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The Beneficial Effect of Chitosan-biochar Blend on the Biosorptive Removal of Heavy Metal Copper from Aqueous Solution

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ABSTRACT

The present study investigates the efficacy of a biochar-chitosan blend in biosorptive elimination of copper from an water. Biochar was prepared from corncob waste by pyrolysis at 600°C under a nitrogen atmosphere and blended with a chitosan solution. The prepared chitosan-biochar (CS-BC) blend was characterized using FTIR, XRD, BET, and SEM analyses. Adsorption tests in batches were carried out to evaluate the adsorption capacity of the CS-BC blend for Cu(II) ions, considering several variables, including pH, starting metal concentration, contact time, and adsorbent dose. The optimal pH for Cu(II) adsorption was found to be 5, having the highest sorption of 313.97mg/g. The adsorption capacity increased with increasing adsorbent dosage up to 4 g and contact time up to 480 minutes. Adsorption isotherm studies revealed that the adsorption process was best explained by the Freundlich model indicating multilayer sorption. According to kinetic analyses, the pseudo-second-order adsorption process was followed. Desorption studies using 0.1M HCl demonstrated a high regeneration capacity of the CS-BC blend, with up to 99% recovery of Cu(II) ions. The results suggest that the chitosan-biochar blend is an effective and economically viable adsorbent for extracting copper, a heavy metal, from water-based solutions.

Keywords: Chitosan, Corncob biochar blend, Copper, Isotherm, Kinetics.

INTRODUCTION

Environmental pollution is steadily rising and having a negative effect on all living things, including people. Numerous groundwater resources are already unusable for both people and wildlife due to water contamination. Heavy metals are already widely distributed in the environment as a result of improper agricultural methods, fast industrial development, and increased pollution. The increasing number of transition metals, which have dangerous qualities in rivers has lately grown to be a significant worldwide issue because of the rapid growth in the industrial activities, lifestyle of people, and the usage of chemicals used in many industries[1].

Typically, industrial and residential effluents from mining, tanneries, and metal plating industries discharge heavy metals into water bodies. It is well known that living organisms require copper as a micronutrient. Among other normal physiological functions in plants, it aids in the synthesis of chlorophyll, photosynthesis, and the metabolism of proteins and carbohydrates[2]. It is commonly recognized that Wilson's illness causes copper to build up in the liver. Since elevated copper levels can result in oxidative stress, hepatic copper deposition is both pathogenic and pathognomonic[3].

To combat the toxicity of heavy metals, numerous treatments have been developed. Techniques for physicochemical treatment including surface sorption, 2D membrane removal, precipitation using chemicals, and photodegradation are used to clean up heavy metal-contaminated locations. These techniques offer benefits like flexibility and convenience of use, as well as the ability to release complicated contaminants with less installation and area needed. Traditional heavy metal removal techniques produce hazardous sludge, and they are highly expensive to run[4]. Conversely, adsorption entails moving sorbate ions from a solution phase to a sorbent phase.

Since surface sorption is one of the most popular and efficient technologies, various adsorbents have been created and applied in systems for treating heavy metals[5]. Because biomass adsorbents are widely available, their use has grown significantly in recent years[6]. The most extensively utilized sorbent for removing harmful heavy metals is activated carbon[7]. However, due to its high cost and limited regenerative behavior, its use is limited[8].

The process of heating organic matter at low temperatures and low oxygen content produces biochar, a substance with a high carbon content. Pyrogenic black carbon, or biochar, is produced when biomass, including wood and grass, is pyrolyzed in an environment with little oxygen or nitrogen[9]. Biochar has been proposed as an inexpensive alternative for soil remediation and water treatment adsorbent due to its unique surface characteristics[10]. When utilized as an adsorbent, the porous structure of biochar is comparable to that of activated carbon (AC) which is widely recognized for its ability to effectively decontaminate a range of pollutants from water. Numerous oxygenated active groups, including alcoholic, carboxylic, and carbonyl groups, are present in biochar, which can be effectively employed to collect pollutants in a variety of matrices. Additionally, these groups can combine to produce complexes that reduce the bioavailability and migratory potential of soil-borne heavy metals[11]. The negative effects of heavy metals are effectively being treated with natural products[12].

