Remediation of Pb2+ and Cd2+ using rice husk biochar produced at low temperatures

Melvin S. Samuel  
Indian Institute of Technology Kharagpur

V.S. Kirankumar  
Kaohsiung Medical University

Selvarajan Ethiraj (selrajan@gmail.com)  
SRM Institute of Science and Technology  https://orcid.org/0000-0002-3447-6432

Research Article

Keywords: Rice husk, Heavy metals, Biochar, Sorption

DOI: https://doi.org/10.21203/rs.3.rs-485313/v1

License: ☑️ ☑️ This work is licensed under a Creative Commons Attribution 4.0 International License.  Read Full License
Abstract

In this study, biochar was obtained under mild conditions by pyrolysis treatment (350 °C) of rice husk, providing energy-efficient and low-carbon footprint synthesis. The pyrolyzed biochar was selected as the basis for solvothermal reaction to combine with ferrite in which the abundant functional groups would facilitate the removal of lead (Pb\(^{2+}\)) and cadmium (Cd\(^{2+}\)). Biochar/Ferrite (MBC) has special physicochemical properties and characterized by XRD, FT-IR, SEM, TEM, and BET. The sorption possessions of the magnetic biochar (MBC) towards the heavy metals Pb\(^{2+}\) and Cd\(^{2+}\) were validated by the batch sorption process. The findings of the batch sorption kinetics propose the mechanism of sorption follows a pseudo-second-order model. The Langmuir and Freundlich isotherm models applied to the sorption equilibrium data for assessment of sorption potential and related mechanism. These findings showed that the sorption occurred through physical and chemical connections among Pb\(^{2+}\) and Cd\(^{2+}\) through MBC functional groups. Pb\(^{2+}\) and Cd\(^{2+}\) had a sorption potential of 147 mg/g, 104 mg/g at pH 5.5, and 300 k. The synthesized MBC was tested for recovery of heavy metal from industrial effluent, and successfully recovered 80% of heavy metals Pb\(^{2+}\) and Cd\(^{2+}\). Finally, the findings obtained showed the MBC adsorbent's ability for extracting trace heavy metals from industrial effluent.

Introduction

Water is a vital natural source that needs fortification from wastes and pollutants. However, effluent from manufacturing plants is the main noxious cause of dirt, which can abolish the environmental marine structure. It has turned out to be a root cause of water contamination. Organic and inorganic matters in the water are a main problem and reason for water contamination: over fifty thousand tons of organic matters are squared in environmental sewages yearly[1, 2]. Along with organic contaminants, the effluents released from industries contain heavy metals such as lead, copper, cadmium, chromium, and iron in large proportions[3, 4]. Worldwide, the existence of lead (Pb) in marine environments has been a significant environmental issue. It poses a significant danger to human health, living species, and marine habitats because of its non-degradable property and propensity for bio-accumulation in the food chain, potentially impacting the entire environment. Most of these heavy metals are hazardous to the environment and healthiness, for example, lead and cadmium contaminants from the fabric manufacturers cause skin epidemics, deteriorated immune systems, respirational illness, modification of hereditary material, and lung tumor[5–6]. The USEPA has listed lead and cadmium as carcinogenic to humans and is considered to have deleterious effects on health and bone de-mineralization by direct bone injury or renal problems[7–9]. Several approaches for eliminating heavy metals from wastewaters have been established, such as sorption[10], degradation [11], ion exchange[12], oxidation[13], and electrocoagulation[14]. Amongst these existing technologies, the sorption process has been extensively used due to its comfort of usage, low cost, no secondary contaminants, selectivity, specificity, easy mode of operation, simple operation and exhibit a great potential for the elimination, retrieval, and reprocessing of heavy metals from wastewater[15, 16]. Modern methods for water treatment, such as absorption, membranes, it has been observed that isolation, sorption, flocculation, and ion exchange are effective in reducing the concentration of Pb\(^{2+}\). However, each of these systems may be correlated with elevated running costs and/or sludge disposal. Biochar is a by-product that is formed under oxygen-limited conditions by the thermal decay of leftover carbon-rich residuals. For heavy metal remediation, Biochar is a relatively low-cost, renewable, and efficient adsorbent. Compared to traditional commercially manufactured activated charcoal, on the basis of its high practical applicability and its useful physico-chemical properties, with versatile surface area, proven porosity and surface functional groups with a fair ability to absorb different compounds. To that end, various forms of chemical modification, with acid and alkali, are used. In order to improve their appearance, activation, metal salt activation, and nanoparticle charging materials have been developed. A one-pot hydrothermal chemical system was used to synthesize manganese ferrite/biochar composites; these composites also demonstrated good efficiency in heavy metal-contaminated wastewater remediation. While most methods of chemical alteration used to achieve real biochar composite materials are moderately simple and specific, these techniques have various disadvantages, such as high costs, rigid laboratory requirements, and several standards for dangerous chemical use[17–19]. Furthermore, in order to make biochar a suitable material for engineering use, a wider surface area and reduced size of the material must be obtained. Therefore, a renewable, reliable, and low-cost method of producing usable biochar is essential for the realistic removal of heavy metals. For fuel and chemical processing, lignocellulosic biomass is an essential feedstock for thermo-conversion. Moreover, a sustainable and green source of energy is the goods produced from it. Cellulose, hemicellulose, and lignin are the major biomass elements, with cellulose being the most abundant. Therefore, the pyrolysis activity of cellulose is more important in understanding the complex lignocellulosic biomass pyrolytic activity. In this study, heavy metal cations (Pb\(^{2+}\), Cd\(^{2+}\)) are introduced to systematically investigate the sorption behavior of biochar derived from rice husk (a source of cellulose) under a wide range of concentrations. The microstructure of the biochar was characterized by TEM and SEM. The sorption properties of the prepared MBC adsorbent towards Pb\(^{2+}\), Cd\(^{2+}\) were elucidated by a batch sorption method. Also, the belongings of contact time, initial metal concentrations, and pH on the sorption performance of Pb\(^{2+}\) by MBC adsorbent were sensibly examined. Due to its high potential for sorption, recyclability, and fast recovery, it could be suggested that Pb\(^{2+}\), Cd\(^{2+}\) should be considered as a suitable candidate to be extracted from wastewater.
Experimental Details: Synthesis And Characterization

