Cadmium remediation from water using low-cost modified Biochar: An Approach towards Sustainable

Abstract

Biochar is considered a promising adsorbent for removing Cadmium (Cd^{2+}), which is commonly found in industrial wastewater. In this study, rice husk biochar was used for the removal of aqueous Cd^{2+}. The rice husk biochar was produced through fast pyrolysis at 450°C. Chitosan-Modified Biochar (CMBC) was employed for Cd^{2+} removal; it was prepared by treating rice husk biochar with a 2% aqueous acetic acid chitosan solution followed by NaOH treatment. Both CMBC and Non-Modified Biochar (NMBC) were characterized using proximate analysis, ultimate analysis, FT-IR, and scanning electron microscopy. The Langmuir maximum adsorption capacity of CMBC at pH 5 was 134 mg/g, compared to 48.2 mg/g for NMBC at 318 K. CMBC demonstrated a higher Cd^{2+} removal capacity than NMBC, indicating that chitosan modification introduces amine groups on the biochar surface, enhancing Cd^{2+} adsorption. The modes of Cd^{2+} adsorption on CMBC were investigated by comparing FT-IR and SEM images before and after adsorption. The modification of rice husk biochar with chitosan significantly increased the Cd^{2+} adsorption capacity. Higher pyrolysis temperatures resulted in reduced biochar yield but increased porosity, surface area, and adsorption capacity. Cd^{2+} adsorption was pH-dependent, with a maximum capacity of 161 mg/g observed at pH 5. The Freundlich model best described the sorption equilibrium data. Both chemisorption and physisorption interactions on the heterogeneous adsorbent surface likely contribute to Cd^{2+} adsorption. Overall, rice husk biochar is a promising, low-cost, sustainable material for removing aqueous Cd^{2+}. The chitosan modification facilitates rapid pollutant removal due to the biochar particle sizes, making CMBC highly effective for removing heavy metal contaminants from aqueous solutions.

Key words: Biochar, Feedstock, Cadmium, Pollutant, Remediation, wastewater**.**

Introduction

Cleaner and more sustainable development can be achieved by implementing efficient and cost-effective technologies for environmentally friendly industrial wastewater treatment **(Tunçsiper, 2019)**. Industrial effluents often contain wastewater with high concentrations of heavy metals, a problem that has been worsening over recent decades **(Zhang *et al.*, 2019).** Various conventional and modern technologies can be used to remove hazardous pollutants, particularly heavy metals harmful to human health, from industrial wastewater **(Liew *et al.*, 2019).** These technologies include thermal treatment **(Safwat, 2018),** membrane-based separation, biological processes, and adsorption processes **(Zhang et al., 2018).** Among these technologies, adsorption is widely recognized for its energy efficiency and cost-effectiveness in pollutant removal from wastewater **(Fernández-González et al., 2019).**

Biochar (BC) stands out as a commonly used adsorbent due to its versatility. As a promising alternative, BC has been investigated for its potential in cost-effective synthesis from various materials for the efficient removal of pollutants from wastewater **(Tang *et al.*, 2019).** To the best of our knowledge, BC derived from rice husk (RH) has not yet been explored for its effectiveness in removing heavy metals, particularly cadmium (Cd^{2+}), for cleaner water production. In this study, BC was synthesized from RH using fast pyrolysis and modified with chitosan. Both the unmodified and chitosan-modified BC were characterized to determine their surface functional groups and structural properties. The BC was then tested for its efficiency in adsorbing heavy metals, especially cadmium, from wastewater. Chitosan, known for its effectiveness in heavy metal removal from aqueous solutions**(Juang *et al.*,2002., Ngah *et al.*, 2011., Zhou *et al.*, 2023)**, has previously been studied in various forms, including chitosan hydrogel, chitosan/PVA hydrogel beads, and chitosan-coated sand **(Wan *et al.*, 2010., Ronghua*et al.*, 2018)**. Therefore, combining chitosan with biochar may result in a novel material with enhanced capacity for lead ion uptake beyond that of biochar alone **(Wang *et al.*, 2018).**

Materials and Method

Chemicals and equipment

All chemicals used were either GR or AR grades and were purchased from HiMedia, India. A 1000 mg L^{-1} Cd^{2+} aqueous stock solution was prepared by dissolving $CdCl_2$ in deionized (DI)

water. Analytical-grade chitosan (0.5 wt% in 0.5% aqueous acetic acid) was also acquired from HiMedia. This chitosan was derived from chitin by deacylating 85% of the amide groups from the parent chitin. Complete deacylation was not necessary.

