



Adsorption of Copper Ions in Aqueous Solution by Montmorillonite-Biochar Composite

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ABSTRACT

A composite adsorbent was prepared by montmorillonite and biochar from peanut shell. The adsorption experiment of the Cu^{2+} ions from aqueous solution by the montmorillonite-biochar composite was carried out in detail. The effects of initial concentration of Cu^{2+} ions in aqueous solution and contact time on adsorption efficiency were studied. FTIR spectroscopy, SEM and TEM analyses, standard N_2 adsorption-desorption techniques, EDS and XPS were used to evaluate the physico-chemical, textural and crystalline properties of the montmorillonite-biochar composite. Results showed that the montmorillonite-biochar composite was mesoporous material. The surface of montmorillonite-biochar composite was rough with irregular layer structure. According to the experimental data, pseudo first order kinetics model and pseudo second order kinetics model were applied. The adsorption process fits well with the pseudo second order kinetics model. The predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent. Adsorption data were correlated well by Freundlich isotherm models and adsorption process was chemical. It is concluded that the montmorillonite-biochar composite can be used as an effective adsorbent for the removal of Cu^{2+} ions from aqueous solutions.

INTRODUCTION

Economic imperatives of productivity and profitability subjected to mining companies and mineral processing industries into products of higher added value significantly reflect the level of pollution by heavy metals. The heavy metals, apart from being hazardous for living organisms when exceeding the specific limits, have accumulating characteristics in nature as they cannot be biodegraded. Removal of heavy metal ions from industrial effluents, drinking water and municipal wastewaters is a matter of serious concern due to their toxicity to various forms of life (Moï se et al. 2017).

Among the variety of heavy metal pollutants of water, copper ions appear and, as other heavy metals, are not degradable and accumulate in the living beings. Moreover, copper is one of the essential elements to human body in trace quantities, but elevated levels of copper may cause various health problems in liver, kidney and the central nervous system (Dalida et al. 2011, Cho et al. 2012). It is necessary to refine wastewaters containing copper ions before their release in the environment.

The heavy metals, having hazardous effects on health, can be treated from wastewater by using various physico-chemical methods (Sevil & Alyüz 2007). Adsorption, ion exchange, chemical settling and reverse osmosis are

the most frequently preferred methods. Among them, adsorption receives considerable interest with the high efficiency in heavy metal removal. Although there are many adsorbents used in adsorption methods, activated carbon is the most common one used in wastewater treatment all over the world (Veli & Öztürk 2005). However, its high cost causes restrictions in use (Babel & Kurniawan 2003). For this reason, many studies have been carried out in order to find out effective and low-cost adsorbents. Different adsorbents are used in copper removal such as chitosan (McKay et al. 1989), eutrophic and oligotrophic marsh peat and agricultural wastes like wheat straw and cacao shell (Chen et al. 1990, Saeed et al. 2005, Qiu & Huang 2017).

The major limitation of these common methods is the production of large amount of sludge, which leads to the disposal problem, requires large capital for electricity, less number of metal ions can be removed and in some methods chemicals used are expensive. Adsorption is more advantageous in terms of its simplicity, fastness, high efficiency, regeneration, low concentrations removal, economic and environmental friendliness. These make it a better option than the common methods and create a research interest in developing low-cost adsorbents.

Copper has been removed by various adsorbents such as agricultural and industrial waste, chitosan, natural zeolite,

natural material, modified biopolymers and marine algae (Meunier et al. 2003, Sarma et al. 2015, Hannatu et al. 2017).

Natural clay is evaluated as an appropriate adsorbent due to its low cost and high removal efficiency. Its sorption capabilities come from high surface area and exchange capacities. The negative charge on the structure of clay minerals gives the capability to attract metal ions. In recent years, special attention has been focused on the use of natural resources as alternatives to conventional adsorbents. Among the alternative adsorbents, clay stands out because of its abundance and low cost compared to other adsorbents such as activated charcoal, zeolites and synthetic ion exchange resins. Moreover, clays are materials that can act as Lewis acids and offer a large ion exchange capacity in a layered structure that presents chemical and physical stability and a high specific surface area (Kumar et al. 2015, Zacaroni et al. 2015).