2.1 Materials. The graphite powder, lead nitrate, cadmium nitrate, and other chemicals were of analytical mark and obtained from Sigma-Aldrich (Bangalore, India).

2.2. Sorption Experiments. Synthesis of MBC adsorbent. The magnetic biochars (MBC) were manufactured at a temperature of 350°C for 4 h at a heating rate of 10°C/min under nitrogen environments via simple pyrolysis of rice husk and Fe(NO$_3$)$_3.9$H$_2$O. The additional extra Fe$^{3+}$, the acquired magnetic-biochar were wash away numerous times by deionized water; then it was oven dried overnight at 105°C. Finally, the sample was called MBC. Pb$^{2+}$ and isothermal sorption of Cd$^{2+}$. The Pb(NO$_3$)$_2$ and Cd(NO$_3$)$_2$ were dissolved in two separate beakers containing deionized water (1000 mL) to provide a concentration of 1000 mg/g for Pb$^{2+}$ and Cd$^{2+}$. In subsequent experiments, this solution was reduced to the desired concentration. The Pb$^{2+}$ solutions (30 mL, 25-100 mg/L) were combined with varying doses of MBC (0.25-1.0 g/L) in 100 mL conical flasks. The HNO$_3$ (0.1 mol/L) and NaOH (0.1 mol/L) were used to change the pH of the Pb$^{2+}$ solution from 2 to 6. At 150 rpm, the flasks containing the adsorbents and solutions of Pb$^{2+}$, Cd$^{2+}$, and the temperature were held throughout the sorption process at 300 K. The adsorbent substance was removed from the solution after the sorption had been done. Atomic absorption spectrophotometry (AA-7000, Shimadzu) was used to calculate the Pb$^{2+}$, Cd$^{2+}$ concentration after sorption. The power of MBC equilibrium sorption ($q_e$, mg/g) was determined using equation 1. RMSE; root-mean-square error equation. 2 and 3.

$$ q_e = \frac{6q_e C_l}{N} \times V $$

$$ R^2 = 1 - \frac{\sum_{i=1}^{n}(Y_{pred,i} - Y_{exp,i})^2}{\sum_{i=1}^{n}(Y_{exp,i} - \bar{Y})^2} $$

$$ RMSE = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n}(Y_{pred,i} - Y_{exp,i})^2} $$

2.3. Regeneration Tests. In regeneration studies, HCl (0.1 mmol/L) has been used as the eluent. The eluent was added to the Pb$^{2+}$-loaded MBC (50 mg) and shaken for 3 h. MBC was consequently isolated by centrifugation at 5000 rpm for 15 min. The separated MBC has been washed with deionized water and used for the subsequent set.

