Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar

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Highlights:

- Date seed biochars adsorption capacity Cu^{2+} and Ni^{2+} were investigated
- Biochar with particle size 0.6-1.4 mm and prepared at 550 °C and 3 h was best
- Ion exchange mechanism accounted for 70% of the ion removal
- Cu^{2+} and Ni^{2+} adsorption was spontaneous and endothermic process

Abstract

This paper reports on Ni^{2+} and Cu^{2+} adsorption kinetics and mechanisms by date-seed derived biochar. Biochar was prepared at different temperatures (350-550 °C), heating times (1-3 h) and particle sizes (<0.3 - >2.0 mm). Biochar prepared at 550 °C and 3 h heating time with particle size range of 0.6-1.4 mm had the highest adsorption capacity for both ions. Further batch experiments revealed that optimal adsorption occurred around pH 6 with maximum adsorption capacity of 0.421 and 0.333 mmol g⁻¹ for Cu^{2+} and Ni^{2+} , respectively. The experimental data were best fit by the Sips isotherm model and the pseudo-second order kinetics models. Ion exchange mechanism accounted for more than two thirds of the ions removal. Complexation with carboxyl and hydroxyl groups also played significant role in ion removal. Column experiments showed that the effluent pH fluctuated overtime buffering to level slightly above 6 which may have facilitated surface precipitation and resulted in the apparent increase in adsorption capacity. The breakthrough curve obtained in the column experiment was reasonably fit by the Adam-Bohart model. Date-seed derived biochar is a promising material for adsorption for heavy metals from aqueous solutions.

Keywords: biochar; date seed; heavy metal; isotherm; mechanism; thermodynamic

1. Introduction

Heavy metal ions Cu^{2+} and Ni^{2+} are classified as micronutrients for plants, animals, and humans. However, they are toxic at high concentrations. Copper exposure may cause lethargy, DNA damage, gastrointestinal bleeding, and hypertension [1]. Exposure to nickel ion can cause skin allergies, lung fibrosis, and respiratory tract cancer [2]. Heavy metals contamination is a result of various industrial activities, such as metal plating, mining, tanneries, petrochemicals and refineries, and pigments and painting. They can be found in industrial wastewater in concentrations that range from a few mg/L up to thousands of mg/L [3].

Considering the harmful effects of heavy metals, their concentrations must be limited to levels acceptable by environmental regulatory agencies prior to discharge into receiving waters. Over the past decades, many treatment methods have been used for heavy metals removal from aqueous solution including ion exchange, chemical precipitation, chemical oxidation and reduction, filtration, membrane separation, and adsorption. However, most of these techniques are costly due to their high energy demand, chemical, and labour requirements, in addition to the production of large amounts of sludge that is difficult to handle [4]. Adsorbents, such as activated carbon (AC), are convenient and therefore widely used. However, the high capital and regeneration costs of AC remain a challenge which motivates the search for more economical alternatives [4,5].

Recently, biochar has received increasing attention as a potential eco-friendly adsorbent for wastewater and water purification [5-10]. Biochar can be prepared from a myriad of organic-based sources, including agricultural wastes. Biochar production from agricultural wastes serves a double purpose: environmentally sound waste management method and valorisation of unwanted material to a value-add product that can be used for removing organic and inorganic pollutants of environmental or economic concern.

Several biochar derived from agricultural wastes were tested for their adsorption ability for heavy metal removal from contaminated solutions including: hickory wood [11], macroalga [12]; peanut straw, soybean straw, and canola straw [13]; hard wood and soft wood [10]; olive pomace, compost, and orange waste [5]; *Sida hermaphrodita* and wheat straw [14]; almond shell biochar [15]. In fact, Mohan et al. [16], Tan et al. [17], and Inyang et al. [4], after reviewing the literature on biochar adsorption for heavy metals, suggested that some biochars were more effective than commercial activated carbon. For example, biochars derived from peanut, canola, and soybean straw prepared at 400 °C were more efficient than activated carbon for Cu^{2+} ion removal [13].

In our previous studies, biochar derived from date seed biomass showed remarkable, adsorption capacities for MB removal from aqueous solution [18]; our preliminary study [19] also suggested a good potential for Ni adsorption. Therefore, date seed derived biochar may be an efficient low-cost adsorbent for heavy metals and dyes. However, the adsorption performance of date seed derived biochar prepared at different pyrolysis conditions for heavy metal ions from aqueous solution and its controlling mechanism must be further studied.

Most of the studies focused on the adsorption aspects including kinetics, isotherms, adsorption capacity, and the influence of solution pH. Limited number of studies examined other important parameters that affect the efficiency of the biochar adsorption, such as pyrolysis conditions, particle size, and reaction temperature. Furthermore, most of the previous adsorption studies were widely carried out in batch mode which, although provides useful information on adsorption parameters, is not the most practical application in wastewater treatment. Fixed bed adsorption provides further information about the adsorption behaviour. Moreover, few studies investigated the adsorption mechanisms governing Cu^{2+} and Ni^{2+} ions uptake onto biochar.

The use of two parameters isotherms such as Langmuir and Freundlich models are very common in the published literature due to their simplicity and ease linearization. However, three parameters, such as Sips, Khan isotherm models offer a better understanding of the adsorption process, especially at low and high concentrations; so far, few studies have used three parameter models to describe the adsorption isotherm of heavy metals on biochar [20].

