# Assessing the mercury removal efficiency of natural adsorbents from wastewater

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**Summary**

Organic waste materials *viz*., coir pith, rice husk, and water hyacinth were studied in the batch experiments to evaluate their potential for mercury removal from wastewater. Five pH (4,5,6,7,8) and five different contact times (1,2,4,6,8 hours) were studied with a constant mercury concentration of 0.1 ppm. SEM (Scanning electron microscopy-energy dispersive spectroscopy) and FTIR (Fourier transform infrared spectroscopy) were used for characterizing the biochars *i.e.*, rice husk biochar (RHBC), coir pith biochar (CPBC) and water hyacinth biochar (WHBC), used for the experiment before and after adsorption studies. Adsorption capacities of each different biochar used for the experiment varied due to their wide range of surface area as well as different shift patterns in the FTIR. Based on the experimental results, among the three adsorbents used for mercury removal from wastewater, coirpith biochar (CPBC) has a maximum removal efficiency of 46.2% followed by rice husk biochar (RHBC–44.8%) and water hyacinth biochar (45.6%) with 6 hours of contact time.

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**Keywords:** Mercury, natural adsorbents, biochar, contact time

## Introduction

Mercury contamination in the soil and sediment has tremendously increased near the places undergoing mining and manufacturing activities (Kumari et al. 2020). As per the “priority list of dangerous substances” released by the Agency for Toxic Substances and Disease Registry, mercury occupies the third position (ATSDR 2015). US Environmental Protection Agency (USEPA) has identified Hg as not only one of the 13 priority pollutant metal elements. Mercury (Hg), being a highly toxic heavy metal, has been labelled by WHO (2017) as one of the "ten most dangerous chemicals". Global mercury emissions to air from anthropogenic sources were reported to be about 2220 tonnes in 2015 (UNEP 2018). Mercury occurs in various forms and it tends to change its chemical nature in the environment and shifts itself from one location to another, ultimately settling deep into soils and sediments. Small-scale gold mining, non-ferrous metal production and cement production are some of the sources of anthropogenic mercury emissions. The anthropogenic mercury released into the environment is higher than natural sources, resulting in a rise in total mercury load and, as a result, encouraging the spread of mercury throughout the world (Kumari et al. 2020).

Mercury exists in three forms namely elemental mercury (Hg°), inorganic mercury ($Hg^{+1}$, $Hg^{+2}$), and dimethyl mercury (organic mercury) (Beckers & Rinklebe 2017). Among these three forms, organic mercury is the most toxic form of the mercury. This organic mercury ($RHg^{+}$) form of mercury is bio-accumulative in nature because it can easily pass through biological membranes and accumulate in cells, and it worsens the issue since its concentration rises with each trophic stage (Cosio et al. 2017). Based on recent research reports, it was found that mercury can damage soil health at even lower levels than the permissible safety cap, demanding more effective treatment strategies (Mahbub et al. 2017).

Adsorption has been found to be a highly competent technique for removing heavy metals from waste streams through the experimental study conducted on effluent-bearing heavy metals (Hegazi 2013). Various researchers have looked into using low-cost agricultural waste by-products like sugarcane bagasse, rice husk, sawdust, coconut husk, oil palm shell, neem bark, and other low-cost agricultural waste by-products to remove mercury from wastewater. The concept of utilization of biochar for the treatment of wastewater has gained attention these days. Hence, the present study has attempted to assess the efficiency of agro-based biochar as a safe and cost-effective method to remove mercury from wastewater.

## Materials and Methods

Natural adsorbents namely coirpith, water hyacinth and rice husks were collected and are washed initially with tap water and later thoroughly with double distilled water. The cleaned adsorbents were shade-dried and processed. The processed coirpith, water hyacinth and rice husk were subjected to slow pyrolysis with temperature ranged from 350-400 $^{0}$C and biochar was obtained for all three natural adsorbents. The batch experiment was conducted with natural adsorbents *viz*., coirpith biochar (CPBC), rice husk biochar (RHBC) and