Results And Discussion

3.1. Characterization of the prepared materials

Analysis by Powder X-ray diffraction (XRD) examination. As illustrated in Figure. 1a, XRD research studied the phase purity and the crystalline structure prepared for Fe$_3$O$_4$ and MBC. The diffraction peak at $2\theta = 30.2^\circ$, 35.6°, 43.3°, 53.7°, 57.3°, and 62.8°, referring to the Fe$_3$O$_4$ reflection of Bragg at (220), (311), (222), (400), (422), (511) and (440). The crystal iron oxide planes were further confirmed by JCPDS no. 19-0629 to indicate the presence of magnetic oxide. Fourier transform infrared spectroscopy (FTIR). FT-IR processing has been used to classify the surface of BC and MBC; the related spectra are shown in Figure 1b. The broadband at 3429 cm$^{-1}$ is assigned to -OH groups. The detailed peaks in BC and MBC at 1586 cm$^{-1}$, 1378 cm$^{-1}$, and 1209 cm$^{-1}$ correspond to the extending vibrations of aromatic C=C or C=O. The MBC adsorbent shows a 560 cm$^{-1}$ peak that could be attributed to the vibration of Fe-O (Reddy and Lee 2014).

Surface Morphology. In the scanning electron microscopy (SEM, Zeiss Auriga instrument) BC exhibited a complete or regular structure (Figure. 2a). Equally, the exterior structure of MBC adsorbent exposed a non-identical, and smooth morphology (Figure. 2b). The Transmission electron microscopy (TEM, Fei-technical-G2 20 Twin) picture of MBC shows regular and rough surface creation (Figure. 3). Brunauer–Emmett–Teller. The specific area for the MBC was 1047 m$^2$/g, Pvol (0.46 cm$^3$/g), Pdiam (66.7 Å), and Psize (38.62 Å). The external surface of MBC was measured by nitrogen sorption-desorption isotherms. The TGA plot showed two main weight losses. The first mass step, occurred at above 80°C was detected; this is probably due to evaporation of the water molecules on biochar surface. The second mass loss step happens at about 200 °C, these are assigned to the functional groups of C-O, C=O and C-OOH. There happens a feeble mass loss in the range of 500 to 600 °C is associated to the removal of more steady functional-groups (Figure. 4).

3.2. Sorption studies
**Concentration effect of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \).** The effect of the initial sorption concentrations of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) on the percentage removal was calculated on a 10-125 mg/L scale by the MBC adsorbent dosage of 0.5 g/L, pH 6.0, 300 K solution temperature, and agitation velocity of 120 rpm. It was also investigated that the levels of adsorbed \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) by MBC adsorbent material were calculated to be 95% at lesser concentrations (50 mg/L) (Figure. 5a). For further laboratory research, 50 mg/L was then found to be the optimum initial \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) concentration. **Impact of agitation speed.** The effect of agitation speed on the removal of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) from MBC was analyzed. 30 mL of the 50 mg/L \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) samples were shaken at varying agitation velocities of 80-150 rpm to perform this research. Other current parameters, such as pH 6.0, incubation time of 360 min, and temperature of 300 K, have been established continuously. Figure. 5b, results show that the removal of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) also significantly facilitates an improvement in rpm speed from 80-150 rpm. Thus, the ideal shaking speed was 120 rpm. **Effect of pH.** In determining the efficacy of sorption, the kinetic adsorbent is more important. As an integral component capable of managing the whole sorption process, the initial pH of the \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) solution is taken into consideration. This is partly because the presence of an extra proton affects the surface of the adsorbent that adsorbs, which essentially leads to the alteration of chemical parameters. The sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) was largely due to the attractive strength between the heavy metals’ positive charge and the adsorbent material's negative charge. The MBC pH adsorbent effect on the removal of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) as seen in Figure. 5c. The percentage elimination of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) at acidic pH was found to be lower. The findings revealed that the sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) improved dramatically by increasing the pH range (> 4.0). This increase is primarily due to the electrostatic force between the MBC and heavy metals. Sorption capacities with respect to pH were studied. At pH 2.0 (\( \text{Pb}^{2+}: 22.5 \) mg/g, \( \text{Cd}^{2+}: 17.5 \)), 4.0 (\( \text{Pb}^{2+}: 65.75 \) mg/g, \( \text{Cd}^{2+}: 60.75 \) mg/g) and 6.0 (\( \text{Pb}^{2+}: 94.8 \) mg/g, \( \text{Cd}^{2+}: 92.34 \) mg/g). It was observed that pH 6.0 was found to be the optimal pH for the greater removal of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \). **Regeneration and reuse.** The MBC adsorbent material reused and 81% of the original sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) was found to be effectively eliminated even after five cycles (Figure. 5d). **The consequence of a dose of MBC adsorbent.** The effect of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) sorption in the aqueous solution depends on the 0.25-1.0 g/L level of the adsorbent MBC dose. MBC’s percentage elimination of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) was observed to be rising with an improvement in the adsorbent dosage at 0.25-1.0 g/L. This improvement in sorption was due to an increase in the MBC adsorbent active site as the dose rose. The sorption potential for \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) decreased from approximately 147.26 mg/g to 87.24 mg/g and from 106.75 mg/g to 70.77 mg/g, with the adsorbent dosage rising from 0.25-1.0 g/L (Fig. 5a). Following the sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) molecules, this reduction in sorption effectiveness with an increase in the sorption dose was noticed this attributed to the remaining of the extra unoccupied locations. Such outcomes were equivalent to previous research[20].