Based on the above considerations, the main objective of this work was to evaluate copper ions in aqueous solution adsorption onto montmorillonite-biochar composite through kinetic and equilibrium studies. In addition, the characterization of the montmorillonite-biochar composite was discussed in detail. The effects of initial concentration of Cu^{2+} ions in aqueous solution and contact time on adsorption efficiency were studied along with the adsorption equilibrium and adsorption kinetics.

MATERIALS AND METHODS

Materials

The montmorillonite was purchased from Shanghai Chemical Co. Ltd. in China and crushed to obtain clay with a diameter less than 50 μm .

The peanut shell was obtained from a local farm in Zhejiang province. It was dried for 24 h at 383 K in a heating oven and milled to obtain powders between 1 mm and 2 mm prior to use. The dried peanut shell was put into a muffle furnace at 873 K for 3 h. They were added into the 250 mL of flask containing 7 mL of distilled water and put into a thermostat water bath and agitated for 2 h. Then, they were dried for 9 h at 383 K in a heating oven and later washed with distilled water into pH value ranging from 7 to 9. They were dried for 5 h at 383 K in a heating oven again, ground and sifted into 100 meshes to finally obtain the experimental biochar.

The 10 wt % montmorillonite suspension was prepared by dispersing its powder in distilled water and stirring for 24 h. Then, the biochar from peanut shell was slowly added to the montmorillonite suspension. During the mixing process, the weight ratio of montmorillonite to biochar was kept 1:1. The reaction mixture was stirred for 2 h, separat-

ed by centrifugation and washed three times with distilled water. Then, they were dried at 383 K for 12 h to obtain the montmorillonite-biochar composite for the adsorption experiment.

All the chemicals in the study were of analytical grade and used without further purification. The wastewater of Cu^{2+} ions in aqueous solution was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Experimental Methods

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing the montmorillonite-biochar composite and 100 mL of Cu^{2+} ion solutions with various initial concentrations. The initial pH was adjusted with 1 mol/L HCl or 1 mol/L NaOH. The flasks were placed in a shaker at a constant temperature and 200 rpm. The samples were filtered and analysed.

Analytical Methods

The textural characteristics of the montmorillonite-biochar composite including surface area, pore volume and pore size distribution were determined using standard N_2 adsorption-desorption techniques. Surface morphology of the samples was determined by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray fluorescence spectroscopy (EDS, Oxford Instruments Link ISIS) for analysing surface elements and transmission electron microscopy (TEM). The montmorillonite-biochar composite was also characterized by FTIR spectroscopy to identify the type of chemical bonds in the molecules present. The samples were also characterized by XPS (Thermo ESCALAB 250 electron spectrometer) using a multidetection analyser with Mg K_α radiation (1253.6 eV) under 10^{-9} Torr pressure. All the peaks were referenced with the C 1s line at 284.4 eV and fitted in terms of the XPSPEAK41 mode. The concentration of Cu^{2+} ions was obtained by atomic absorption spectrophotometry (AAS).

The amount of adsorbed Cu^{2+} ion q_t (mg/g) at different times, was calculated as follows:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad \dots(1)$$

Where, C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Cu^{2+} ions respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical Analyses of Data

All experiments were repeated in duplicate and the results were represented as the mean with standard deviation (SD). The value of the SD was calculated by Excel Software. All

error estimates given in the text and error bars in figures are standard deviation of means (mean \pm SD). All statistical significances were noted at $\alpha = 0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

Characterization of Montmorillonite-Biochar Composites

The textural characteristics of the montmorillonite-biochar composite including surface area, pore volume, and pore size distribution were determined using standard N_2 adsorption-desorption techniques. The surface area, pore volume and average pore size of montmorillonite-biochar composites are 6.1784 m^2/g , 0.01971 cm^3/g and 12.76 nm respectively. The International Union of Pure and Applied Chemistry-IUPAC (1985) classified the diameter of pores

with width greater than 50 nm as macropores, pores from 2 to 50 nm width as mesopores, and those with diameter of less than 2 nm as micropores. Therefore, it tends to be more suitable for mesoporous materials. The characterization of montmorillonite-biochar composites can contribute to metal adsorption (Chen et al. 2008).

