Removal of Pb(II) from wastewater using activated carbon prepared from the seeds of Reptonia buxifolia

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Abstract: The potential of activated carbon as a cheap bioadsorbent prepared from Reptonia buxifolia seeds, for the removal of Pb(II) from wastewater was investigated. The morphology and structure of the prepared activated carbon was characterized using different techniques. Adsorption phenomenon was studied by varying the metal ion concentration, contact time, temperature, and pH, in a batch process. The SEM results showed that the thermal treatment significantly altered the topography of synthesized activated carbon due to formation of numerous pores on the surface of the adsorbent. At equilibrium, the Langmuir model gave a better fit to the adsorption isotherm results than the Freundlich model. Kinetics data indicate that equilibrium is established within the first 60 min. The results showed that activated carbon obtained from seeds of R. buxifolia have the potential to be used as alternative economical biosorbent for the removal of heavy metals from wastewater.

Keywords: bioadsorbent; thermal treatment; adsorption model.

INTRODUCTION

With the rapid development of modern industrial technology over the last sixty years, tremendous changes have been brought in human standards of living. However, this industrial revolution is one of the major sources of pollution of the natural environment. In most developing countries, different industries discharge their waste directly or indirectly into the open environment.1 Most of the heavy metals are toxic or carcinogenic and are persistent in the environment. It tends to deposit in different parts of living organisms and create various types of problems. Among toxic metals, copper, nickel, zinc, cadmium, mercury, Pb(II) and chromium are of concern in the treatment of industrial wastewaters. These metals may accumulate to a toxic concentration level, in body parts, which can lead to

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adverse effects on the quality of human lives. Exposure to heavy metals, such as Pb(II), Cd and Hg, are the main threat to human health. Pb(II) has adverse effects on the whole body. It can damage the nervous system, kidneys, and reproductive system and is responsible for high blood pressure. Long-term exposure to Pb(II) may lead to prolonged reaction times, memory loss and reduced ability to understand. Exposure to Pb(II) may bring critical changes in children’s behavior, learning and concentration abilities. Hence, the treatment and the removal of heavy metals, from water, receive considerable attention. Various chemical and physicochemical methods were attempted for removal of heavy metals from wastewaters, such as, oxidation/reduction, electrochemical ion exchange, chemical precipitation, reverse osmosis, filtration, and absorption. However, new, economical, eco-friendly, easily accessible and most effective adsorbents are still under investigation. There is an increasing interest in the application of materials of biological origins for heavy metal ions removal from wastewater since the last few decades. As they are available in large quantities, cheap and have a good performance in removal of heavy metals from aqueous solutions. Several agricultural wastes have been investigated as a bioadsorbents for removal of heavy metals from water such as macro-algal biomass, cassava peel, sawdust and so on. Different biomasses were tried for the removal of Pb(II) from water. Some researchers also have used chemicals and pretreatments for the modifications of these bioadsorbent. The conversion of these biomasses to activated carbons (ACs), is one of the cost effective materials of natural origin and their applicability in recovery as well as removal of heavy metals from the industrial wastewater. In this study, Reptonia buxifolia seed has been used as precursor for synthesis of ACs because it is considered superior to those obtained from other sources, as it contains high carbon/oxygen ratio and low ash content. R. buxifolia is grown in hilly areas of the south-west of Khyber Pakhtunkhwa, Pakistan. The fruits of these plants are used by local people while seeds are discarded. Therefore, the main aim of this study is to prepare high porous ACs from R. buxifolia seeds, and investigate their use as bioadsorbent for removal of Pb(II) from wastewater.