**Contact Time Effect.** The effect of the contact period on the sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) on the MBC adsorbent content was analyzed at various concentrations of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) (25-100 mg/L). According to the results obtained, complete removal of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) occurred at a lower concentration of 50 mg/L at 360 min, indicating a 96 percent clearance. The sum of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) adsorbed on the MBC content grew about the rise in reaction time. This is partly attributed to the versatility of a wide number of accessible locations and pores on the MBC adsorbent content that allows sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \). The sorption potential of MBC adsorbent reached an equilibrium state after 360 min, after which no additional sorption was observed. The reaction time of 360 min was then determined to be the optimum contact time.

**Kinetic studies.** The kinetic tests for sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) on MBC adsorbent material were performed using various \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) concentrations (25-100 mg/L) and the findings were shown in Fig. 6. For the estimation of the sorption process, kinetic models such as pseudo-first-order (Figure. 6a and b) and pseudo-second-order (Figure. 6c and d) models were used in this experiment. Then the kinetic parameters were determined and stated in Table 1. **Sorption isotherm studies.** The isothermal sorption of \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) on MBC material was examined at different dosages (0.25-1.0 g/L). The Langmuir (Figure. 7a and b) and Freundlich isotherm (Figure. 7c and d) models were used to assessing the isotherms in this analysis and the results obtained were seen in Figure. 7. Compared to the Freundlich model, the Langmuir isothermal model was found to be the best match (Table 1). This suggested that the surface of MBC might have been homogenous. The values of root mean square error (RMSE) values are presented in Tables 2 in order to assess the fitness of the kinetic models. The obtained rate constants reduced with increasing C_D. This displayed that the adsorption system was concentration dependent. Real wastewater was used to examine the realistic implementation capabilities of the MBC material. For sorption tests, wastewater was taken from the leather industry in Vellore, Tamil Nadu. White suspended floccules and stable particles were found and pH 4.5 was the wastewater effluent. \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) ions were added to the actual wastewater and the concentration reaches 50 mg/L. MBC content demonstrated sorption potential in actual wastewater only 80 % for \( \text{Pb}^{2+} \) and 72 % for \( \text{Cd}^{2+} \). The drop in the amount of sorption could be attributed to containing organic matter, inorganic salts, etc in the wastewater. Therefore, in adsorbing \( \text{Pb}^{2+} \) and \( \text{Cd}^{2+} \) ions from industrial wastewater, this substance is economically efficient.

**Conclusion**
To extract Pb$^{2+}$ and Cd$^{2+}$ from water, the synthesized MBC adsorbent was added, and sorption conditions were optimized through a series of systematic experiments. The sorption mechanism follows pseudo-second-order kinetics, and the Langmuir isotherm model, according to the sorption results. The $q_{\text{max}}$ value was 148 mg/g for Pb$^{2+}$ and 107 mg/g for Cd$^{2+}$, as calculated by applying the sorption effects to the Langmuir isotherm model. For both Pb$^{2+}$ and Cd$^{2+}$ sorption, the sorption time which reached balance was 360 min, and the optimum pH was defined as 6.0. The easy preparation and efficient adsorbent regeneration (over five consecutive cycles) suggest that MBC can be used to adsorb Pb$^{2+}$ and Cd$^{2+}$ from industrial wastewater.

Declarations

Acknowledgement

Authors are thankful SRMIST, Kattankulathur, India for providing resources to carry out the work.

Competing interests: The authors declare no competing interests.