The micrographs are shown in Fig.1. A heterogeneous grain size was observed in the montmorillonite-biochar composite. The surface of montmorillonite-biochar composite is rough with irregular layer structure.

The montmorillonite-biochar composite was also characterized by EDS. Results of EDS analyses are shown in Fig. 2 and Table 1. It shows that C, O and Si are the major constituents in montmorillonite-biochar composite while Al, Mg, Ca, K and Fe are the minor substitute element in this layer silicate mineral. So, the montmorillonite-biochar composite possesses a negatively charged surface which

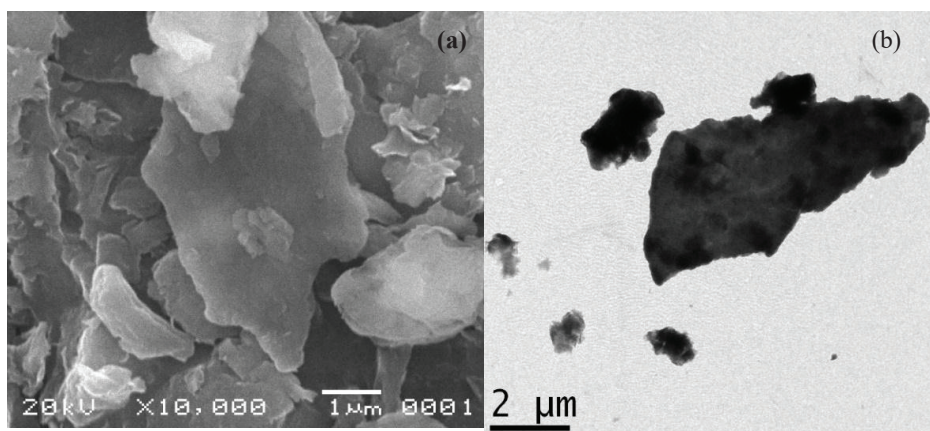


Fig. 1: SEM (a) and TEM (b) of the montmorillonite-biochar composite.

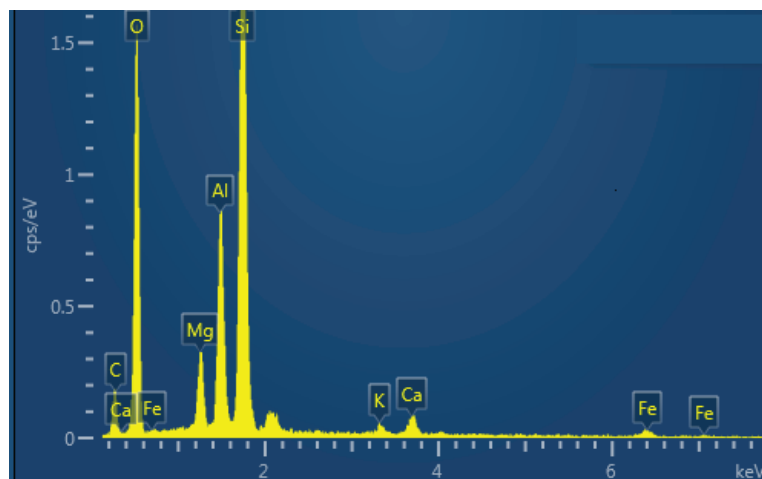


Fig. 2: EDS spectra of the montmorillonite-biochar composite.

Table 1: Chemical composition from EDS analysis.

Element	C	O	Mg	Al	Si	K	Ca	Fe
Components (% wt)	21.40	54.96	2.34	5.51	14.04	0.29	0.79	0.67

is favourable for cationic ion adsorption (Bertagnolli et al. 2011).

Fig. 3 presents the FTIR adsorption bands of the montmorillonite-biochar composite. As shown in Fig. 3, the bands at 3417 cm^{-1} , 1837 cm^{-1} and 1511 cm^{-1} could be attributed to the stretching vibration of $-OH$, $-C=O$ and $-C=C-$ groups, respectively. The peaks at 1400 cm^{-1} and 1034 cm^{-1} were ascribed to $-OH$ and $-C-O$ groups. The bands at 839 cm^{-1} , 796 cm^{-1} , 520 cm^{-1} and 488 cm^{-1} are due to $C-O$ and $-O-$ vibrations (Lin & Juang 2002, Weng et al. 2007).