EXPERIMENTAL

The Reptonia buxifolia seeds (R. B. seeds) were collected from Karbogha Sharif, Doaba, District Hangu, Khyber Pakhtunkhwa, Pakistan, in June–July 2017. The seeds were washed repeatedly with water and left to dry under sunlight for a few days. The seeds were then crushed to powder form. The particle sizes in, the range of 90–212 µm, were used for further analysis. AC was synthesized by heating ground seeds of R. buxifolia in furnace at 773 K for 30 min and was characterized by TGA, EDX and (SEM). Thermal stability of the synthesized AC was analyzed by heating the sample in nitrogen atmosphere from 300 to 1073 K with the ramp of 10 K/min using TG/DTA6300 thermal analyzer. Surface morphology of the prepared raw and prepared AC was performed by a JEOL (JSM-7600F, Japan). A stock solution of 1000 mg/L was prepared by dissolving 1.83 g of Pb(II) acetate trihydrate (Pb(CH3CO2)2
3H₂O) in distilled water and made up to 1000 ml in a flask. All the other samples were prepared from the stock solution, by dilution method, using the following formula:

\[ C_1V_1 = C_2V_2 \]  \hspace{1cm} (1)

where \( C_1 \) represent 1000 mg/L solution (stock solution), \( V_1 \) volume taken from stock solution, \( C_2 \) concentration of required solution and \( V_2 \) volume of the required solution. Batch mode adsorption experiments were performed by mixing raw R. B. seeds and AC with 100 ml of different Pb(II) initial concentration (1–1000 mg/L), different periods of contact (1–180 min) and pH range 2–12. All these experiments were performed in a thermal shaker with a constant agitation speed of 140 rpm. After finishing the adsorption experiments, the remaining Pb(II) concentration after filtration process was determined by atomic absorption spectrometer (AAnalyst 400, Perkin Elmer) in each sample. The condition of the instrument was: flame, acetylene–air, slit width, 2.7 mm/1.05 mm, wavelength, 283.31 nm, lamp current, 5 mA.

**RESULTS AND DISCUSSION**

The raw R. B. seeds and prepared AC were characterized using different techniques which are discussed below.

*Thermogravimetric analysis*

To determine the temperature at which the prominent pyrolysis process of raw materials is completed, thermogravimetric process was performed from 50 to 800 °C in N₂ atmosphere (Fig. 1). The first weight loss (50 to 100 °C) corresponds to the surface bound water and moisture adsorbed on the materials. A major weight loss occurred between the temperature regions of 300 to 500 °C. This weight loss is assigned mainly to the decomposition of cellulose and other low molecular weight organic compounds, such as lactone and furan derivatives.15

![Fig. 1. TGA analysis of R. B. seeds; residual weight (—) and heat flow (—).](www.shd.org.rs/JSCS/)

Hence, the range 300 to 550 °C, in this study, is considered the carbonization temperature. The TGA analysis of sesame seeds and grapes gave similar results, however, in the current results weight loss completed relatively at high tempe-
rature, i.e., 520 °C. The weight loss at high temperature suggests a high C/H ratio of the R. B. seeds.16

**Scanning electron microscopy analysis**

The physical morphology of the samples was investigated by SEM analysis. The surface of raw materials was rough and irregular (Fig. 2a). It can be seen from SEM images that significant change occurred in the morphology of the AC, in terms of size and the formation of pores, as shown in Fig. 2b. It indicates that heat treatment creates honeycomb-like structure in AC prepared from R. B. seeds. Previously, the porous materials were obtained by using different chemically activating agents (ZnCl₂, HCl and KOH) from the coconut shell and seeds of Tamarind.17,18 However, in the current project, porous AC was obtained without chemically activated agent. These porous materials may be obtained due to the calcination procedure of R. B. seeds during carbonization.

![Fig. 2. SEM micrograph of: a) R. B. seeds and b) AC after heat treatment at 500 °C.](image)

**Energy dispersive X-ray spectroscopy**

EDX results of raw and AC prepared from these seeds are given in Table I.

