



Harnessing Agricultural Byproducts: Rice Husk-Derived Adsorbents for Heavy Metal Remediation in Water

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This study investigates the removal of heavy metals Pb(II), Cr(VI) and Ni(II) from water using rice husk-derived materials. The adsorption effectiveness of rice husk charcoal and its refined forms, including carbon-silica, silica, and carbon, was assessed after activation with HCl. The results revealed that activation improves the adsorption of Pb(II) and Cr(VI), particularly at lower concentrations, due to increased surface area and active sites. However, the influence of activation on Ni(II) is less significant. This research highlights the potential of using eco-friendly, cost-effective rice husk-derived adsorbents for water purification, offering a sustainable solution to heavy metal contamination and agricultural waste management.

Keywords: Heavy metal adsorption, Rice husk-derived adsorbents, HCl activation, Sustainable water treatment.

INTRODUCTION

The presence of heavy metals in water and wastewater poses substantial threats to both the environment and the health of all living things. There are a variety of health issues that can be brought on by the accumulation of heavy metals in the body over time [1,2]. They threaten aquatic ecosystems and human health due to their persistent and recalcitrant nature and bioaccumulative ability in the environment [3-5]. Heavy metals contamination can result from industrialization, urbanization and climate change, causing ecological balance disruptions and biodiversity loss [3,4].

To mitigate these risks, effective water treatment methods are essential. Materials like rice husk have been extensively studied and found to be effective for this purpose due to their cost-effectiveness, easy availability, high adsorption efficiency and reusability [6-9]. Rice husk, a low-cost and renewable bio-based adsorbent, offers a promising solution for treating wastewater contaminated with heavy metals. The application of rice husk not only facilitates the removal of heavy metals but also offers an environmentally beneficial and cost-effective approach to ensuring the safety of water bodies [7,9].

In addition to posing health risks, heavy metals in water and wastewater harm the environment. Their propensity to contaminate soil, water and ecosystems disrupts ecological equilibrium and engenders biodiversity loss [3]. Owing to their persistent nature, heavy metals may linger in the environment over extended periods and bioaccumulate within organisms, culminating in enduring damage to ecosystems [5]. The necessity for efficacious water treatment methodologies to mitigate the perils associated with heavy metals in water and wastewater is unequivocal [4]. Among the studied methods, adsorption utilizing materials such as rice husk has garnered considerable attention as a viable technique for extirpating heavy metals from water and wastewater [6,7].

An advantage of employing rice husk as an adsorbent is its abundance and economic viability. As an agricultural byproduct generated in copious amounts, especially within developing nations, rice husk embodies a promising resource [6,7]. The primary constituents of rice husk, carbon and silica, render it a promising material for adsorption endeavors [6]. In present study, rice husk was subjected to a charring process to obtain charcoal. The rice husk-derived charcoal was further refined to yield carbon-silica, silica and carbon materials. These mater-

ials were then subjected to activation using HCl. The efficacy of these activated materials in adsorbing heavy metals, specifically Pb(II), Cr(VI) and nickel Ni(II) ions, was meticulously evaluated.

EXPERIMENTAL

The chemicals and solvents used in this research *viz.* rice husk charcoal, lead nitrate, silver nitrate, deionized water, HCl 37% *v/v*, sodium hydroxide, ethanol, absolute ethanol, *n*-hexane, potassium dichromate and nickel sulphate hexahydrate were purchased from Sigma-Aldrich, USA.

Preparation of rice husk charcoal: The rice husk charcoal was subjected to a grinding process utilizing a ball mill (Star Trace-Planetary) operating at a rotational speed of 250 rpm for 2 h, after which it was sieved through a 50-mesh sieve (Retsch ASTM E11). After that, 6 g of powdered rice husk charcoal were introduced into a beaker followed by the addition of 12 mL of ethanol. The mixture was homogenized within an incubator (GFL Type 1086) maintained at 45 °C. After 1 day, the charcoal and ethanol mixture was decanted and repeated the process twice more, the last time using absolute ethanol.

Upon separation, the resultant residue was mixed with *n*-hexane in a volume twice that of the precipitate and agitated within an incubator at 45 °C. Following a day, the charcoal-hexane mixture was decanted and the process was repeated twice. The precipitate was then desiccated in an oven (Carbolite Type PF120) at 100 °C over 4 h. After drying, the rice husk charcoal was sieved utilizing an 80-mesh sieve (Retsch ASTM E11).