Chitosan's hydroxyl and free amino sites improve its capacity for crosslinking and chelating. To strengthen the connection between amine functional groups and enhance the adsorption capacity for heavy metals, chitosan is commonly employed as a surface modification. Not much research has been done on the application of chitosan to change the surfaces of biochars to improve their affinity for heavy metals. Chitosan and biochar have recently been effectively mixed by several researchers, offering fresh perspectives on how to address the issues of soil and aqueous solution pollution. The combination may benefit from the high chemical affinity of chitosan and the vast surface area of biochar[13]. The novelty of the current study is that, both chitosan and biochar are inexpensive, readily available, and "green" materials, this combination is non-toxic and do not form secondary pollutants. The benefits of chitosan's strong chemical affinity, porous network, and relatively large surface area of biochar would be combined in chitosan-modified biochars. Corncobs are the waste byproducts after the removal of corn seeds from corn. Hence in the present research work biochar prepared from corn cob was blended with chitosan solution and tested for its efficacy in the extraction of copper, a heavy metal, from water.

MATERIALS AND METHODS

Materials

Chitosan (deacetylation 92%) was procured from India Sea Foods, Cochin, Kerala, India. Corncobs were collected from the local market in Vellore, India. Copper sulphate and glacial acetic acid were obtained from S.D. Fine-Chem Limited in Mumbai. All the chemicals utilised in this study were of analytical quality.

Biochar (BC) preparation

Ten grams of dry corncob were precisely weighed and put through pyrolysis in a muffle furnace with a restricted oxygen feed. For four hours, at 600°C, the pyrolysis setup was operated, with a steady supply of N_2. After that, the prepared biochar was treated with 2% sodium hydroxide and stored for further analysis.

Preparation of chitosan-Biochar Blend

100 mL 7% acetic acid was used to dissolve one gram of chitosan (CS) and agitated for two hours in a magnetic stirrer. The solution was allowed to stand for few hours to remove air bubbles and then mixed with 1g of the biochar of corncob and stirred again for 4 h in a magnetic stirrer. The mixture was allowed to stand and then filled in a petri dish and allowed to air dry. The dried sample for stored in airtight container until further use.

Instrumental analysis

FTIR spectroscopy was performed using Shimadzu's IR Affinity-1S Spectrometer, with 4000 to 400 cm^{-1} wavelength range. The D8 advance Bruker (Germany) diffractometer with Cu $K\alpha$ line as its radiation source, was used to do the Powder XRD investigation. The TESCAN VEGA3 Model at a voltage of 30 kV was used to study surface imaging with Scanning Electron Microscopy (SEM). Using the sorption isotherms with N_2 gas at 77 K and the BET technique, the examination of the surface area of corncob biochar was computed (NOVA-2200 e, Quantachrome NovaWin).

Batch adsorption experiments

Using a batch adsorption technique, the effectiveness of the CS-BC sample in removing Cu(II) from a synthetic solution made with copper sulphate was evaluated. Batch adsorption tests were performed using One hundred millilitres of a 200 mg/L solution of copper and 1 g of dried CS-BC in a 250 mL conical flask. The orbit shaker was used to mechanically shake the flasks at 200 rpm throughout the one-hour contact period.

To change the pH of the initial solution, a 1M HCl or NaOH solution was added. Following pH adjustment, conical flasks containing the CS-BC blend and copper solutions were agitated at 200 rpm in an orbit shaker. After an hour of storage, the final product was made to pass through filter paper. An Atomic Absorption Spectrometer (AAS) (Shimadzu Model: AA-7000F) was used to analyze Cu(II) in the filtered solution. The effects on the biosorption ability of the CS-BC mixture were analyzed with sorbent dose (1-6 mg/L), sorbate pH (range 2-8), residence period (1-6 hours), and copper solution strength (50-1000 mg/L) in order to examine the interaction between Cu(II) and the sample. The following equations are used to compute the kinetic models and adsorption isotherms from the experimental measurements.

The Langmuir isotherm model is used to describe monolayer adsorption outside the adsorbent; at equilibrium, no further sorption occurs on the sorbent. Below is a linear representation of the Langmuir isotherm model:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{1}$$

$$\frac{C_q}{C_{ad}} = C_q C_{max} + 1K_L C_{max} = K_L b \tag{2}$$

Where,

The amount of adsorbed Cu(II) (mg/g) is designated as C_{ad}.

Cq is the Cu(II) ultimate equilibrium concentration (mg/g).

The Langmuir constants-K_L and b (dm^3/g).

C_{max} is the max-adsorption of Cu(II) on 1 g sorbent (mg/g)

The mathematical isotherm model's degree of agreement with experimental data is shown by the R^2 value. This is derived from the Cq Vs. Cq/C_{ad} plot of equilibrium adsorption data.