Preparation of Rice Husk Biochar

The biochar used in this study was a byproduct of fast pyrolysis bio-oil production. Rice husk was pyrolyzed in a continuous auger-fed reactor, where it was preheated and then passed through the pyrolysis zone at 450°C for 20–30 seconds. The resulting biochar was collected, washed several times with DI water to remove salt impurities and ash, and then ground. The biochar was sieved to a uniform particle size distribution of 0.1 to 0.5 mm, oven-dried at 105°C for 10 hours to remove moisture, and stored in a sealed container for future use. This non-modified rice husk biochar is referred to as Non-Modified Biochar (NMBC).

Preparation of Chitosan-Modified Biochar

Chitosan-modified biochar was prepared following the method described by Y. Zhou et al. Briefly, 3 g of chitosan was dissolved in 180 mL of 2% aqueous acetic acid, and 3 g of biochar was added. The mixture was stirred for 30 minutes at ambient temperature. The biochar-chitosan suspension in aqueous acetic acid was then added dropwise to a 900 mL NaOH (1.2%) solution over approximately 2 hours. The suspension was allowed to stand for an additional 12 hours. The solid was then filtered through Whatman no. 1 filter paper. The chitosan-modified biochar was washed with DI water to remove excess NaOH and oven-dried for 24 hours at 70°C. The final weight of the dried sample was 4 g, indicating that 1 g of chitosan had been complexed with the biochar, resulting in approximately a 25% w/w ratio of chitosan to biochar. This chitosan-modified biochar is referred to as CMBC.

Biochar characterization

Fourier transform Infrared spectroscopy (FT-IR) analysis of the samples were obtained after grinding and pressing into a 5% by weight adsorbent KBr pellet. A total of 62 scans were taken from 4000 cm^{1} to 600 cm^{-1} with a resolution of 4 cm^{-1}. Scanning electron microscopy (SEM) analysis was performed using a JEOL JSM-6500F SEM operated at 5 kV. The biochar was applied to a carbon stub attached to carbon tape and then sputtered-coated under argon with a 5 nm layer of gold.