The montmorillonite-biochar composite was also characterized by XPS (Thermo ESCALAB 250 electron spectrometer) using a multidetection analyser with Mg K_{α} radiation (1253.6 eV) under 10^{-9} Torr pressure. The results are shown in Fig. 4.

As shown in Fig. 4, the C 1s XPS spectra of montmorillonite-biochar composites can be deconvoluted into three bands at 295.2 , 292.3 and 284.4 eV , which were assigned to $C/N-O$, $C-O$ and $C-$, respectively.

Adsorption Studies

Effect of contact time: In order to study the effect of contact time on the adsorption of Cu^{2+} ions by the montmo-

illonite-biochar composite, the samples were determined at 5, 10, 15, 20, 30, 40, 50, 60, 120, 180 and 240 min. The experimental results are shown in Fig. 5. At first stage, the adsorption capacity of Cu^{2+} ions increased with contact time quickly. After 30 min, there is no considerable change in Cu^{2+} ions removal. The optimum time for copper removal was 40 min. As a result of the experimental studies, it is seen that high efficiency for copper adsorption can be obtained at short time periods.

Effect of initial concentration: As presented in Fig. 6, the adsorption capacity for Cu^{2+} ions in aqueous solution increases with increase in the initial concentration of Cu^{2+} ions.

It is clear that the removal of heavy metal depends on the initial concentration. This is due to the fact that the initial Cu^{2+} ions concentration provided the necessary driving force to overcome the resistance to the mass transfer of Cu^{2+} ions between the solution and adsorbent (Langmuir 1918).

Adsorption Kinetics

In order to investigate the adsorption kinetics and mechanism, two kinetic models were used. They are the pseudo

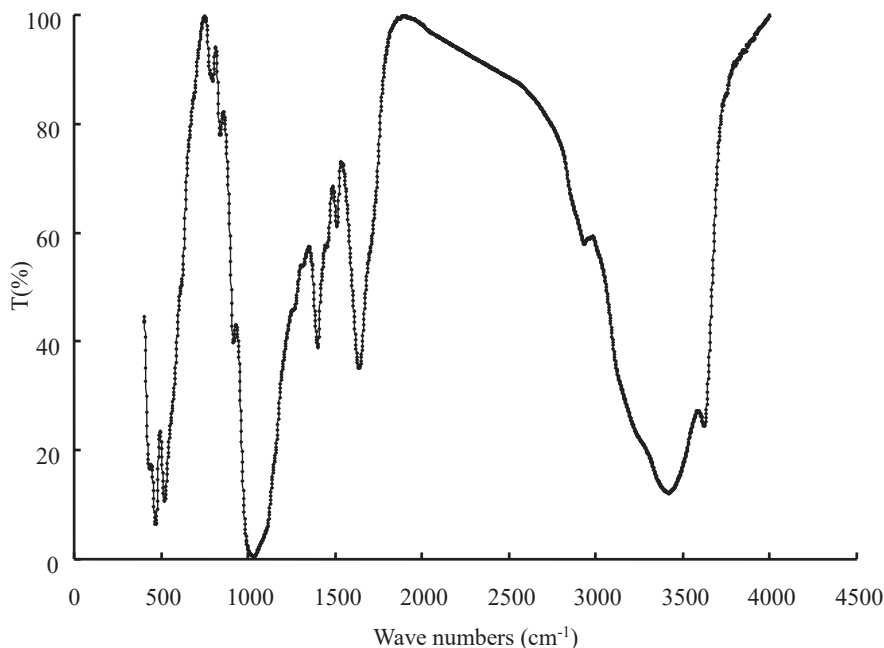


Fig. 3: FTIR spectra of the montmorillonite-biochar composite.