The Freundlich equation's linear form can be shown by

$$\log q_e = \log K_F + (1/n)\log C_e \quad (3)$$

Where
K_F is the Freundlich constant (mg/g)
The dimensionless coefficient = 1/n.
Ce is the eqm concentration of Cu (II).
q_e is the quantity of Cu(II) absorbed/1g at eqm.
Similarly, in kinetic research,
PFO's equation is computed by

$$\log (q_e - q_t) = \log q_e - k_1\, t/2.303 \quad (4)$$

Where,
At equilibrium (e) and duration (t) in minutes, the amount of Cu(II) adsorbed (mg/g) by the biosorbent is represented by q_e and q_t. PFO rate constant is k1

The PSO linearised variant equation is

$$t/q_t = 1/k_2\, q^2e + t/q_e \quad (5)$$

In this case, t/q_t was plotted against time (t) on the graph. PSO rate constant is k_2.

Nevertheless, an intra-particle diffusion (IPD) model was also employed, utilizing the subsequent formula:

$$q_i = k_i t^{0.5} + C_i \quad (6)$$

C_i is the intercept of the intraparticle diffusion rate, while ki is its rate.

Desorption studies

The process of desorption was carried out using 0.1 M HCl. 200 mL Erlenmeyer flasks containing the desorption agent were loaded with the recovered adsorbent, and the combination was shaken for one to five hours in order to test the treated biosorbent's capacity for regeneration. Cu (II) ions was evaluated by AAS. Percentage desorption calculated by the following formula.

$$\text{Desorption (\%)} = C_d - C_a)/(C_a \times 100) \quad (7)$$

Where the amounts of copper desorbed and adsorbed are denoted by Cd and Ca respectively.

RESULTS AND DISCUSSION

The CS-BC prepared was subjected to different analytical techniques and the results are presented below.

FTIR Studies

FTIR studies indicate the various functional groups present in different samples. Fig. 1 and 2 represent the FTIR spectra of pure chitosan and CS-BC blend.

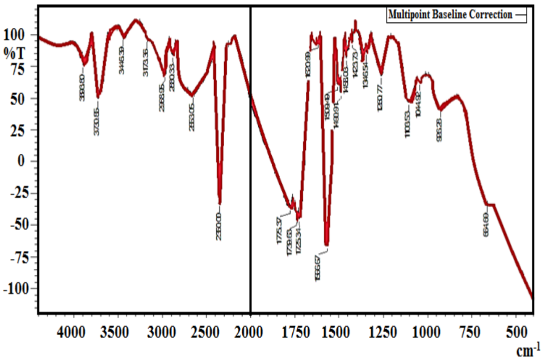


Fig. 1. FTIR spectrum of pure chitosan

In Fig. 1 the approximate peaks at around 3900 to 3800 cm^{-1} are due to -NH and -OH groups stretching vibrations[14]. The band 3400 cm^{-1} is due to the formation of hydrogen bonds. The peak at 2968 cm^{-1} was proven by aliphatic C-H and O-H stretching, which suggested a chitosan structure. Chitosan showed peaks at 1725 cm^{-1} suggesting -C=O group. The peak at around 1100 cm^{-1} is due to the availability of -C-O-C- linkage of pyranose ring structures of chitosan[15].

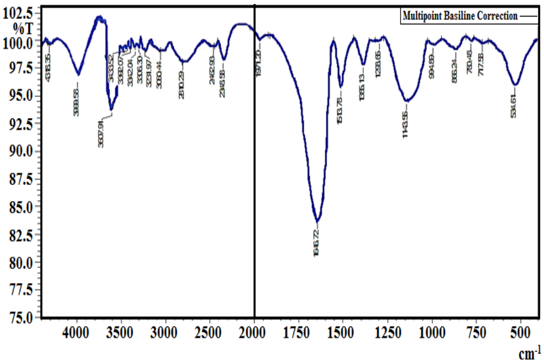


Fig. 2. FTIR spectrum of CS-BC blend

Figure 2 represents the FTIR analysis of the freshly made CS-BC mixture. Peaks around 3900 cm^{-1}, and 3400 cm^{-1} are that of -OH and -NH stretching, and hydrogen bonding which are shifted compared to pure chitosan. A sharp and strong peak at around 1660 cm^{-1} represents the -C=O groups of carbonyl groups of amide and acid of both chitosan and biochar. Thus, it is confirmed that the CS-BC blend has been effectively formed.

XRD studies

X-ray diffraction studies confirm the samples' crystalline and amorphous nature and the particle size.