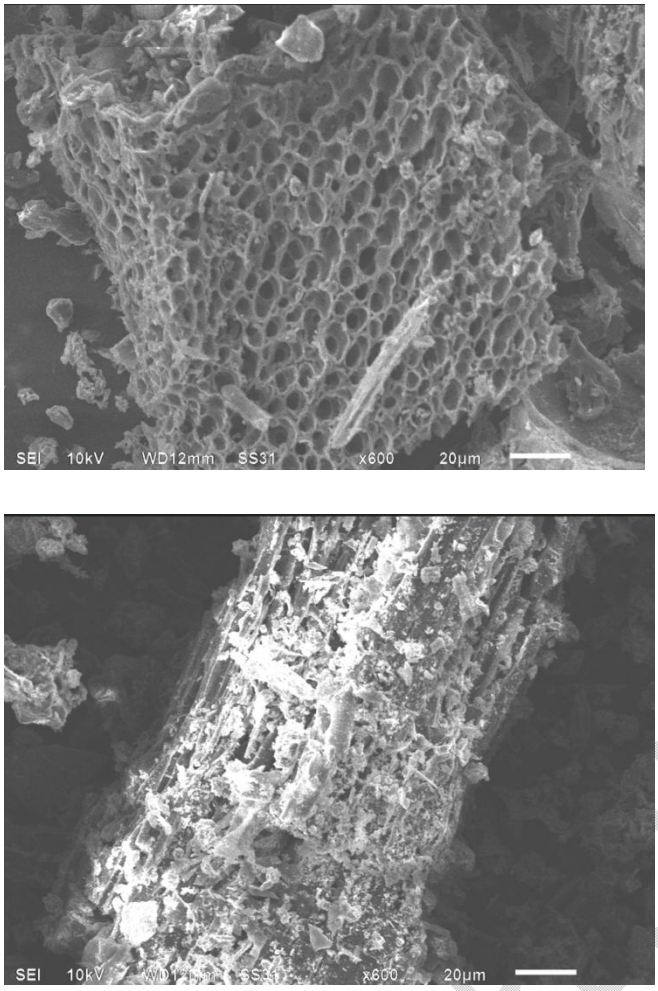

Fig. 1 SEM images of CMBC before and after adsorption

Batch sorption studies

The effects of pH, contact time, and Cd^{2+} concentration on uptake were carried out using the batch adsorption method **(Ramola *et al.*, 2020)**. Both kinetic and adsorption isotherm studies for Cd^{2+}were carried out at pH 5 and temperatures at 298, 308, and 318 K. A known amount of CMBC was added to 25 mL solutions of adsorbate containing 150 to 200 mg L^{-1} of Cd^{2+} from the 1000 mg L^{-1} Cd^{2+} stock solution prepared by dissolving $CdCl_2$ into DI water. This range was selected based on the natural levels of Cd in soil (range between 50 and 200 mg L^{-1}). Samples were then shaken using a mechanical shaker at 250 rpm for 18 h. Supernatants were then filtered through Whatman no. 1 filter paper. (As a test to determine if Cd^{2+} was adsorbed or retained on the filter paper, an aqueous $CdCl_2$ solution (150 mg L^{-1}) was filtered through the filter paper and

the Cd^{2+} concentration in the filtrate was measured. It was found that the Whatman no. 1 filter paper can hold about 3.3% total wt of Cd^{2+} in solution. The Cd^{2+} concentration remaining in the filtrate was measured with Atomic Absorption Spectrometry (AAS) and the amount of Cd^{2+} removed by adsorption was calculated by:

$$Q_e = \frac{V(C_0 - C_e)}{M}$$

here Q_e is the amount of Cd^{2+}(mg) removed per gram of CMBC, C_o and C_e are the initial and equilibrium Cd^{2+}concentrations (mg L^{-1}) in solution, V is the solution volume (L), and M is the CMBC weight (g).

Result and Discussion

Chitosan-modified biochar characterization

The FTIR spectra for CMBC is shown in Fig. 2 The IR bands from 3300 to 3500 cm^{-1} are characteristic of N–H and O–H stretching vibrations. Chitosan shows the typical FTIR spectrum of chitosan with N–H and O–H vibrations centered in the 3300 to 3500 cm^{-1} regions. The bands at 1653 cm^{1} and 894 cm^{-1} are due to the N–H bending and N–H wagging respectively. The NMBC surface has a large number of alcohols and ethers, phenolic O–H (3200–3550 cm^{-1}), and cyclic alkene (1566–1650 cm^{-1}) The CMBC surface contains amine and amide functional groups from chitosan and a few functional groups from the biochar including phenolic OH and carbonyls (Fig. 2)