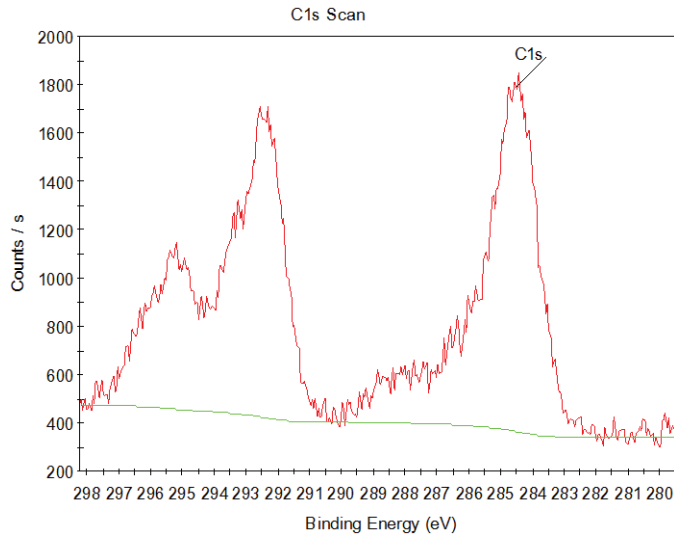


Fig. 4: XPS spectra of the montmorillonite-biochar composite.

first order kinetic model and pseudo second order kinetic model.

Pseudo first order kinetics model is generally expressed as follows (Ho 2004):

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad \dots(2)$$

Where k_1 (min^{-1}) is the adsorption rate constant for the first order adsorption, q_t is the amount of copper ion adsorbed at time t (mg/g) and q_e is the amount of copper ion adsorbed at saturation (mg/g).

The integration of the Eq. (2) gives the following expression:

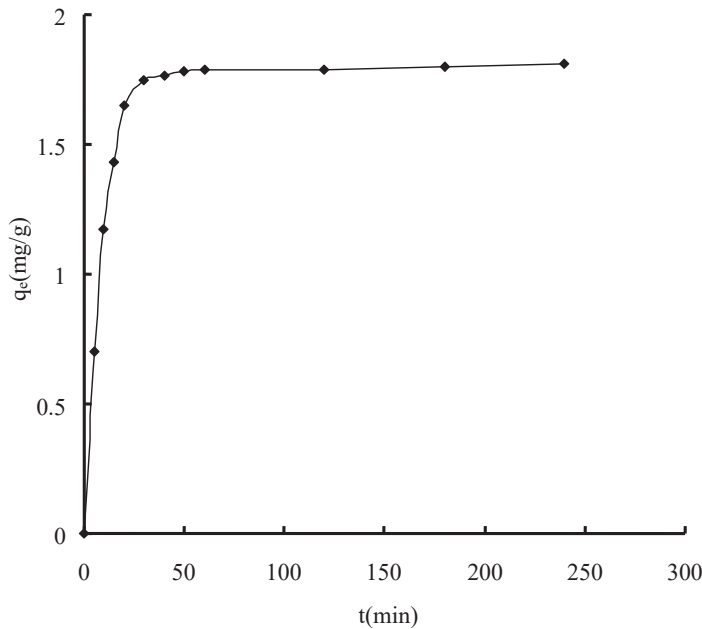


Fig. 5: Effect of contact time on the removal of copper ions by the montmorillonite-biochar composite. Initial concentration of Cu²⁺ ions 40 mg/L, dosage of the montmorillonite-biochar composite 4 g/L, pH 4 and temperature 303 K.

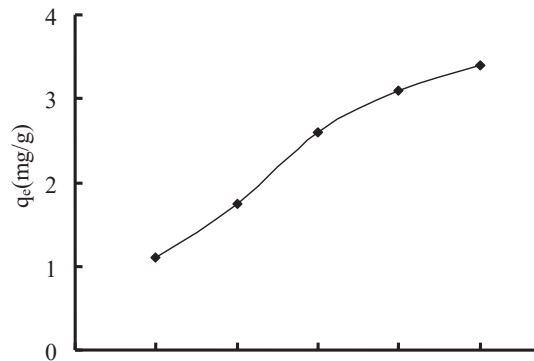


Fig. 6: Effect of initial concentration of Cu^{2+} ions on the removal of Cu^{2+} ions by the montmorillonite-biochar composite. Dosage of the montmorillonite-biochar composite 4 g/L, pH 4, contact time 180 min and temperature 303 K.