Preparation of carbon-silica: Powdered rice husk charcoal (6 g) was mixed with NaOH at varying molar ratios of 1:0.4 and 1:2 by following the reported procedure [10]. Subsequently, the charcoal and NaOH mixture were introduced into 225 mL of deionized water and subjected to heating whilst under continuous agitation. The resulting mixture was then titrated with HCl until pH of 8-9 and left for 1 day. After the acid addition, a carbon-silica precipitate formed, which was then washed with deionized water until free of chlorine.

The carbon-silica precipitate was then mixed with ethanol, the volume of which was twice that of the precipitate and homogenized within an incubator maintained at 45 °C. The mixture encompassing carbon-silica and ethanol was allowed to stand for 1 day and then decanted. This procedure was repeated twice more, with absolute ethanol as solvent in the final the process. Thereafter, the carbon-silica precipitate was combined with *n*-hexane in a volume twice that of the precipitate and agitated within an incubator at 45 °C. The mixture of carbon-silica and *n*-hexane was allowed to stand for 1 day, after which it was decanted and this procedure containing *n*-hexane as solvent was replicated twice. The subsequent addition of *n*-hexane solvent resulted in the formation of a precipitate, which was dried in an oven at 100 °C for 4 h. Following desiccation, the carbon-silica was sieved utilizing an 80-mesh sieve.

Preparation of silica and carbon: Powdered rice husk charcoal (6 g) was combined with 4 g of NaOH and 225 mL of deionized water. The mixture was subjected to heating and stirring until it reached a boiling state, filtered to obtain silica

filtrate and carbon residue. The silica filtrate and carbon residue were titrated with HCl until a pH range of 8-9 and left for 1 day. After the acid addition, the resulting precipitates were filtered and then rinsed with deionized water.

Each fraction of silica filtrate and carbon residue was separately mixed with ethanol, twice the volume of the precipitate and homogenized in an incubator at 45 °C with stirring. The mixture was then allowed to stand for 1 day followed by decantation. This procedure was repeated twice with ethanol addition at the final process. The precipitates were then mixed with *n*-hexane, twice the volume of the precipitate, in an incubator at 45 °C with stirring and then left for 1 day. The mixture was decanted and this procedure of incorporating *n*-hexane as solvent was replicated twice. The resulting silica and carbon precipitates were dried in an oven at 100 °C over 4 h. The dried silica and carbon were sieved utilizing an 80-mesh sieve.

Activation of charcoal, carbon-silica, silica and carbon: A 2% HCl solution was separately added to 2 g of charcoal, silica carbon, silica and carbon until the pH reached 2. Each mixture was heated at 60 °C for 2 h and then cooled down. The filtered residue was washed with deionized water until reaching a neutral pH to ensure chlorine-free conditions. Then, the residue was dried at 100 °C for 4 h.

Adsorption studies: A total of 20 mg of each adsorbent were added to 20 mL of heavy metal solution containing Pb(II), Cr(VI) and Ni(II) at different concentrations of 30, 50 and 100 ppm. The pH of the solution was adjusted to pH 2 using HCl. The mixture was stirred on a shaker for 20 min at 100 rpm and the solution was then left at room temperature for 1 day. The final concentrations of heavy metals [Pb(II), Cr(VI) and Ni(II)] in the filtrate were analyzed using an atomic absorption spectrophotometer (AAS; Shimadzu AA-7000). The reduction in the concentrations of the adsorbed heavy metals Pb(II), Cr(VI) and Ni(II) was calculated from the difference between the initial and final concentrations. The percentage of adsorption efficiency of each adsorbent was calculated using the following equation [11]:

$$\text{Adsorption efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100$$

where C_i is the initial concentration (ppm) and C_e is the final concentration (ppm).

RESULTS AND DISCUSSION

Rice husk charcoal: Rice husk charcoal, obtained from the combustion of rice husks, typically has large size and retains the shape of the original husks. The rice husk charcoal was subjected to grinding and sieving processes through a 50-mesh sieve to enhance its adsorption capacity. The rationale behind this is that smaller particle sizes equate to an increased surface area, thereby facilitating more efficient adsorption of adsorbates onto the adsorbent surface [7]. This is primarily because smaller adsorbent particles exhibit higher effective surface areas, providing more available sites capable of binding metal ions. The adsorption of heavy metal ions on the surface of adsorbents is attributed to the small size of adsorbent, which presents larger surface areas to metal ions present in the aqueous solution.