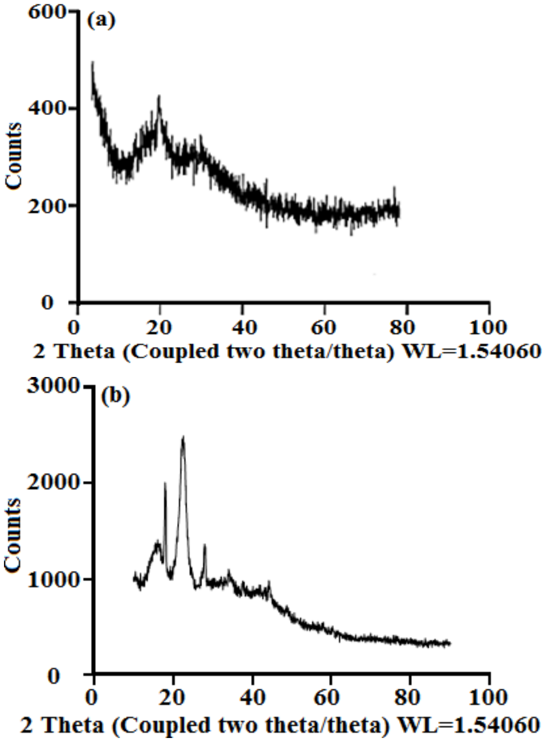


Fig. 3. X-Ray diffractogram of (a) chitosan, (b) CS-BC blend

Figures 3a and 3b represent the X-ray diffractograms of pure chitosan and CS-BC blend, respectively. Peaks at 20° and 20° confirm the partially crystalline structure of chitosan. When blending with corncob biochar, new peaks are observed at 22°, 28°, and 30°, in addition to 10° and 20°. The diffractogram shows very broad peaks, showing the amorphous nature of the blend, which is very suitable for adsorption.

BET Analysis

When evaluating a material for adsorption applications, the surface area of the material and also the pore volume are significant. N_2 sorption isotherm at 25°C was carried out for plain chitosan and CS-BC blend by BET method. Chitosan Surface area 21.20 m^{2}g^{-1} and that of CS-BC blend was 98.4 m^{2}g^{-1}. The CS-BC blend's large surface area caused the size of the pore to decrease from larger to smaller (34.5 to 17.20 nm). When compared to pure chitosan, the pore volume rose from 1.022 cc/g to 3.12 cc/g, indicating that the chitosan-biochar blend had good surface characteristics[16]. This makes it evident that larger sorption effectiveness is due to the higher surface area and smaller pore size. Therefore, this CS-BC blend is a suitable adsorbent for copper heavy metal removal.

SEM analysis

The SEM micrograph of the CS-BC blend is shown in Figure 4.

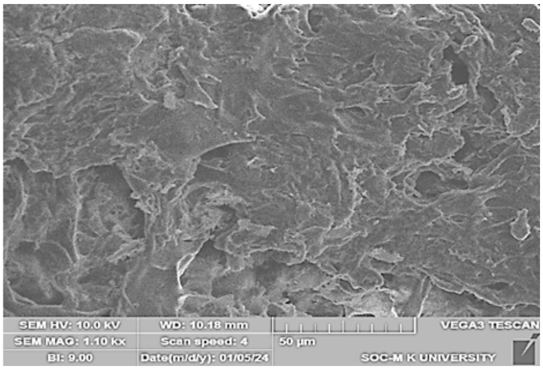


Fig. 4. SEM micrograph of CS-BC blend

The SEM image showed a very rough surface morphology with lots of fissures and holes. The rough surface proves that the surface is suitable for adsorption as mentioned by Wan *et al.,*[17].

Adsorption studies

The adsorption studies were carried out using the chitosan-modified biochar in the synthetic stock solution of copper chloride. The operating parameters such as solution's starting pH, the starting copper strength, contact duration, and the weight of the adsorbent.

Effect of pH

The highly significant parameter is considered the solution pH that influence the chemical reactions in wastewater. As the medium's pH varies, so do the adsorbent's and adsorbate's chemical characteristics. This is due to the fact that the degree of ionization of particular pollutants varies along with changes in pH. Therefore, the starting pH of metal solutions was adjusted from 3 and 8 to find pH's influence in the Cu(II) adsorption by chitosan-modified biochar.