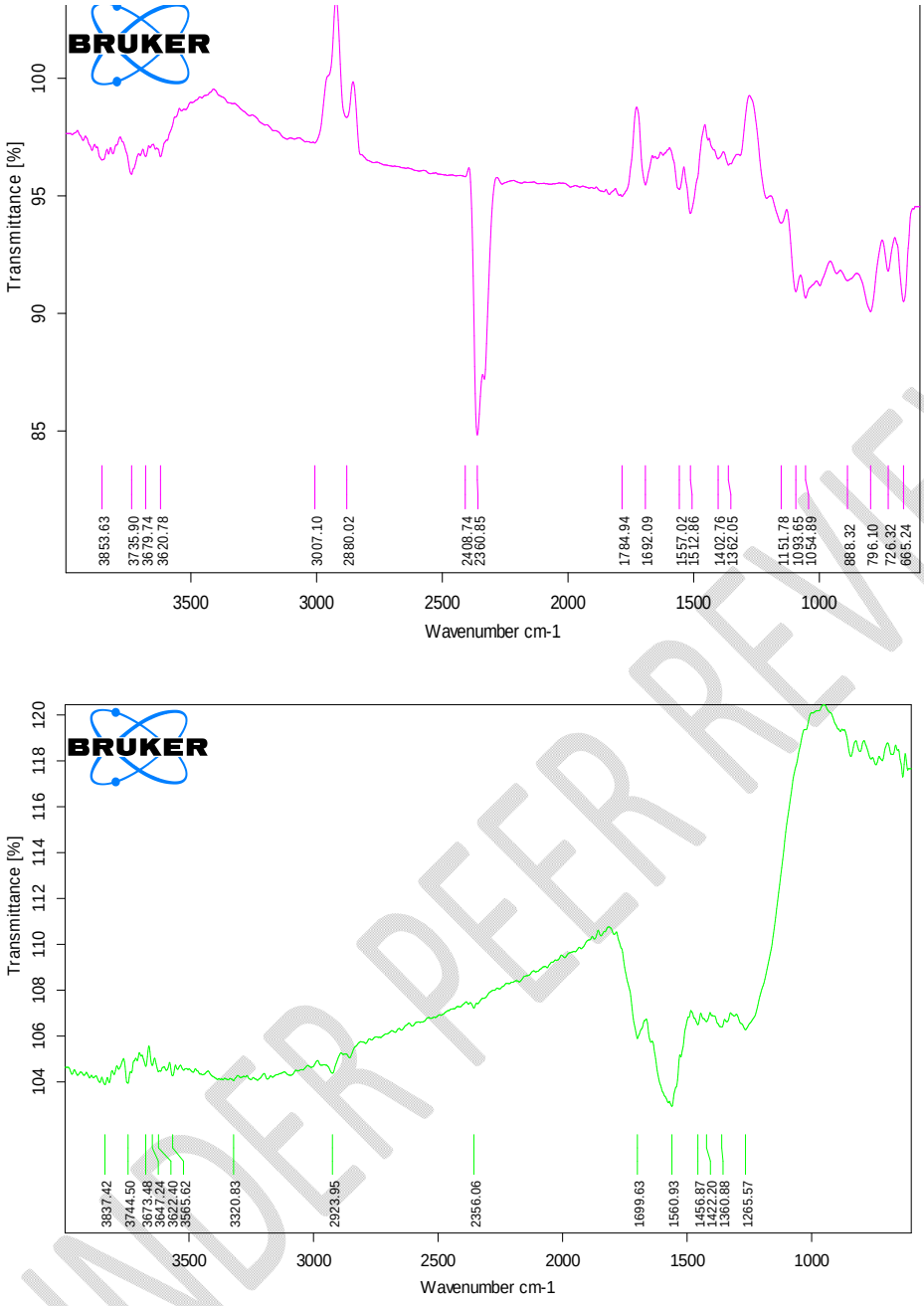

Fig. 2. FT-IR spetra of CMBC before and after treatment

Batch sorption studies

Effect of pH on adsorption

The Cd^{2+}adsorption of CMBC and NMBC at different initial pH values is shown in Fig.1 . The maximum pH studied was 5 to avoid Cd^{2+}precipitation (another remediation technique). Cd^{2+}removal by CMBC at equilibrium is more than two times higher than that of

NMBC at every solution pH's except at pH 2. Cd^{2+}removal by both CMBC and NMBC increases with increased pH.However, the maximum removal of $Cd^{2+}$is at pH 5, where the net surface charge is positive and cadmium ion repulsion still exists. Therefore, the mechanism of Cd^{2+}adsorption on CMBC must include specific non-electrostatic interactions to achieve this removal. Possible mechanisms include specific sorption by amine group coordination of Cd^{2+}physical attraction, precipitation, and reduction.

Adsorption mechanism

pH dependent mechanism

Possible Cd^{2+} ion adsorption sites on CMBC include chitosan amino groups, biochar carboxylic acid groups, aliphatic hydroxyl groups on chitosan, and phenolic hydroxyls on biochar. Many studies have investigated the role of chitosan amine groups in metal chelation, reporting that C, O, and H atoms are not involved in cadmium adsorption. In this study, maximum percentage removal was observed at pH 5 (Fig. 1). Chitosan's surface on CMBC undergoes pH-dependent protonation of its primary amine functions. Since 85% of the chitosan used had its $–NHCOCH_3$ functions hydrolyzed to amine groups, 85% of its monosaccharide rings contain primary amine functions.

Depending on the solution pH, chitosan's basic $–NH_2$ groups will be protonated to $–NH_3^+$. As pH increases, the fraction of protonated amine sites decreases, as shown in Table 1. At pH 5, only about 5–6% of chitosan amine groups are not protonated. Nevertheless, every monomer ring contains an $–NH_2$ or $–NH_3^+$ function, so even at pH 3, chitosan can still adsorb a significant amount of Cd^{2+} through amine coordination.