**TABLE I. EDX results of raw R. B. seeds and AC**

<table>
<thead>
<tr>
<th>Element</th>
<th>Raw R. B. seeds Content, wt. %</th>
<th>Content, at. %</th>
<th>AC Content, wt. %</th>
<th>Content, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>58.70</td>
<td>67.40</td>
<td>C</td>
<td>78.28</td>
</tr>
<tr>
<td>O</td>
<td>34.96</td>
<td>30.14</td>
<td>O</td>
<td>14.40</td>
</tr>
<tr>
<td>Ca</td>
<td>3.88</td>
<td>1.34</td>
<td>Ca</td>
<td>0.65</td>
</tr>
<tr>
<td>K</td>
<td>0.64</td>
<td>0.23</td>
<td>Si</td>
<td>0.47</td>
</tr>
<tr>
<td>Mg</td>
<td>0.22</td>
<td>0.13</td>
<td>K</td>
<td>0.65</td>
</tr>
<tr>
<td>Al</td>
<td>0.38</td>
<td>0.20</td>
<td>Mg</td>
<td>0.20</td>
</tr>
<tr>
<td>Si</td>
<td>0.82</td>
<td>0.40</td>
<td>Total</td>
<td>100.00</td>
</tr>
<tr>
<td>S</td>
<td>0.40</td>
<td>0.17</td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Available on line at www.shd.org.rs/JSCS/ (CC) 2020 SCS.
Table I indicates that the amount of carbon and oxygen contents, in raw material, was 67.40 and 30.14 %, respectively. On the other hand, the carbon content of AC was increased to 85.66 % while the oxygen amount was decreased to 11.83 %. A significant change between the amount of carbon/oxygen ratio in the R. B. seeds and AC sample were observed. The results show that the carbon contents increased with calcination, indicating that AC was formed, which is also supported by the SEM results. The C/O ratios of the given AC (85 %/11 %) were comparable to the AC (70 %/25 %) obtained by using chemical activation agent (H₃PO₄).¹⁹ Hence, it can be deduced that calcination procedure and selection of biomass play a key role in the synthesis of high carbon/oxygen ratio activated carbon. Moreover, different metals such as Mg, Al, Si, S, K and Ca were detected both in raw and AC.

**Adsorption of Pb(II) on raw R. B. seeds and AC**

To determine the adsorption capacity of the prepared bioadsorbents, adsorption experiments were conducted by taking different initial metal ion concentrations, contact time and pH.

*Initial Pb(II) concentration effect on adsorption.* Batch adsorption experiments were performed to assess the effects of initial metal concentration of Pb(II), on raw and AC (Fig. 3). The determination of optimum initial metal concentrations in solutions play a key role in the adsorption study because it greatly influences the mass transfer of metal ions from the solution to biosorbent.²⁰ The experiments were performed using Pb(II) solutions ranging from 1 to 1000 mg/L. Stronger adsorption of Pb(II) (51 mg/g) was observed compared to the raw materials. This result validates that the formation of AC, from raw materials, increased the surface area, which creates more active sites compared to the raw materials. These results support the formation of more pores in AC, as is obvious from SEM results. The amount of Pb(II) uptake per unit weight of carbon (mg/g) increased with an increase in Pb(II) concentration and equilibrium achieved at
100 mg/g of adsorbent in case of AC. These results indicate that after equilib-
rium, no change in adsorption of Pb(II) occurred, because of the lack of the more
vacant active sites on the adsorbent. Adsorption of Pb(II), on the AC, was com-
pared with different bioadsorbents, reported in the literature, as shown in Table II.

### TABLE II. Comparison of adsorption capacities, mg/g, of Pb(II) by various bioadsorbents

<table>
<thead>
<tr>
<th>Bioadsorbent</th>
<th>$q_{\text{max}}$ / mg g$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spirogyra neglecta</td>
<td>132.00</td>
<td>21</td>
</tr>
<tr>
<td>Cladophora fascicularis</td>
<td>198.5</td>
<td>22</td>
</tr>
<tr>
<td>Pyrolusite-modified sewage sludge carbon</td>
<td>69.87</td>
<td>23</td>
</tr>
<tr>
<td>Oryza sativa L husk</td>
<td>8.6</td>
<td>24</td>
</tr>
<tr>
<td>Tobacco stems</td>
<td>5.54</td>
<td>25</td>
</tr>
<tr>
<td>Tea waste</td>
<td>1.35</td>
<td>26</td>
</tr>
<tr>
<td>Rhizopus arrhizus</td>
<td>76.40</td>
<td>27</td>
</tr>
<tr>
<td>Reptonia buxifolia seeds(AC)</td>
<td>51.0</td>
<td>Present work</td>
</tr>
</tbody>
</table>

The current results show that the AC, prepared from the seeds of *R. buxi-
folia*, has comparable adsorption capacity with most of the bioadsorbents. From
this, it can be concluded that prepared AC is potential biosorbent for removal of
Pb(II) for waste water treatment.