Similarly, methodologies utilizing rice husk and its derived charcoals as effective adsorbents have demonstrated the critical role of adsorbent particle size in achieving optimal adsorption performance [12]. In addition, the specific particle size fractions are achieved by grinding and screening the activated carbons from rice husk, which further highlights the importance of particle size in adsorption applications [13].

The silica content in rice husk charcoal was analyzed using X-ray fluorescence (XRF) technique, which revealed that the average silica content in rice husk charcoal is 49.86%. Various factors such as temperature, combustion duration, heating rate, variety and acid activation may influence the silica content in rice husk charcoal. The resulting silica content analysis was then used in calculating the mass of rice husk charcoal and NaOH required to produce silica carbon, silica and carbon according to the stoichiometric ratios of mole comparison. Based on Table-1, the mole ratios of silica to NaOH were chosen as 1:0.4 and 1:2.

TABLE-1
SILICA CONTENT (SiO₂) IN RICE HUSK CHARCOAL

Replication	Silica content (%)
1	49.82
2	49.91
Average	49.86

Activation of silica carbon, silica and carbon from rice husk charcoal: The sieved rice husk charcoal was then treated using NaOH to extract silica. Since silica is poorly soluble at pH values below ten and greatly enhances at pH values above ten, alkaline solutions like NaOH are ideal for removing silica from rice husk charcoal as a raw material [14]. Referring to the study of He *et al.* [10], a mole ratio of silica to NaOH for silica extraction was used. The production of silica carbon was carried out using a different mole ratios of silica to NaOH (1:0.4 and 1:2). The mole ratio of 1:0.4 involves rice husk charcoal (6 g) and NaOH (0.8 g) in deionized water up to 225 mL. On the other hand, the mole ratio of 1:2 utilizes 6 g of rice husk charcoal and 3.9 g of NaOH in deionized water up to 225 mL. The reaction that occurs during the extraction of silica using NaOH to obtain sodium silicate solution (Na₂SiO₃) is as follows in eqn. 1:



To speed up the reaction and get more silica dissolved in the NaOH solution, the mixture was heated and constant stirring helped to distribute the heat evenly and get the charcoal to dissolve more easily [15]. Sodium ions accelerate the condensation reaction by reacting with the negative charge of silica, leading to coagulation, gel formation and sol formation alternately, resulting in a larger surface area [16].

No filtration was involved in the extraction of silica carbon. In contrast, in silica extraction, filtration was carried out using a Buchner funnel, resulting in silica filtrate and carbon residue. Addition of 1 N HCl solution until pH 7.0 to each system leads to silica carbon and silica formation (eqn. 2) [17]:



The resulting carbon-silica precipitates were mixed with ethanol to replace water molecules, which may be present in the pores. The subsequent addition of *n*-hexane was intended to substitute ethanol molecules. Such solvent exchange was performed to minimize the capillary pressure since polar liquid evaporation in the pores may increase capillary pressure, leading to pore collapse [10].

Treatment with 2% HCl solution enhances the pore structure of silica and carbon materials. When inorganic minerals dissolved in HCl, the adsorptive qualities of pores were improved and thereby their porosity increased. Dilute HCl treatment has been demonstrated to diminish ash content in activated carbon and expand the holes within the carbon structure, leading to a proliferation of micropores and an increase in the pore volume ratio [18].

Adsorption of heavy metals Pb(II), Cr(VI) and Ni(II) by activated and non-activated charcoal, silica carbon, silica and carbon: The adsorption efficiency of heavy metals Pb(II), Cr(VI) and Ni(II) at different concentrations (30, 50 and 100 ppm) were evaluated by various activated and non-activated adsorbents, including charcoal, silica carbon, silica and carbon.

Charcoal, silica and silica carbon in both activated and non-activated forms exhibit varied adsorption efficiencies across different concentrations of 30, 50 and 100 ppm for Pb(II) (Fig. 1). At 30 ppm, activated silica carbon 1:0.4 shows the highest efficiency, indicating its suitability for low concentration Pb(II) adsorption. At higher concentrations of 50 and 100 ppm, activated forms generally maintain higher efficiency, suggesting that activation enhances Pb(II) adsorption capacity, possibly due to increased surface area and active sites.