Surface carboxylic acid sites on the biochar can also complex with Cd^{2+}, similar to their interaction with Ca^{2+} and Mg^{2+} ions via chelation ($2RCOO^- + Cd^{2+} \rightarrow [(RCOO^-)_2\ Cd^{2+}]$). These are acidic sites (pKa∼4.20–4.75) because their carboxylate conjugate bases are stable and can complex with metal cations like Cd^{2+}.

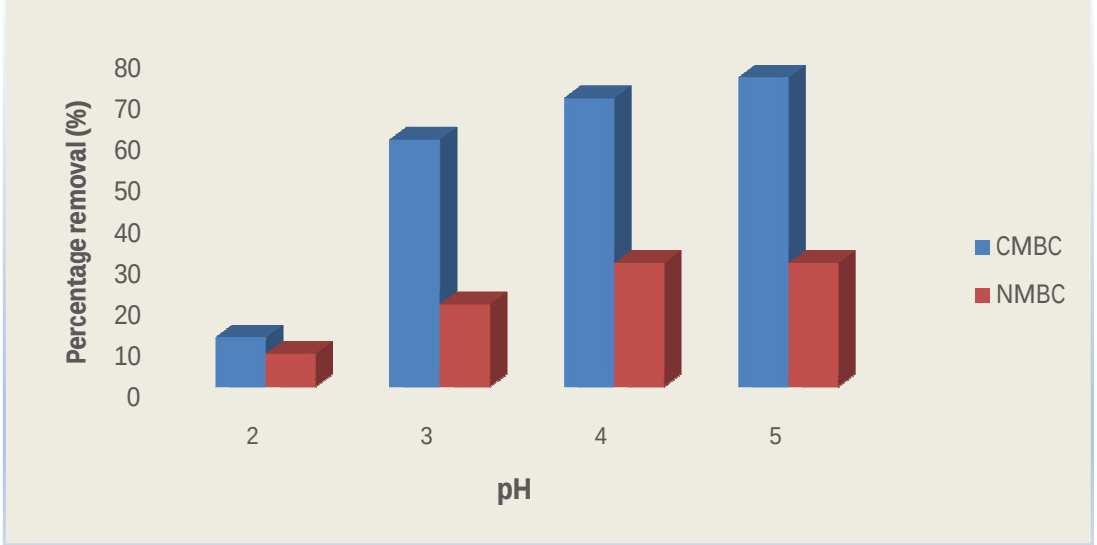

Fig.3. Percentage removal of lead at equilibrium by NMBC and CMBC at different pH values by 0.05 g adsorbent in 25 mL of aqueous $CdCl_2$, concentration = 150 mg L−1 at 25°C.

Functional groups studies by FTIR

Comparison of the FTIR spectra before and after Cd^{2+} adsorption suggests the nature of Cd^{2+} adsorption on the CMBC surface (Fig. 2). A slight shift in the N–H vibration band from 3282 to 3290 cm^{-1} after Cd^{2+} adsorption indicates the interaction of Cd^{2+} with the N group, affecting the N–H vibration. This finding is consistent with previous studies where binding of iron ions to the NH_2 group of chitosan caused a shift in the N–H bending vibration from 1638 to 1681 cm^{-1}**().**Additionally, the subtracted spectrum shows a reduction in transmittance in the 3534, 1612, 1396, and 1045 cm^{-1} regions, corresponding to N–H stretching, bending, scissoring, and wagging, and C–N stretching bands, respectively. These changes likely result from Cd^{2+} ions binding to the amino groups.

Sorption dynamics

The effect of temperature on cadmium adsorption was studied using 2 g L^{-1} of CMBC, 150 mg L^{-1} Cd^{2+} , shaking for 24 hours, with a pH of 5 at 298, 308, and 318 K. Significant Cd adsorption was observed within 1 hour, with equilibrium reached after approximately 6 hours.

Adsorption at 298 and 308 K was similar, but greater at 318 K, suggesting endothermic behavior. All kinetic studies were conducted over 6 hours to ensure equilibrium was achieved.

The effect of Cd^{2+} concentrations on adsorption was investigated using 25 mL solutions of 150, 175, and 230 mg L^{-1} Cd^{2+}, 2 g L^{-1} CMBC, and 6 hours of shaking at pH 5. Adsorption capacity increased with higher initial Cd^{2+} concentrations, with a significant increase observed when Cd^{2+} concentration was raised from 175 mg L^{-1} to 230 mg L^{-1}.