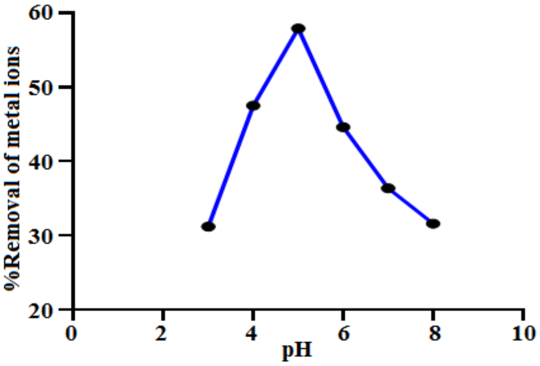


Fig. 5. Influence of pH on the sorption of copper on the chitosan-modified biochar

Figure 5 shows the impact of pH on heavy metal copper adsorption on the prepared chitosan-modified biochar. At the starting pH 2, the adsorption was only 31.2%. As the pH increased there is a rise in the adsorption percentage reaching a maximum of 57.9% at pH 5. The adsorption of copper then declined as the medium's pH was raised to 8. This demonstrated that the ideal pH for copper adsorption on the produced sorbent is 5. Hence pH 5 was fixed for the other experiments. The low adsorption rate at pH 3 may be due to the influence of the H$^+$ ions on the sorption of copper ions. Additionally, at pH 5, there are fewer protons, which reduces the opposition of the ions in the solution brought on by the acid's breakdown and increases the amount of copper adsorbed[18]. Therefore, the biochar-modified chitosan's amino groups get protonated in acidic conditions, preventing copper adsorption, which decreases as pH rises. After the optimum pH, the copper tends to slowly precipitate and thus the adsorption is reduced[19].

Effect of Adsorbent Dose

One factor that significantly influences sorption efficiency is the sorbent's dosage. The dosage of the adsorbent was raised from 1 g to 7 g in the current study and the results are presented in Figure 6.

The adsorbent percentage rose sharply at first, as seen in the above Fig. 6, and then decreased as the dosage was raised after 4 grams. Because a larger sorbent surface means more adsorption sites, an increase in dosage typically increases the mass of the adsorbed metal[20]. Low binding efficiency is typically the result of inadequate metal availability in the solution to cover the sorbent's accessible active sites at high adsorbent dosages[21].

Effect of Contact Time

In wastewater treatment by adsorption, contact time is important. The effectiveness of the adsorbent is indicated by the rapid uptake of contaminants and the rapid achievement of equilibrium.

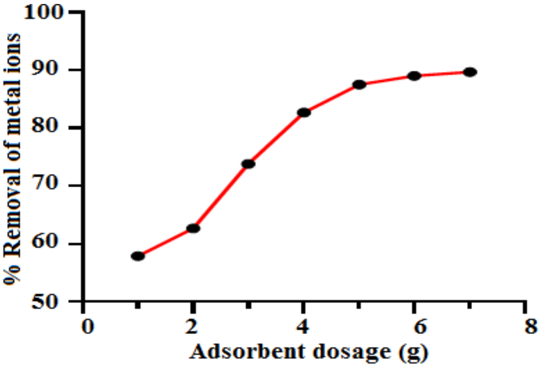


Fig. 6. Effect of dose of CS-BC blend on the adsorption of copper

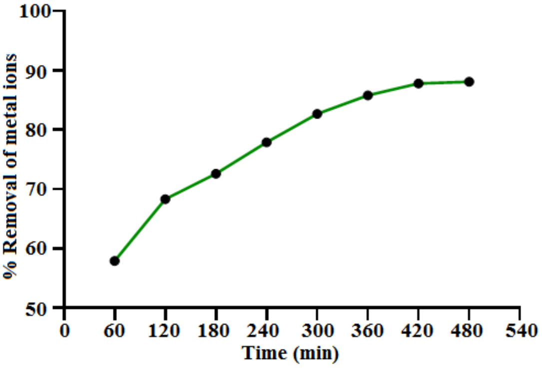
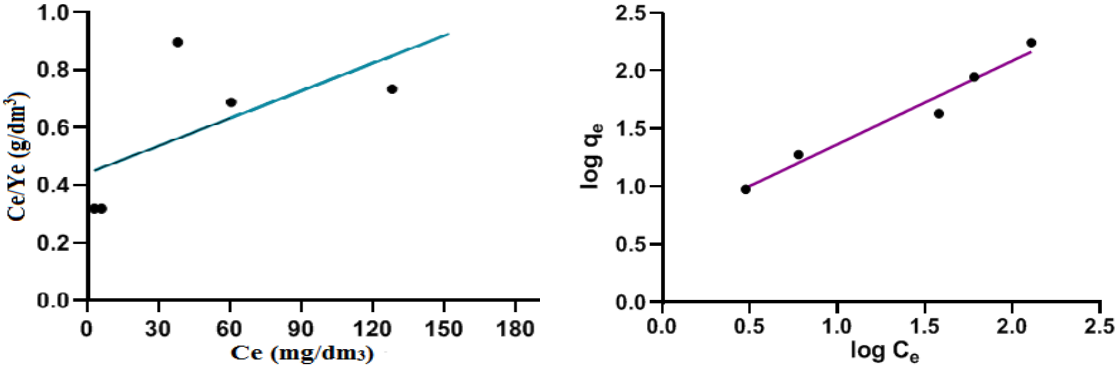


