd and 82% to 88% for Pb). It is readily understood that the number of available adsorption sites increased by increasing the adsorption dose. However, 0.4 g of adsorbent showed almost the similar removal efficiency. This is due to the particle interactions, such as aggregation, resulting from high sorbent concentration. Such aggregations would lead to a decrease in the total surface area of the sorbent.

Figure 6. Effect of Adsorbent dose on removal of Cd (II), Cr (III), and Pb (II) by adsorption onto the BP.

Effect of contact time

The equilibrium time is one of the parameters for economical wastewater treatment plant applications [2]. (Fig. 7) shows the effect of contact time on removal of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$. The adsorption of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ was increased as a function of time up to 50 min at an initial concentration of 10 mg/L and remain constant. The rate of sorption of Cr, Cd and Pb on BP was rapid, with 50-60% of Cr, Cd and Pb adsorption occurring within the first 10 min and attaining equilibrium was at 60 min. This behavior suggest that at the initial stage, sorption takes place rapidly on the external surface of the sorbent followed by an internal diffusion process, which may be the rate determining step. The trend in adsorption of Cr, Cd and Pb suggests that the binding may be through interactions with functional groups located on the surface of BP. According to these results, the agitation time was fixed as 90 min for the rest of the batch experiments to make sure that equilibrium was attained.

Figure 7. Effect of contact time on removal of Cr, Cd and Pb.

Effect of initial concentration

The experimental studies were carried out with varying initial metal ion concentrations of Cr, Cd and Pb, ranging from 10 to 50 mg/l using 0.3g of adsorbent dose at pH 4.0; the results are shown in (Fig. 8).

Figure 8. Effect of initial concentration on removal of Cr, Cd and Zn (pH 4.1, contact time 60 min; dose 3.0 g).
The results demonstrate that at a fixed adsorbent dose, the percentage of adsorption decreased with increasing concentration of solution. At lower concentrations, the ratio of number of metal ions to the available sorption sites is low and subsequently the fractional adsorption becomes independent of initial concentration. At higher concentrations, however, the available sites of adsorption become fewer and subsequently the removal of metals depends on the initial concentrations. Hence, the removal of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ metals depends on the initial metal ions concentrations and decreases with increase in initial metal ions concentration.

**Effect of initial volume of solution**

As it is desired to obtain the optimum conditions for the development of a noble method for heavy metals removal; the effect of initial volume was also investigated. Different initial volumes with optimized concentration 10 mg/L of Mn$^{+}$ solution were treated onto betel-nut peel and results were summarized in (Fig. 9). It shows clearly that removal efficiency decreases with increase of initial volume. The removal efficiency varied from 83 to 55 % for Pb, 85 to 62% for Cr and 98 to 95% for Cd with initial volume 50 mL to 200 mL. Decrease of the removal efficiency suggests that it happened due to the decrease of contact of heavy metals with active sites on BP. At lower volume of Mn$^{+}$ solution, most of heavy metals (Cd$^{2+}$, Cr$^{3+}$ and Pb$^{2+}$) might get available adsorbent sites. Moreover, increasing volume of the Mn$^{+}$ solution, active adsorbent sites were unavailable due to filled by the previous metal ions. On the other hand, metal adsorption (mg/g) significantly increased with increasing volume of metal solution. This happens due to the increase in the number of ions in the solution which favors for the increase of metal adsorbed (e.g., For Cd(II) 0.98 mg to 3.80 mg/g of BP as a function of 50 to 200 mL of the solution). The two parameters Removal efficiency (%) and metal adsorbed (mg/g) were not coherent, which is shown in the (Fig. 9).

**Desorption studies**

To achieve practical adsorption, the adsorbate has to be desorbed and the spent adsorbent reused. Studies were attempted to use chemical regeneration for adsorbate desorption. Desorption of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ using HCl by disruption of coordination of metal ions and subsequent release from the BP surface into the desorption medium was studied. The results relating to desorption of Cr$^{3+}$, Cd$^{2+}$ and Pb$^{2+}$ by HCl are shown in Table 4. The results show that with increase in concentration of HCl desorption also increased.

**Table 4. Desorption studies of chromium, cadmium and lead ions onto BP by HCl**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Desorption agent (50mL)</th>
<th>Metal</th>
<th>Desorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP</td>
<td>2.0 M HCl</td>
<td>Cd$^{2+}$</td>
<td>47.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr$^{3+}$</td>
<td>38.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb$^{2+}$</td>
<td>46.25</td>
</tr>
<tr>
<td></td>
<td>4.0 M HCl</td>
<td>Cd$^{2+}$</td>
<td>56.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr$^{3+}$</td>
<td>43.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb$^{2+}$</td>
<td>53.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cd$^{2+}$</td>
<td>71.72</td>
</tr>
<tr>
<td></td>
<td>6.0 M HCl</td>
<td>Cr$^{3+}$</td>
<td>67.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb$^{2+}$</td>
<td>72.17</td>
</tr>
</tbody>
</table>
Conclusion

The study indicated that BP could be used as an effective adsorbant material for the treatment of Cr, Cd and Pb bearing aqueous wastewater. The adsorption of $\text{Cr}^{3+}$, $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ on BP is dependent on contact time, initial concentration, pH and initial volume and dose of the adsorbent. The studied adsorbent is not only economical but also an agricultural waste product. Hence BP would be useful economical treatment of wastewater containing Cr, Cd and Pb metals.

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References