Adsorption kinetics

The pseudo first order linear kinetics modelwas fit to

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

where, q_t is the amount of lead adsorbed at time "*t*", q_e is the amount adsorbed at equilibrium, and k_1 (h^{-1}) is the first order adsorption rate constant. The parameters, correlation coefficients (0.915–0.970) for the first order kinetics model and the calculated *versus* observed q_e values (Table2) were not satisfactory. Thus, pseudo second order fittings were conducted.

The linear version of the pseudo second order kinetics model is given by,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e}$$

where, q_t is the amount of lead adsorbed at time "*t*", q_e is the amount adsorbed at equilibrium, and k_2 (h^{-1}) is the second order adsorption rate constant. Linear plots of t/q_t *vs.* t (slope of $1/q_e$).The correlation coefficients for the second order kinetics model are all larger than 0.991, and the calculated q_e values and the experimental q_e values matched well.

Adsorption isotherm models

Cadmium adsorption on CMBC was analyzed using various adsorption isotherm models. Data were collected at 298, 308, and 318 K, with Cd^{2+} concentrations ranging from 3 to 350 mg L^{-1}, over a 12-hour shaking period. The data were evaluated using the Langmuir and Freundlich models**.**

The Langmuir model provided a better fit than the Freundlich model, with R^2 values greater than 0.988. This suggests a monolayer lead adsorption mechanism for Cd^{2+} binding. This observation aligns with previous studies of heavy metal ion adsorption ontoamine-functionalized materials.

The Langmuir adsorption capacity for CMBC is 134 mg g^{-1} at 318 K, compared to 48.2 mg g^{-1} for NMBC, despite CMBC having only 68% of NMBC's surface area. This value is also much higher than previously reported biochar capacities for cadmium adsorption.

Table 1. Pseudo-second order parameters for lead adsorption (pH = 5) at (a) 298 K, (b) 308 K, and (c) 318 K for Pb2+ concentrations of 150, 175, and 230 mg L−1, using 2 g CMBC/L

Temp. (K)	Initial conc. (mg L^{-1})	q_e exp. (mg g^{-1})	q_e calc. (mg g^{-1})	k_2 (g m g^{-1} h)	R^2
298	150	63.8	62.5	0.085	0.999
	175	79.6	71.4	0.049	0.991
	230	88.3	83.3	0.072	0.996
308	150	63.6	66.7	0.056	0.998
	175	76.1	83.3	0.048	0.999
	230	91.3	90.9	0.061	0.996
318	150	73.4	76.9	0.084	0.999
	175	79.5	83.3	0.072	0.998
	230	96.1	100	0.100	0.999

Table 2. Langmuir and Freundlich model parameters for Cd2+ adsorption on CMBC

Isotherm parameters		298 K	308 K	318 K
Langmuir	Q^0 (mg g^{-1})	50.5	103	103
	b	0.0791	0.0149	0.0113
	R^2	0.996	0.994	0.988
Freundlich	K_f (mg g^{-1})	13.5	6.58	6.33
	n	3.82	2.09	1.93
	R^2	0.999	0.996	0.994

Adsorption isotherms at 298, 308, and 318 K [pH = 5; adsorbent concentration = 2 g/L; 102 Shaking time = 12 h].

Conclusions

Rice husk biochar modified with chitosan significantly increased the Cd^{2+} adsorption capacity. The chitosan deposition facilitated rapid flow through columns or beds due to the biochar's particle size. Maximum cadmium removal occurred at pH 5 and 318 K, demonstrating pH-dependent and endothermic behavior for Cd^{2+} adsorption. The pseudo-second-order kinetics model provided the best fit with regression coefficients of 0.991 or higher. Sorption was evaluated from 298 to 318 K using the Freundlich and Langmuir isotherm models, with the Langmuir model providing the best fit. A fixed-bed column study for Cd^{2+} indicated a column capacity of 5.8 mg g^{-1}. The Cd^{2+} adsorption mechanism on CMBC biochar was mainly governed by the coordination between chitosan amine groups and Cd^{2+} ions, supported by FT-IR evidence. CMBC shows great potential for removing heavy metal contaminants from aqueous solutions.