Fig. 7. Influence of time of contact on the adsorption of copper on chitosan-modified biochar

During the first 120 min of the process (Fig. 7), the adsorption %increased quickly; after that, it increased moderately until the end of 480 minutes. Therefore, in practical adsorbent applications, the time factor is an essential component[22].

Adsorption Isotherms

A specific amount of adsorbate can only be adsorbed by a given dosage of adsorbent. In adsorption operations, the removal efficiency of the adsorbent is greatly influenced by the starting concentration of the adsorbate solution. In this study, the sorption of Cu(II) by chitosan-BC blend at several initial strengths of copper solution ranging from 50 to 1000 mg/L was carried out.



Langmuir isotherm plot for Cu adsorption

Freundlich isotherm plot for Cu adsorption

Fig. 8. Adsorption Isotherm plots of copper adsorption on CS-BC blend

Table 1: The adsorption isotherm constants of copper adsorption on CS-BC blend

Metal ions	Langmuir constants				Freundlich constants		
	K_L (dm^3/g)	b	C_{max}	R^2	K_F	n	R^2
Cu(II)	2.26603	0.00721	313.97	0.3909	4.3642	1.3835	0.9954

When the sorption results of copper on the CS-BC blend were fitted in both the Langmuir and Freundlich isotherm equations, the adsorption process was found to follow Freundlich isotherm, proving that the sorption process followed multilayer adsorption and also physisorption than chemisorption. Hence the results confirm that physical interactions such as Vander Waals forces, and hydrogen bonding dominated electrostatic operations and π-π interactions[23].

Adsorption kinetics

By measuring the residual concentration in the aqueous phase at different intervals until an equilibrium value was attained, the sorption rate of copper ions onto the CS-BC blend was determined.