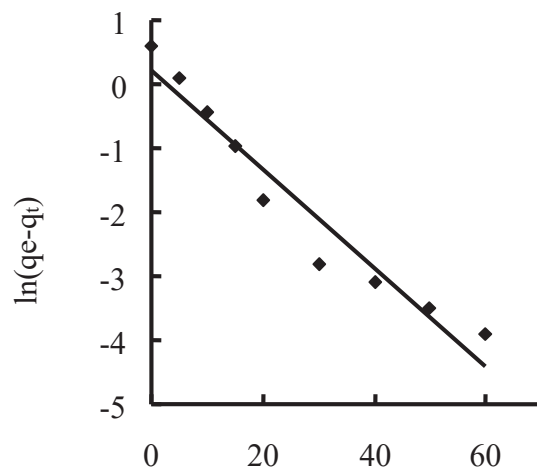


Fig. 7: Pseudo first order kinetics of Cu^{2+} ions in aqueous solution adsorption by the montmorillonite-biochar composite.

$$\ln(q_e - q_t) = -k_1 t + C_1 \quad \dots(3)$$

Where, C_1 is the integration constant for first order reaction kinetic.

If it is supposed that $q = 0$ at $t = 0$, then:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \dots(4)$$

Pseudo second order kinetics model is generally expressed as follows (Ho & McKay 1998):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad \dots(5)$$

Where k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the second order reaction constant. The integration of the Eq. (5) gives the following expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(6)$$

According to experimental data, the rate constants k_1 , k_2 and q_e were calculated from the slopes and intercepts of the

linear plot of $\ln(q_e - q_t)$ or $\frac{t}{q_t}$ respectively (Fig.7 and Fig.

8). The values of k_1 , k_2 and q_e are listed in Table 2.

Table 2: Parameter values and correlation coefficients of pseudo first order kinetics model and pseudo second order kinetics model for the adsorption of Cu^{2+} ion onto the montmorillonite-biochar composite.

Pseudo first order kinetic model			Pseudo second order kinetic model		
k_1 (min)	q_e (mg/g)	R^2	k_2 (mg/g min)	q_e (mg/g)	R^2
0.077	1.23	0.94	0.071	2.04	0.99

From Table 2, it can be shown that the adsorption process fits well with the pseudo second order kinetics model according to the value of R^2 . It implies that the predominant

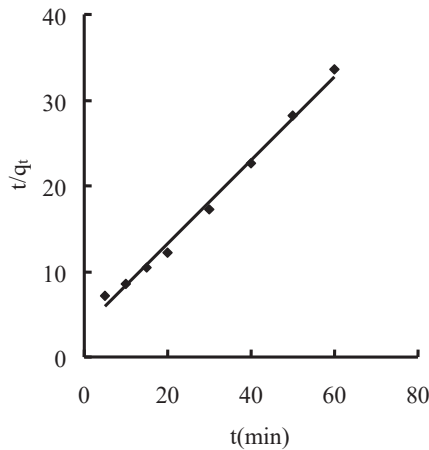


Fig. 8: Pseudo second order kinetics of Cu²⁺ ions in aqueous solution adsorption by the montmorillonite-biochar composite.

process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent (Vanessa et al. 2015).

Adsorption Isotherms

For solid-liquid system, adsorption isotherm is important in description of adsorption behaviour. To research on the mechanistic parameters associated with Cd²⁺ ion adsorption, the results obtained by the adsorption experiments were analysed by Freundlich model (Freundlich 1918) and Langmuir model (Langmuir 1918).

The Langmuir isotherm equation is represented by the following Eq. (7):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \dots(7)$$

The integration of the Eq.(7) gives the following expression:

$$\frac{C_e}{q_e} = \frac{1}{K_L} q_m + \frac{C_e}{q_m} \quad \dots(8)$$

Where, C_e is the equilibrium concentration of Cu²⁺ ions (mg/L), q_e is the amount of Cu²⁺ ion adsorbed (mg/g), q_m is the maximum adsorption capacity of Cu²⁺ ion (mg/g), and K_L is the Langmuir adsorption equilibrium constant (L/mg) related to the affinity of the binding sites.