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water hyacinth biochar (WHBC) for evaluating its potential for mercury removal in an aqueous solution. Aqueous solution of mercury was prepared for 0.1 ppm by using analytical grade Mercuric chloride in deionized water. The different pH namely 4, 5, 6, 7, 8 used for the experiment were obtained using 0.5 M NaOH or 0.5 M HCl. Batch experiments were conducted in the 100 mL Erlenmeyer flasks containing 50ml of 0.1 ppm mercuric chloride solution and mixed with 0.5g of all three adsorbents in different sets of flasks at room temperature of 26$^{0}$C. The Erlenmeyer flasks were agitated on a rotary shaker at 150 rpm. at different time intervals (1, 2, 4, 6 hours). After the required time intervals, the supernatant solutions were filtered immediately through the Whatmann number 42 filter paper and were subjected to further analysis (Mulu Berhe Desta 2013). The experimental procedure is slightly modified from Mulu Berhe Desta, 2013 in the concentration of the mercury aqueous solution, contact time and also in the pyrolysis temperature. To obtain the accuracy in the results, the experiments were performed in triplicate and the mean value was used for data interpretation. The surface morphology of the adsorbents used for the experiment was studied through scanning electron microscopy (SEM). The SEM images of the RHBC and CPBC taken at a high voltage of 10kV with 1000 x were taken. The structure of these adsorbents is suitable for mercury adsorption which is confirmed through FTIR analysis.

## Results and Discussion

### SEM images of adsorbents

The morphology of the adsorbents varied and there was a significant change among the adsorbents. The SEM images of the RHBC, CPBC and WHBC were taken at a high voltage of 10kV with 1000 x is given in Fig.1a, 1b & 1c. In the case of CPBC, the pores were arranged like honeycomb and the pore size varied between 50 to 300 µm. In the case of RHBC, the presence of macropores with irregular patterns and fibrous structures with large surface area was seen due to the presence of cellulose and the pore size varied between 10 to 300 µm. In the case of WHBC, the SEM was found to have a nebulous and striated structure. The structure of these adsorbents is suitable for mercury adsorption which is confirmed through FTIR analysis.

### Influence of pH on adsorption

Adsorption is the separation process of molecules from the environment to the bulk or surface of the solid or liquid phase. Adsorption outperforms other separation and purification methods, such as photo remediation, membrane technology, ion exchange, and electrochemical separation due to its unique characteristics of low cost and ease of operation combined with high performance (Pourhakkak et al. 2021). An important factor to influences the adsorption of metal ions from the wastewater by the adsorbents is pH. This pH significantly affected the adsorption mechanism as it affects the interaction between the adsorbate and the adsorbent by altering the surface charges and functional groups. In the case of CPBC, an adsorption experiment was carried out at various pH 4 to 8. It was observed that the maximum adsorption of mercury on CPBC (90%) occurred at pH of 8. This could be due to the protonation of C=O and amine groups in the adsorbent leading to strong binding of mercury ions from the aqueous solution. The batch experiment was conducted at different pH ranges from 4 to 8 for RHBC. When the pH was low, the adsorption capacity of the absorbents was very less. It was observed that the maximum adsorption of mercury on RHBC (96%) occurred at a pH of 6. The adsorption of RHBC at near neutral may be attributed to the cellulose part of the rice husk. This could be due to the surface complexation phenomenon that OH facilitates, Sulfur groups present in rice husk biochar. The subsequent decrease of Hg (II) uptake at higher pH values may result from the weak binding between the target metal ions and the amphoteric silanol or aluminol groups when the solution is alkaline. At moderate pHs of 4-6, $H^+$ ions are released from the adsorbents' active sites, thereby facilitating the adsorption of metallic cations like mercury. Many factors influence the ability or efficiency of rice husk adsorption, including pH, temperature, initial contaminant concentration, adsorbent dosage and particle size, agitation or contact period, as well as the flow rate and characteristics of the column in continuous service (Shamsollahi & Partovinia 2019). Johari et al. (2016) demonstrated that coconut pith-derived chars could be potential as low-cost adsorbent alternatives for the removal of elemental mercury in gas streams

### Influence of Contact time on adsorption

The contact time is an important parameter in determining the adsorption rate between the adsorbent and the adsorbate. The variations of per cent adsorption of mercury with contact time were studied using 0.1 ppm Hg solution and 0.5 g of all the adsorbents *viz*., CPBC, RHBC and water hyacinth biochar (WHBC). The shaking time varied from 1 hour to 8 hours for all the adsorbents at their desired pH. It has been found that percentage adsorption increases with an increase in shaking time in an end-to-end shaker at 120 rpm. The percentage of adsorption of $Hg^{2+}$ gradually increased with the contact tie ranging from 1 to 8 hours. The mercury removal efficiency (%) of different adsorbents is calculated using the formulae

$$P = (C_o - C_e)/C_o \times 100\%$$

where $C_o$ is the Hg (II) initial concentration, $C_e$ is the Hg (II) concentration at the equilibrium stage.