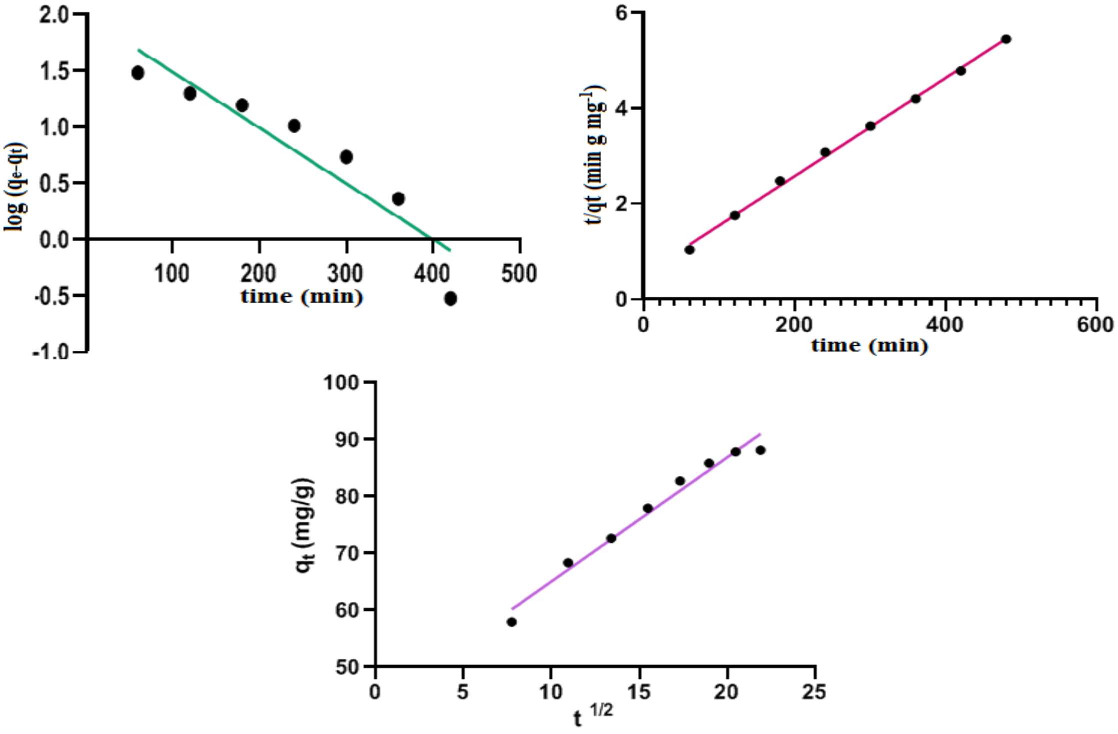


Fig. 9. Kinetic plots of copper sorption on CS-BC blend

Table 2: Kinetic parameters of sorption of copper on CS-BC blend

Metal ions	PFO kinetic model			PSO kinetic model			IPD model		
	q_e(mg/g)	k_1(min^{-1})	R^2	q_e(mg/g)	k^2(g mg^{-1}min^{-1})	R^2	K_{id}	I	R^2
Cu(II)	96.161	-0.0114275	0.8705	97.4659	0.000198356	0.9978	2.179	43.24	0.9753

The kinetic studies results are presented in Table 2 and Figure 9.

The results confirm that the adsorption of copper on CS-BC blend followed PSO kinetics as evidenced by the higher R^2 values (0.9978 for PSO model). The high R^2 value indicated that the adsorption was predominantly controlled by chemical adsorption[24].

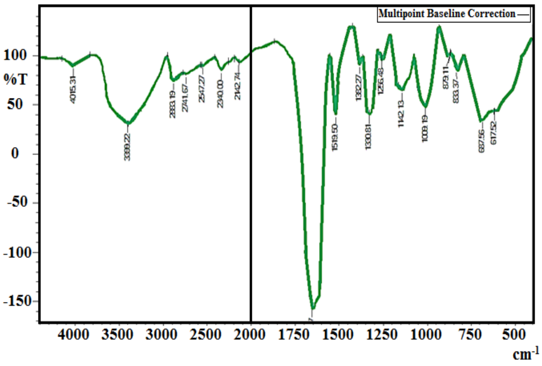


Fig. 10. FTIR spectrum of CS-BC blend after copper adsorption

Figure 10 shows the FTIR spectrum of the CS-BC blend after copper ions got adsorbed. The peaks such as the ones at 3400 cm^{-1}, 1600 cm^{-1}, and 1100 cm^{-1} to lower wave numbers suggest the influence of H bonds and C=O moieties in the adsorption process. Additional broad peaks around 600 cm^{-1} also indicate the availability of inorganic copper ions in the adsorbed sample.

Desorption studies

Desorption studies are crucial for examining the potential for both adsorbent regeneration for later use and the recovery of metals adsorbed on the adsorbent surface. Here the copper metal adsorbed chitosan-modified biochar adsorbent was subjected to desorption studies using 0.1M HCl. The desorption process was undertaken with HCl and the desorption efficacy was analyzed for every hour of shaking for consecutive 5 h the same process was repeated for three cycles and the desorption results are presented in Figure 11.

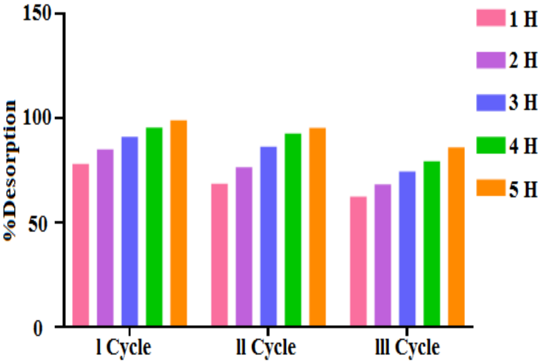


Fig. 11. Desorption studies of copper from CS-BC blend

The results indicate that the recovery of copper increased from 1 to 5 h to the extent of around 99%. The recovery slowly decreased on the third cycle which still was 86%. The chosen desorbing agent, 0.1M HCl is found to be very suitable and the adsorbent has a very high regeneration capacity proving the economic viability of the sorbent. Similar results were reported by many researchers such as Chauhan and Sankararamakrishnan[25], who studied the use of EDTA and HCl to desorb Pb(II) ions adsorbed on chitosan functionalized with xanthate, with a 48% recovery rate.

CONCLUSION

Thus, in the present research, the corncob biochar's structure was altered using a chitosan solution and the prepared blend showed effective linking of both the materials by both chemical and many physical interactions. The CS-BC blend was tested for its suitability for the sorption of copper ions by batch sorption work. The results indicated that the CS-BC was an effective adsorbent for removing copper ions from the solution with promising regeneration efficacy. The adsorbent can be further tested for the removal of multimetal solutions and also real-time effluents.