**Adsorption model.** Adsorption model is key parameter to design how ads-
orbate interacts with adsorbents. It is critical in optimizing the structure of ads-
orbents for further use. Among different isotherms, Langmuir and Freundlich are
well studied and compared. The Langmuir and Freundlich models were applied
on the experimental data to determine the maximum adsorption capacity of the
amount of Pb(II) adsorbed on adsorbent on the equilibrium concentration in sol-
utions.

The linear form of Langmuir model can be represented by the following
equation:

$$
\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}
$$

(2)

where $Q_e$ is the amount of Pb(II) adsorbed per unit gram of adsorbent (mg/g), $C_e$
(mg/L) is the concentration of Pb(II), at equilibrium, $Q_m$ is the optimum adsor-
ption capacity and $K_L$ is Langmuir isotherm constant which has a correlation with
free energy of adsorption. The plot of $C_e/Q_e$ against $C_e$ gives a linear rela-
tionship with the slope of $1/Q_m$ and intercept of $1/Q_m K_L$, which is obtained from
experimental data (Fig. 4), suggesting the applicability of Langmuir isotherm
model with a correlation coefficient ($R^2$) of 0.990 (R. B. seeds) and 0.998 (AC).
Higher value of $R^2$ suggests that current results well follow the Langmuir model
and a monolayer adsorption of Pb(II) is prevalent. This result has close agree-
ment with previous literature, where Pb(II) adsorption on *Phytolacca americana* biomass follow Langmuir model.\(^2^9\)

The Freundlich model considers a heterogeneous surface with a non-uniform distribution of heat of biosorption sites over the surface. The Freundlich model is given by the equation below:

$$\log \frac{X}{M} = \log K_F + \frac{1}{N} \log C$$  \hspace{1cm} (3)

where \(1/N\) is the Freundlich indicator of adsorption intensity and \(K_F\) is the Freundlich indicator of adsorption capacity of adsorbent. The plot of \(\log x/m\) (amount of adsorbate adsorbed per gram of adsorbent) against \(\log C\) gives a straight line with the slope of \(1/N\) and intercept of \(K_F\), with the correlation coefficient \((R^2)\) of 0.95 and 0.87, for R. B. seeds and AC, respectively (Fig. 5). From the value of \(R^2\) it can be suggested that the current results are matching with the previous studies.\(^3^0\)

![Fig. 4. Langmuir adsorption isotherm of Pb(II) on raw R. B. seeds (■) and AC (●).](image)

![Fig. 5. Freundlich adsorption isotherm of Pb(II) on R. B. seeds (■) and AC (●).](image)

The value of the intercept \(K_F\) obtained from the plot for R. B. seeds and AC were 3.12 and 148.70 mg/g, respectively. The value of the slope \(1/N\), obtained
from the plot, for R. B. seeds and AC were 0.69 and 0.22, respectively. The value of $K_F$ indicates the adsorption capacity and $1/N$ indicates characteristic constant for the adsorption system, under study. The result demonstrates that the adsorbent has several different types of adsorption sites. Value of $N$, greater than 1, represents a favorable adsorption condition. The value of $N$ for R. B. seeds and AC were found to be 1.44 and 4.65, respectively. This indicates that adsorption conditions were favorable for Pb(II) on AC.

**Adsorption kinetics.** In order to find out the mechanism of the adsorption on AC, two kinetic models were applied on the data. The batch adsorption experiments were studied at different contact time ranging from 1 to 180 min at 298 K to help in determining the adsorption capacities of R. B. seeds and AC by keeping the biosorbent concentration fixed at pH 6. The results indicate that the adsorption rate increased very rapidly, and equilibrium was established within the first 60 min for both R. B. seeds and AC adsorbents. This suggests that all the adsorption sites available have been occupied by the cation under investigation in the first 60 min. The equilibrium time was found 60 min as compared to 100 min described in a previous study. Thus, the equilibrium of Pb(II) adsorption, in this project, was obtained quicker than those reported in the literature. However, the amount of Pb(II) adsorbed (221.9 mg/g) was greater than the amount of the current study (50 mg/g). The fast metal adsorption, in the early stage, occurred due to the presence of the active sites on R. B. seeds and AC. As the active sites become occupied, the adsorption rate slows down due to the occupation of the active sites by metal. Furthermore, the equilibrium position was significantly higher for AC compared to the R. B. seeds. This may be due to the high surface area of the AC.