Among the three adsorbents used for mercury removal from wastewater, rice husk biochar (RHBC) has a maximum removal efficiency of 44.8% followed by coirpith biochar (CPBC – 46.2%) and water hyacinth biochar (WHBC - 45.6%) with 6 hours of contact time. Okoume sawdust was found to be an excellent adsorbent for the removal of mercury (II) from aqueous solutions and it tends to get an increased sorption rate with an increase in contact time, stirring speed and initial solution pH and decreases with an increase in temperature and sorbent particle size. The maximum sorption capacity of Okoume sawdust was found to be 112.36 mg $g^{-1}$ at 20°C. Langmuir and the Freundlich isotherms were used to analyse the equilibrium isotherm data. The Langmuir model yields a much better fit than the Freundlich model (Chakraborty et al. 2020). Liu et al. (2020) evaluated the influence of Hg (II) ion concentration, pH, and contact time for the removal of mercury from aqueous solution using the rice husk-activated carbon with KOH (RHAC). Adsorption results concluded that maximum adsorption capacity for Hg (II) was obtained within 60 min and was regarded as the most suitable time for the experiment.

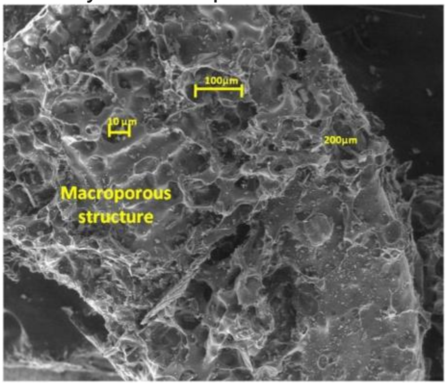


**Fig 1a.** SEM image of Rice husk biochar (RHBC)

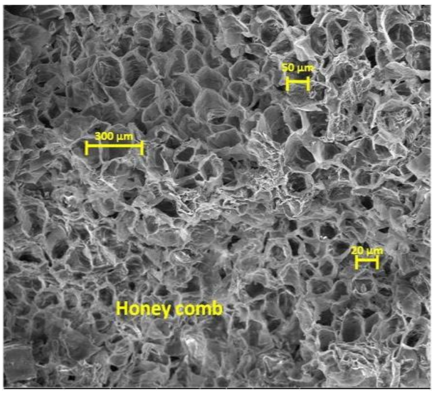


**Fig 1b.** SEM image of Coirpith biochar (CPBC)

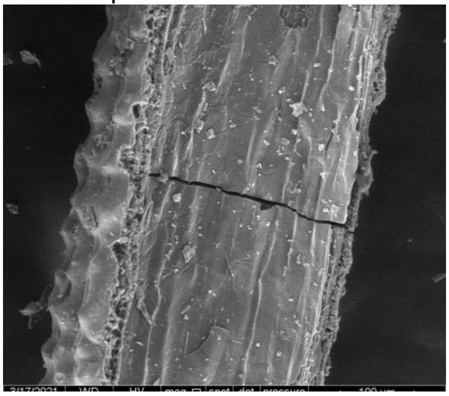

**Fig 1c.** SEM image of Water hyacinth biomass (WHBC)

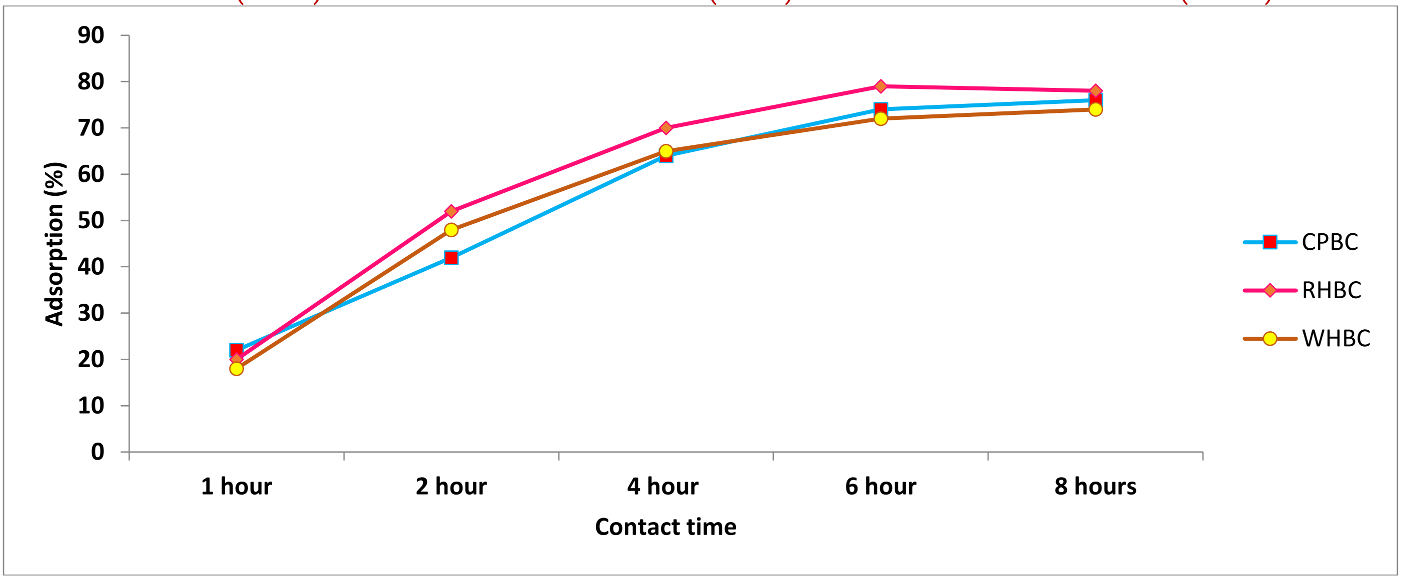


**Fig 2.** Effect of contact time on the adsorption capacity of different adsorbents

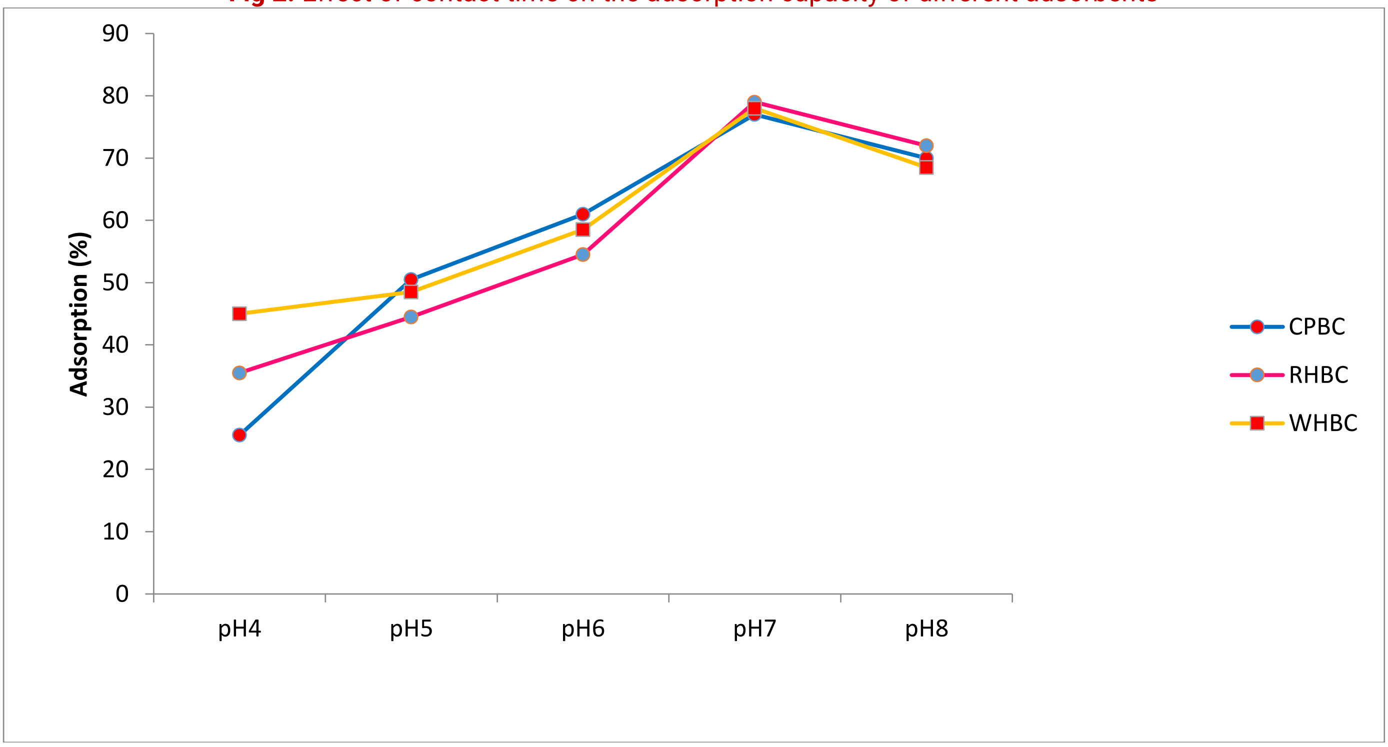