For Cr(VI) adsorption, activated charcoal and silica carbon forms tend to show higher efficiency across all concentrations (Fig. 2). This suggests that activation plays a significant role in Cr(VI) adsorption. Significantly, activated silica carbon 1:0.4 and 1:2 show high efficiency at 30 ppm, highlighting their potential for low-concentration Cr(VI) removal. The trend of higher efficiency in activated adsorbents is consistent at 50 and 100 ppm, reinforcing the importance of activation for Cr(VI) adsorption.

For Ni(II) adsorption, the adsorption efficiency varies significantly across different adsorbents and concentrations (Fig. 3). At 30 ppm, activated carbon and silica carbon 1:0.4 show significant efficiency, indicating their effectiveness in low concentration Ni(II) adsorption. At higher concentrations (50 and 100 ppm), both activated and non-activated forms of various adsorbents demonstrate comparable efficiencies, suggesting that the impact of activation might be less pronounced for Ni(II) compared to Pb(II) and Cr(VI).

Overall, activation generally enhances the adsorption efficiency for Pb(II) and Cr(VI), with significant differences observed at lower concentrations. For Ni(II), the activation impact is less consistent, with both activated and non-activated adsorbents showing comparable performances at higher concentrations. The choice of adsorbent and its activation status is crucial and should be tailored based on the specific heavy metal ions and concentration for optimal removal efficiency.

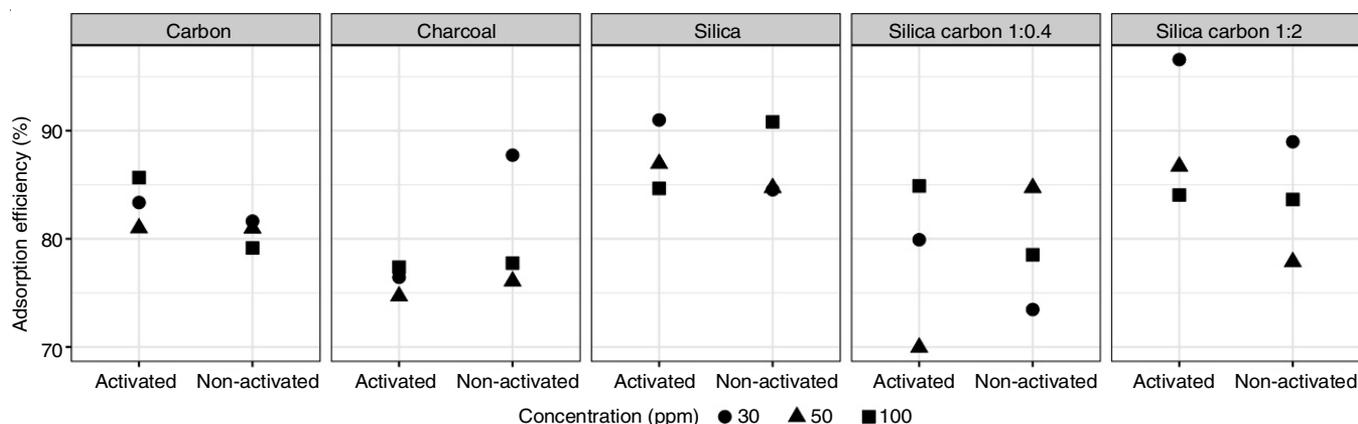


Fig. 1. Pb(II) adsorption efficiency at different concentrations by various activated and non-activated charcoal, silica, silica and carbon. The concentration variations used were 30, 50 and 100 ppm, represented in black circle, triangle and square shapes, respectively