The kinetics of metal removal from aqueous solution are elucidated, in the literature, using pseudo-first-order and pseudo-second-order models. These kinetic models were used to examine the process and mechanism of Pb(II) removal from an aqueous phase on AC. The integrated form of pseudo-first-order and pseudo-second-order were used to find out the mechanism of metal adsorption. From the results, it was found that the adsorption of Pb(II) on R. B. seeds does not follow the pseudo-first-order kinetics (details are given in Supplementary material to this paper).

The adsorption kinetics was also evaluated by a pseudo-second-order kinetic equation. The mathematical form of pseudo-second-order kinetic equation is:

$$\frac{t}{Q_t} = \frac{1}{K_2Q_e^2} + \frac{t}{Q_e}$$

(4)

where $t$ is time (min), $Q_t$ is the amount of Pb(II) adsorbed (mg/g) at any time, $Q_e$, is the amount of Pb(II) adsorbed (mg/g) at equilibrium and $K_2$ is the rate constant. The intercept and slope of the linear plot of $t/Q_t$ against $t$ yielded the values...
of $Q_e$ and $K_2$, when this equation was applied in the experimental. It was found that data are well fitted in pseudo-second-order equation, having $R^2$ value 0.971 and 0.973 for R. B. seeds and AC, respectively (Fig. 6). This result illustrates that rate determine steps might be chemisorption of Pb(II) on both R. B. seeds and AC. The pseudo-second-order kinetic equation was also followed by adsorption of Pb(II) on the orange peel, peanut shell and tea waste reported in literature.\textsuperscript{20}

![Figure 6. Pseudo-second-order kinetic plot for the biosorption of Pb(II) on R. B. seeds (■) and AC (●).](image)

Intra-particle diffusion model. Weber and Morris model was applied to check whether adsorption of Pb(II) on R. B. seeds and AC is intra-particle diffusion controlled or boundary layer diffusion controlled. This model states that the rate-limiting step is intraparticle diffusion if a plot of adsorbate adsorbed against the square root of the contact time yields a straight line, passing through the origin:

$$Q_t = K_i t^{1/2} + I$$

where $Q_t$ represents the amount of adsorbate at a particular time, $K_i$ the intra-particle diffusion rate constant (mg g\textsuperscript{-1} min\textsuperscript{-0.5}) and $I$ is the intercept of the graph.\textsuperscript{32} The amount of Pb(II) adsorbed, $Q_t$, was plotted against square root of time $t^{1/2}$ for both the R. B. seeds and AC (Fig. 7). The figure shows that adsorption of Pb(II) on adsorbent took place in two steps. In the first step the adsorption of Pb(II) sharply increased up to six minute. This change in adsorption of Pb(II) in an initial six minutes may correlate to the diffusion of biosorbate through the solution to the external surface of the biosorbent or the boundary layer diffusion of the biosorbate molecules. In the second step no apparent change in the adsorption of Pb(II) was observed, which indicates that the equilibrium of the adsorbate was achieved after six minute. The extrapolation of the data does not pass through the origin and hence it is not well fitted in the Morris model. These results indicate that adsorption of Pb(II) is not intraparticle diffusion controlled but it is more likely boundary layer controlled.\textsuperscript{33}
Effect of pH. pH of solution is a key parameter in governing the metal adsorption on biomass. The pH of the solution alters the chemical composition on the surface of the adsorbent, as well as, the precipitation of the metal in the solution.\textsuperscript{34} It was deduced from the literature that when Pb(II) salt is dissolved in water, Pb(II) exists in seven different forms at different pH. These different forms significantly reshuffled from one to another form between pH 6 and 9.\textsuperscript{35} The adsorption of Pb(II) was checked in pH ranging from 2 to 12 on both R. B. seeds and AC. These experiments helped in selecting a suitable pH of the solution for achieving maximum efficiency in metal removal by AC obtained from R. B. seeds. Fig. 8a shows that maximum adsorption was achieved (19.91 mg/g for R. B. seeds and 39.10 mg/g for AC) in acidic pH range. In contrast to the previous studies, the current results show higher adsorption at lower pH.\textsuperscript{35} This contradictory result is not fully understood. However, it can be explained that at low pH, the adsorbent becomes highly protonated and favors exchange of Pb(II) with the proton.\textsuperscript{34} With the increase of pH, the degree of protonation of the surface decreases gradually and that results in the low adsorption of Pb(II). Hence, acidic range was the most appropriate pH to remove the Pb(II) from aqueous solution using R. B. seeds and AC as adsorbents. Furthermore, the decrease in Pb(II) in basic medium could be due to competitive adsorption with sodium cation because the NaOH was used for achieving basic pH.