**Fig 3.** Effect of pH on the adsorption capacity of different adsorbents

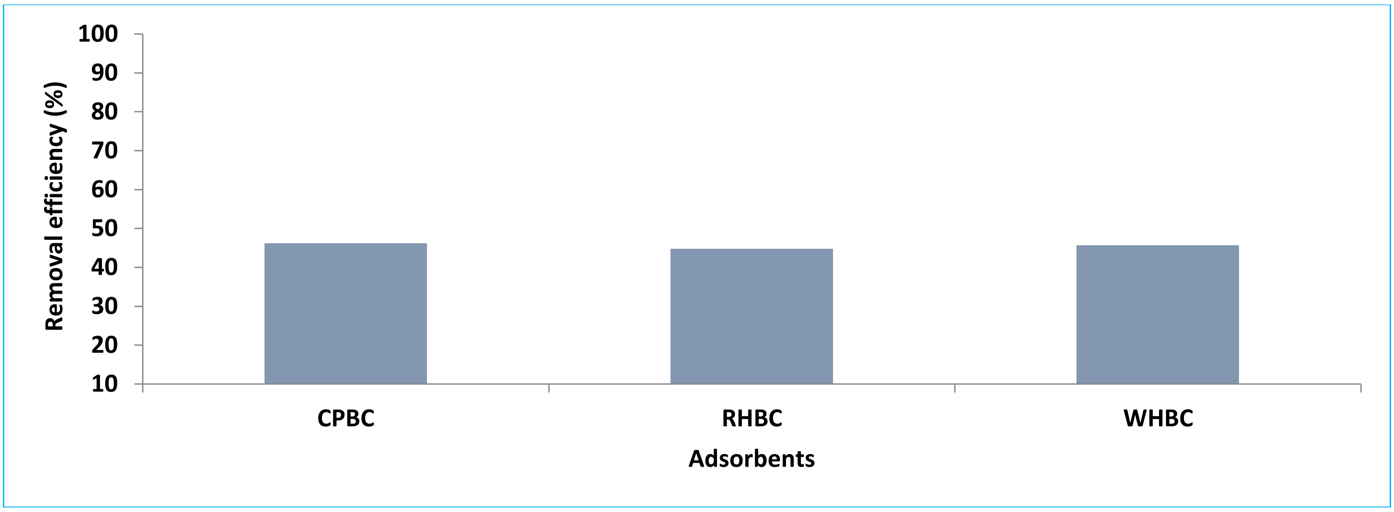


**Fig 4.** Hg removal efficiency of different adsorbents

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## Conclusion

Based on the results obtained in the laboratory experiment conducted it was found that the **v**arious adsorbents *viz.,* rice husk biochar (RHBC), coirpith biochar (CPBC), and water hyacinth biochar (WHBC) were useful for the removal of mercury from wastewater and it was found that all the adsorbents were on par in mercury removal from wastewater. Since water hyacinth is a weed, it can be used as an adsorbent effectively compared to rice husk or coirpith, which have their own economic values and importance.

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