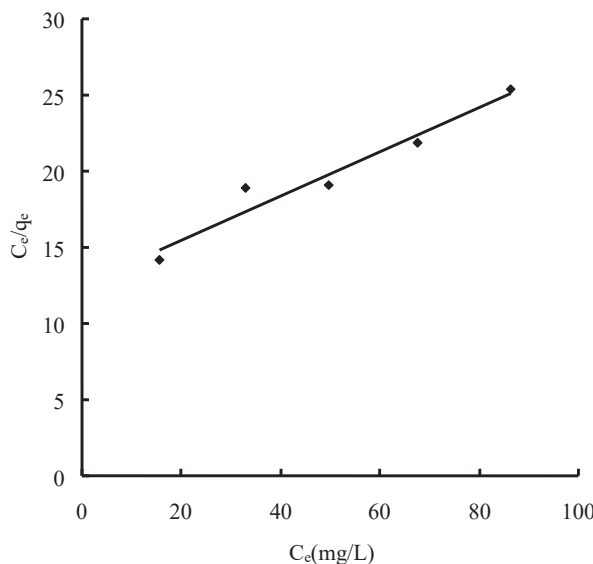


Fig. 9: Langmuir plot for the adsorption of Cu²⁺ ions onto the montmorillonite-biochar composite.

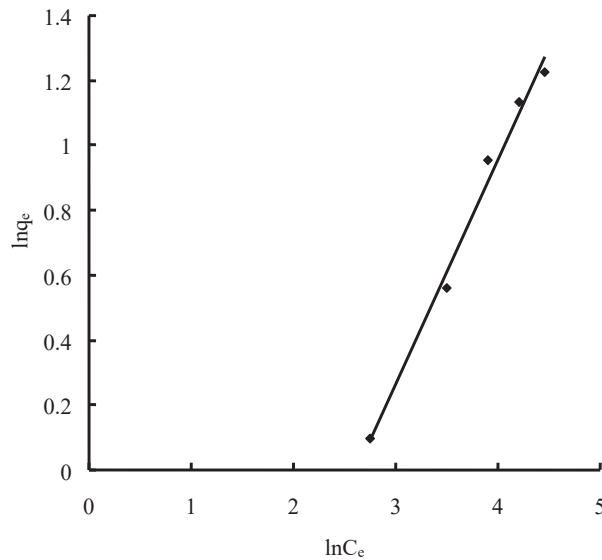


Fig. 10: Freundlich plot for the adsorption of Cu^{2+} ions onto the montmorillonite-biochar composite.

The Freundlich isotherm equation is described by the following Eq. (9):

$$q_e = K_F C_e^{\frac{1}{n}} \quad \dots(9)$$

The integration of the Eq.(9) gives the following expression:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \dots(10)$$

Where, K_F and n are the Freundlich adsorption isotherm constants, which are indicators of adsorption capacity and adsorption intensity respectively.

Two isotherm models were applied to experimental data, and results are shown in Fig. 9, Fig. 10 and Table 3.

Table 3 Parameters of Langmuir isotherm model and Freundlich isotherm model for the adsorption of Cu^{2+} ion onto the montmorillonite-biochar composite

Langmuir isotherm model		Freundlich isotherm model			
$q_m(\text{mg/g})$	K_L	R^2	K_F	n	R^2
6.92	0.55	0.948	0.17	1.45	0.989

The Freundlich constant (n) for Cu^{2+} ions is within the range of 1 and 10, suggesting the adsorption of Cu^{2+} ions on the adsorbents is favourable (Das et al. 2011). The correlation coefficient (R^2) of Freundlich model for Cu^{2+} ions is higher than that of Langmuir, indicating that it has high degrees of heterogeneous distribution of active sites on the surface, presumably due to the uneven surface distribution. The adsorption process is chemical.

CONCLUSIONS

A composite adsorbent was prepared by montmorillonite and biochar from peanut shell. The adsorption experiment of the Cu^{2+} ions from aqueous solution by the montmorillonite-biochar composite was carried out in detail. Results showed that the montmorillonite-biochar composite was mesoporous material. The surface of montmorillonite-biochar composite has roughness and irregular layer structure. It is also determined that the adsorption is completed in relatively short time periods. The Cu^{2+} ions in aqueous solution adsorption onto the montmorillonite-biochar composite are well described with the pseudo second order reaction kinetics and Freundlich isotherm models respectively.

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