To assess the electrostatic charge on the surface of AC, pH–PZC analysis were performed for both R. B. seeds and AC (Fig. 8b). At pH 7.3 and 8.3, PZC was observed for R. B. seeds and AC respectively. These results further support the pH analysis which illustrates that change in adsorption of Pb(II) on R. B. seeds and AC are observed after pH 7. It indicates that before pH 7 the functional groups or electrostatic charge present on the surface of R. B: seeds and AC are similar. However, after pH 8.3 the nature of the electrostatic charge changed and hence the adsorption of Pb(II) altered. The results indicated that with a change of pH the electrostatic charge present on the surface of R. B. seeds and AC changed with similar patterns.
CONCLUSIONS

AC was prepared from the seeds of *Reptonia Buxifolia* by heat treatment at 823 K without chemical agent. From the structure and morphological studies, it was found that the AC obtained thermal stability before 823K and thermal treatment gave high porous structure which has a high potential for removal of Pb(II) from wastewater. The batch experiment showed that equilibrium was achieved within the first 60 minutes and the experimental data follow the pseudo-second-order kinetics. The biosorption of Pb(II) preferred monolayer formation on R. B. seeds and AC (Langmuir model). The pH for PZC was 8.3 and the optimum pH was found to be 2 for the adsorption of Pb(II) on AC. Based on the results, it can be concluded that the AC produced from the seeds of *R. Buxifolia* have high potential to adsorb Pb(II) from solutions. Consequently, it can be used as a cost-efficient bioadsorbent for the removal of Pb(II) metal.

SUPPLEMENTARY MATERIAL

Additional data are available electronically from the journal web site: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

Acknowledgment. Department of Chemistry, KUST is highly appreciated for providing lab facilities to perform this research work.
активног угља карактерисани су различитим техникама. Адсорпција је проучена варирањем концентрације металних јона, времена контакта, температуре, дозе адсорбента и pH у шаржном процесу. Резултати SEM анализе су показали да је термални третман значајно променио топографију синтетисаног активног угља због формирања бројних пора на површини адсорбента. У равнотежи, Лангмиров модел је дао боље слагање са адсорпционом изотермом него Фројндлихов.

Кинетички подаци указују да се равнотежа успоставља у оквиру првих 60 min. У испитивању утицаја температуре од 273 до 333 K, максимална адсорпција добијена је при 283 K. Резултати су показали да активни угљ добијен од сеума R. buxifolia има потенцијал да се користи као економичан биоадсорбент за уклањање тешких метала из воде.
WASTEWATER TREATMENT USING BIOMASS

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    (https://doi.org/10.1260/0263-6174.29.5.495)
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    (http://dx.doi.org/10.1155/2013/146092)
    http://bcc.bas.bg/index.html
    (https://www.ingentaconnect.com/content/doaj/09740546/2010/00000003/00000001/art00003)
    (https://doi.org/10.1515/chem-2015-0087)
    (https://doi.org/10.1080/19443994.2014.992974).