References

1. Fernández-González, C., Martínez-Alonso, A., &Tascón, J. M. D. (2019). Adsorption is widely recognized for its energy efficiency and cost-effectiveness in pollutant removal from wastewaterJournal of Hazardous Materials, 378, 1207296.
2. Jin, L., & Bai, R. (2002). Mechanisms of lead adsorption on chitosan/PVA hydrogel beadsLangmuir, 18(25), 9765–97704.
3. Juang, R. S., & Shao, H. J. (2002). A simplified equilibrium model for sorption of heavy metal ions from aqueous solution on chitosanWater Research, 36(12), 2999–30081.
4. Juang, R. S., Wu, F. C., & Tseng, R. L. (2002). Chitosan, known for its effectiveness in heavy metal removal from aqueous solutions, has previously been studied in various formsJournal of Hazardous Materials, 93(2), 233-2488.
5. Liew, R. K., Tan, L. L., & Leo, C. P. (2019). Various conventional and modern technologies can be used to remove hazardous pollutants, particularly heavy metals harmful to human health, from industrial wastewaterJournal of Environmental Management, 232, 858-8693.
6. Ngah, W. S. W., & Hanafiah, M. A. K. M. (2011). Chitosan, known for its effectiveness in heavy metal removal from aqueous solutions, has previously been studied in various formsBioresource Technology, 102(3), 933-9409.

7. Ramola, R. B., Joshi, H. C., & Pant, K. K. (2020). Kinetics of liquid phase batch adsorption experimentsAdsorption, 27, 353–3681.
8. Ronghua, L., Xiaoyan, L., & Xue, D. (2018). Chitosan, known for its effectiveness in heavy metal removal from aqueous solutions, has previously been studied in various formsJournal of Environmental Sciences, 63, 1-1012.
9. Safwat, M. (2018). Thermal treatment is one of the effective methods for removal of heavy metals from wastewaterJournal of Cleaner Production, 185, 723-7314.
10. Tang, W., Zhang, Y., & Zhang, Y. (2019). Biochar (BC) has been investigated for its potential in cost-effective synthesis from various materials for the efficient removal of pollutants from wastewaterBioresource Technology, 272, 372-3797.
11. Tunçsiper, B. (2019). Cleaner and more sustainable development can be achieved by implementing efficient and cost-effective technologies for environmentally friendly industrial wastewater treatmentJournal of Cleaner Production, 185, 723-7311.
12. Wan, Y., Jin, Z., & Xiao, Q. (2010). Chitosan, known for its effectiveness in heavy metal removal from aqueous solutions, has previously been studied in various formsJournal of Hazardous Materials, 177(1-3), 126-13211.
13. Wan Ngah, W. S., Teong, L. C., &Hanafiah, M. A. K. M. (2011). Adsorption of dyes and heavy metal ions by chitosan composites: A reviewCarbohydrate Polymers, 83(4), 1446–14562.
14. Wang, Y., Zhang, Y., Pan, X., & Zhang, X. (2018). Combining chitosan with biochar may result in a novel material with enhanced capacity for lead ion uptake beyond that of biochar aloneEnvironmental Science and Pollution Research, 25(35), 35001-35002
15. Yan, W. L., & Bai, R. (2005). Adsorption of lead and humic acid on chitosan hydrogel beadsWater Research, 39(4), 688–698
16. Zhang, S., Wang, Y., Li, Y., & Li, X. (2018). Adsorption processes are widely recognized for their energy efficiency and cost-effectiveness in pollutant removal from wastewaterEnvironmental Science and Pollution Research, 25(35), 34999-350005.
17. Zhang, S., Wang, Y., Li, Y., & Li, X. (2019). Industrial effluents often contain wastewater with high concentrations of heavy metals, a problem that has been worsening over recent decadesEnvironmental Science and Pollution Research, 26(35), 35911-359122.

18. Zhou, Y., Gao, B., Zimmerman, A. R., Fang, J., Sun, Y., & Cao, X. (2013). Sorption of heavy metals on chitosan-modified biochars and its biological effectsChemical Engineering Journal, 231, 512–5183.
19. Zhou, Y., Gao, B., Zimmerman, A. R., Chen, H., Zhang, M., & Cao, X. (2023). Chitosan, known for its effectiveness in heavy metal removal from aqueous solutions, has previously been studied in various formsBioresource Technology, 132(2), 202-21210.