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Conflict of Interest

All the authors declare no conflict of interest.

REFERENCES

1. Qu, L.; Huang, H.; Xia, F.; Liu, Y.; Dahlgren, R. A.; Zhang, M.; Mei, K., *Environmental Pollution*., **2018**, *237*, 639-649.
2. Mitra, S.; Chakraborty, A. J.; Tareq, A. M.; Emran, T. B.; Nainu, F.; Khusro, A.; ... Simal-Gandara, J., *Journal of King Saud University-Science*., **2022**, *34*(3), 101865.
3. Immergluck, J.; Anilkumar, A. C. **2023**, Wilson Disease. StatPearls.
4. Sodhi, K. K.; Mishra, L. C.; Singh, C. K.; Kumar, M., *Current Research in Microbial Sciences*., **2022**, *3*, 100166.
5. Ifthikar, J.; Wang, J.; Wang, Q.; Wang, T.; Wang, H.; Khan, A.; Chen, Z., *Bioresource Technology*., **2017**, *238*, 399-406.
6. Gao, N.; Du, W.; Zhang, M.; Ling, G.; Zhang, P., *International Journal of Biological Macromolecules*., **2022**, *209*, 31-49.
7. Kaveeshwar A. R.; Kumar P. S.; Revellame E. D.; Gang D. D.; Zappi M. E.; Subramaniam R., *J. Cleaner Prod*., **2018**, *193*, 113.
8. Vardhan K. H.; Kumar P. S.; Panda R. C., *J. Mol. Liq*., **2019**, *290*, 111197.
9. Hussain, A.; Maitra, J.; Khan, K. A., *Applied Water Science*., **2017**, *7*(8), 4525-4537.
10. Amalina, F.; Abd Razak, A. S.; Zularisam, A.; Aziz, M.; Krishnan, S.; Nasrullah, M., *Physics and Chemistry of the Earth*, Parts A/B/C., **2023**, *2022*, 103508.
11. Lu, Y.; Cheng, J.; Wang, J.; Zhang, F.; Tian, Y.; Liu, C.; Cao, L.; Zhou, Y., *Processes*., **2022**, *10*(8), 1627.
12. Tchounwou, P. B.; Yedjou, C. G.; Patlolla, A. K.; Sutton, D. J. Molecular, clinical and environmental toxicology: 2012, 3,133-164. Xiao, F.; Cheng, J.; Cao, W. Yang, C.; Chen, J.; Luo, Z., *Journal of Colloid and Interface Science*., **2019**, *540*, 579-584.
13. Song, C. L.; Vardaki, M. Z.; Goldin, R. D.; Kazarian, S. G., *Analytical and Bioanalytical Chemistry*., **2019**, *411*, 6969-6981.
14. Sharma, R.; Dhamodharan, R., *Journal of Polymer Research*., **2024**, *31*(2), 46.
15. Rekha, A.; Vijayalakshmi, K.; Alswieleh, A.; Sudha, P. N.; Rani, J.; Vidhya, A., *Biomass Conversion and Biorefinery*., **2024**, 1-14.
16. Wan, M. W.; Wang, C. C.; Chen, C. M., *International Journal of Environmental Science and Development*., **2013**, *4*(5), 545.
17. Nie, X.; Li, G.; Wang, Y.; Luo, Y.; Song, L.; Yang, S.; Wan, Q., *Journal of Hazardous Materials*., **2022**, *424*, 127504.
18. Zhang, M.; Liu, Y.; Yin, Z. Feng, D.; Lv, H., *Sci Rep.,* **2023**, *13*(1), 20937.
19. Esposito, A.; Pagnanelli, F.; Lodi, A.; Solisio, C.; Veglio, F., *Hydrometallurgy*., **2001**, *60*(2), 129-141.
20. Fomina, M.; Gadd, G. M., *Bioresource Technology*., **2014**, *160*, 3-14.
21. Azizkhani, S.; Mahmoudi, E.; Emami, A.; Hussain, S. A.; Mohammad, A. W., *Science and Technology Indonesia*., **2018**, *3*(4), 141-146.
22. Wang, Q.; Zhang, Y.; Li, F.; Liu, W.; Ma, L., *Journal of Chemical Technology & Biotechnology*., **2024**.
23. Qian, L. W.; Yang, M. X.; Zhang, S. F.; Hou, C.; Song, W. Q.; Yang, J. F.; Tang, R. H., *Cellulose*., **2018**, *25*, 2021-2036.
24. Chauhan, D.; Sankararamakrishnan, N., *Bioresour. Technol*., **2008**, *99*, 9021-9024.