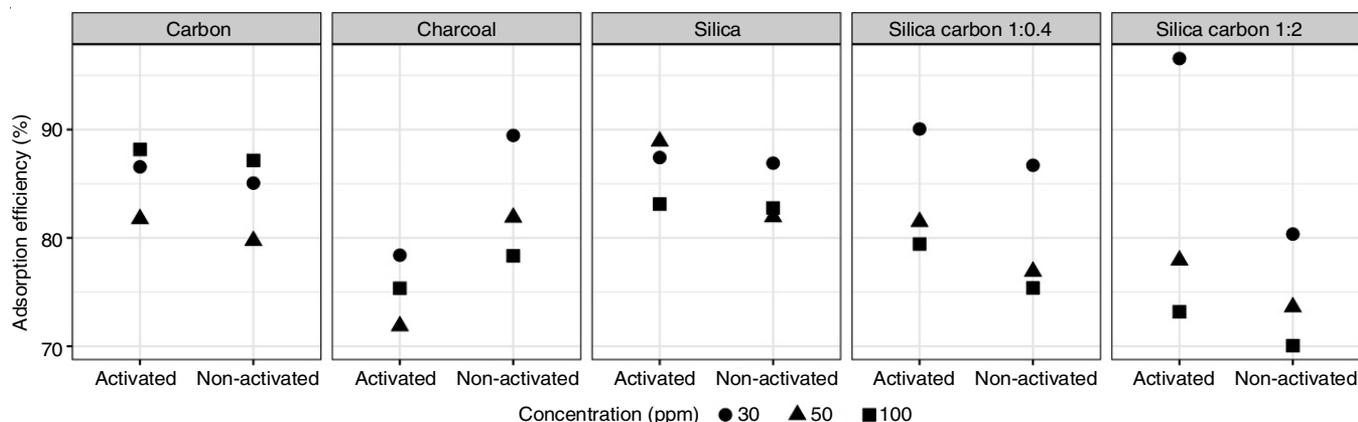


Fig. 2. Cr(VI) adsorption efficiency at different concentrations by various activated and non-activated charcoal, silica, silica and carbon. The concentration variations used were 30, 50 and 100 ppm, represented in black circle, triangle and square shapes, respectively

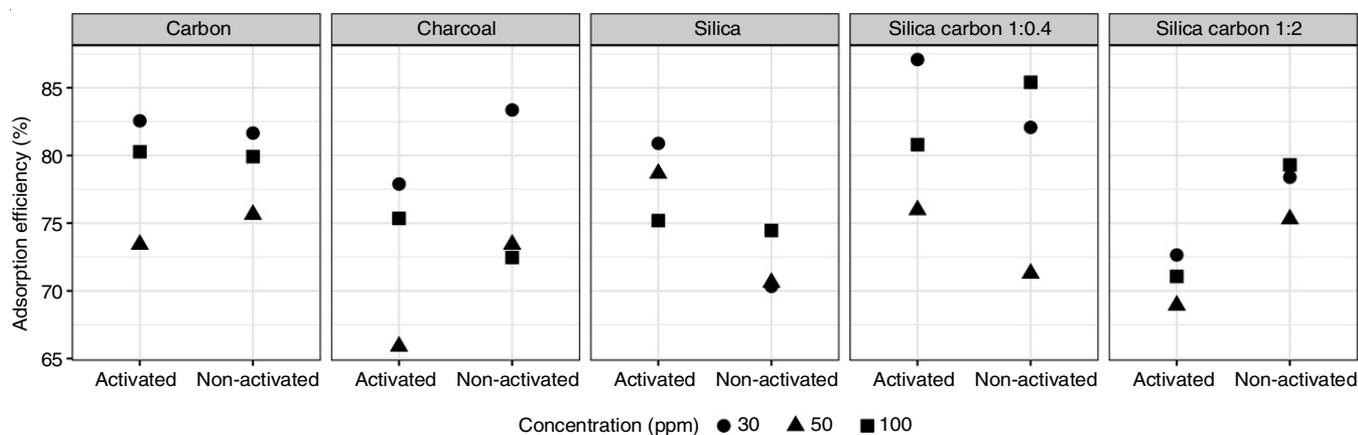


Fig. 3. Ni(II) adsorption efficiency at different concentrations by various activated and non-activated charcoal, silica, silica and carbon. The concentration variations used were 30, 50 and 100 ppm, represented in black circle, triangle and square shapes, respectively

Conclusion

The present study has successfully demonstrated the potential of rice husk-derived materials as effective adsorbents for the removal of hazardous heavy metal ions *e.g.* Pb(II), Cr(VI) and Ni(II). This study has demonstrated the importance of material activation and the role of various adsorbents in reducing heavy metal pollution, which is a critical issue for both the environment

and public health. The findings indicate that activation of adsorbents generally enhances the adsorption efficiency for Pb(II) and Cr(VI), particularly at lower concentrations. This improvement is likely attributable to the increased surface area and active sites available for heavy metal ion binding post-activation. In case of Ni(II), however, the activation of adsorbents shows a less pronounced impact on the adsorption efficiency, suggesting that the choice of adsorbent and its activation state

is also crucial and should be specifically tailored to the heavy metal ion in question.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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