References


Tables

**Table 1.** Equilibrium isotherm parameters for the Pb^{2+} and Cd^{2+} adsorption on MBC sorbent

| Experimental | Isotherm model | | | | |
|----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | Adsorbent dosage (g L^{-1}) | q_{e} (mg g^{-1}) | | | | |
| | | | Langmuir | | | |
| | | | q_{max} (mg g^{-1}) | K_{L} (L mg^{-1}) | R^2 | | |
| | | | | | | |
| Pb^{2+} | 0.25 | 147.29 | 148 | 0.046 | 0.9917 | 10.65 | 1.514 | 0.9875 |
| | 0.50 | 128.71 | 133.84 | 0.139 | 0.9921 | 21.06 | 1.879 | 0.9868 |
| | 0.75 | 117.35 | 115.13 | 0.510 | 0.9930 | 36.09 | 1.980 | 0.9848 |
| | 1.0 | 97.24 | 100 | 0.485 | 0.9962 | 28.49 | 1.995 | 0.9605 |
| Cd^{2+} | 0.25 | 106.75 | 107.85 | 0.050 | 0.9958 | 9.55 | 1.791 | 0.9789 |
| | 0.50 | 88.10 | 93.07 | 0.133 | 0.9921 | 14.04 | 1.879 | 0.9860 |
| | 0.75 | 77.33 | 82.64 | 0.654 | 0.9985 | 26.21 | 2.331 | 0.9444 |
| | 1.0 | 73.77 | 75.74 | 0.597 | 0.9992 | 23.88 | 2.063 | 0.9487 |

**Table 2.** Kinetics parameters of the Pb^{2+} and Cd^{2+} adsorption on MBC sorbent using different models.
<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Concentration (mg L(^{-1}))</th>
<th>Experimental (q_0) (mg g(^{-1}))</th>
<th>pseudo-first-order</th>
<th></th>
<th>pseudo-second-order</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(K_1) (min(^{-1}))</td>
<td>(q_e) (mg g(^{-1}))</td>
<td>(R^2)</td>
<td>(RMSE)</td>
<td>(K_2) (min(^{-1}))</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>25</td>
<td>64.28</td>
<td>(4.14 \times 10^{-3})</td>
<td>7.62</td>
<td>0.8822</td>
<td>0.526</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>106.26</td>
<td>(9.21 \times 10^{-3})</td>
<td>61.47</td>
<td>0.9660</td>
<td>1.250</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>127.22</td>
<td>(8.29 \times 10^{-3})</td>
<td>72.66</td>
<td>0.9667</td>
<td>1.057</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>147.51</td>
<td>(9.44 \times 10^{-3})</td>
<td>82.09</td>
<td>0.8504</td>
<td>1.364</td>
</tr>
<tr>
<td>Cd(^{2+})</td>
<td>25</td>
<td>57.14</td>
<td>(4.13 \times 10^{-3})</td>
<td>9.14</td>
<td>0.9180</td>
<td>0.527</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>89.94</td>
<td>(9.44 \times 10^{-3})</td>
<td>47.18</td>
<td>0.9710</td>
<td>1.269</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>102.16</td>
<td>(8.52 \times 10^{-3})</td>
<td>61.09</td>
<td>0.9839</td>
<td>1.105</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>105.35</td>
<td>(9.21 \times 10^{-3})</td>
<td>69.54</td>
<td>0.8845</td>
<td>1.321</td>
</tr>
</tbody>
</table>

**Figures**

(a) XRD patterns of Fe3O4 and MBC sorbents. (b) FT-IR spectra of BC and MBC sorbents
Figure 2

The SEM images of (a) BC and (b) MBC sorbents, EDX results of selected areas of MBC

Figure 3

The TEM images of MBC sorbent

Figure 4

TGA analysis of MBC sorbent
Figure 5

Effect of initial Pb\(^{2+}\), Cd\(^{2+}\) concentration (a), shaking speed (b), pH (c), (d) recycle times of MBC (Pb\(^{2+}\) and Cd\(^{2+}\) solution of C\(_0\) = 50 mg/L; T = 300 K; MBC dosage = 0.25 g/L; V = 25 mL; pH = 6.0)

Figure 6

The fitting lines of Pb\(^{2+}\) pseudo-first-order model (a), pseudo-second-order model (b); fitting lines of Cd\(^{2+}\): pseudo-first-order model (c), pseudo-second-order model (d)
Figure 7

The fitting lines of Pb2+: Langmuir model (a), Freundlich model (b); fitting lines of Cd2+: Langmuir model (c), Freundlich model (d)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- Biochar.001.tiff