This study presents a comprehensive investigation of the adsorption of Cu^{2+} and Ni^{2+} on biochar derived from date seed in batch and fixed bed settings. The main objectives of the present study were (1) to identify the optimal biochar preparation conditions including pyrolysis temperature (350, 450, 550 °C), heating time (1, 2, 3 h) and particle size (<0.3, 0.3-0.6, 0.6-1.4, 1.4-2.0, and >2.0 mm); (2) to identify the optimal operating conditions including solution pH, initial metal concentration, temperature, and contact time using batch adsorption experiments; (3) to evaluate adsorption isotherms, adsorption kinetics, and thermodynamics of the Cu^{2+} and Ni^{2+} adsorption on the biochar; (4) to study the adsorption of Cu^{2+} and Ni^{2+} from aqueous solutions in fixed bed experiments; (5) to investigate the adsorption mechanisms of the Cu^{2+} and Ni^{2+} on the biochar; and (6) to investigate the desorption potential of Cu^{2+} and Ni^{2+} from laden biochar.

2. Materials and methods

2.1 Biochar preparation and characterization

Nine biochars were prepared from date seed by varying the final pyrolysis temperature (350, 450, and 550 °C) and heating times (1, 2, and 3 h). The biochar samples were characterized to determine their physicochemical properties including surface area, pH, ash content, CEC, surface structure, and surface chemistry (Table 1). Further details about preparation and physicochemical characterization of the biochar were discussed in our previous works [18,21]. The biochar was gently crushed and sieved to particle size ranges (<0.3, 0.3-0.6, 0.6-1.4, 1.4-2.0, and >2.0) mm. Date seed biochar (DSB) samples were washed with deionized

(DI) water several times to remove impurities (e.g., ash) and soluble salts. The biochar was then oven-dried (105 °C) for 2 h, and stored in air tight container labelled clearly according to its pyrolysis temperature and time (DSBTemp-time) as: DSB350-1; DSB350-2; DSB350-3; DSB450-1; DSB450-2; DSB450-3; DSB50-1; DSB550-2; and DSB550-3.

Table 1

Physicochemical data seed biochar properties samples prepared at various pyrolysis condition [18,21]

Biochar	C %	Ash %	pH	Total acidic groups, meq g ⁻¹	Specific surface area, m ² g ⁻¹
DSB350-1	64.4	6.670	6.95	15.6	23.88
DSB350-2	66.7	10.67	6.99	15.4	69.52
DSB350-3	69.0	10.67	7.48	11.0	73.78
DSB450-1	63.7	9.000	7.61	11.2	29.86
DSB450-2	71.5	11.67	7.69	11.0	97.48
DSB450-3	79.3	11.94	7.71	11.2	100.2
DSB550-1	69.8	12.00	8.36	11.2	29.56
DSB550-2	76.0	12.33	8.43	13.5	88.16
DSB550-3	82.2	12.67	8.58	11.0	104.2

2.2 Chemicals

All chemicals used in the experimental work were of the analytical grade. Chemicals including Cu(NO₃)₂ 2.5H₂O and Ni(NO₃)₂ 6H₂O with a minimum assay of 99% purity obtained from (AJAX chemicals) and (Scharlau chemicals), respectively. A stock solution of 5 mM of Cu²⁺ and Ni²⁺ were prepared. Then working metals solutions of (0.3, 0.5, 1.0, 1.5, 3.0, 3.5, 4.0 mM) were prepared by further diluting with deionized water to the required concentrations. For atomic absorption spectroscopy analysis, the standard solutions were freshly prepared before use and discarded after use. All the prepared solutions were stored in pre-cleaned glass containers at room temperature for further use.

2.3 Analysis of metal ion concentrations

Atomic absorption spectroscopy (AAS) (Avanta-GBC, USA) operating with an air–acetylene flame was used to analyse single heavy metal samples. Inductively coupled plasma ICP (Perkin Elmer-Optima 8300) were used for the quantitative determination of light metals

concentration including Na^+ , K^+ , Ca^{2+} , and Mg^{2+} released during adsorption experiments as well as the concentration of Cu^{2+} and Ni^{2+} ions.

2.4 Batch adsorption experiments

2.4.1 Biochar screening for copper and nickel adsorption

The nine (9) biochar samples prepared at different pyrolysis temperature and time were first screened to identify the best candidate for Cu^{2+} and Ni^{2+} adsorption. Batch experiments were run by mixing 0.1 g of each biochar sample in 10 ml of working solutions (0.5 mM Cu^{2+} or 1.0 mM Ni^{2+}) in 50 ml glass containers. The samples were then agitated using rotary shaker (30 rpm) for 24 h at $23 \pm 2^\circ\text{C}$. At the start of the experiment, initial pH was adjusted to $\text{pH } 6.0 \pm 0.1$ using 0.1 M NaOH or HCl solutions. The solution was filtered using pre-cleaned glass syringe combined with 0.45 μm Millipore filters. The adsorption capacity of each metal ion adsorbed by the biochar were determined (q_e , mmol g^{-1}) as the difference between their initial and final concentrations as given in Eq.(1):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where, C_o is initial metal concentration (mM), C_e metal concentration at equilibrium (mM), V is volume of metal solution (L), and W is amount of biochar (g).

All adsorption experiments were conducted in triplicate and the average values and the standard error was used to express the error bar. Following preliminary adsorption studied Cu^{2+} and Ni^{2+} adsorption kinetics, isotherm, and thermodynamic studies were conducted on the best performing biochar.

2.4.2 Effect of pH solution

Solution pH has been identified as one of the significant parameter governing adsorption of metal ions onto different adsorbents such as biochar. The influence of solution pH on adsorption of Cu^{2+} and Ni^{2+} ions was investigated for the initial pH range between 2.0 and 6.0. The initial pH of solution was adjusted to the required values using 0.1 M HCl and

NaOH solutions. In these experiments, a biochar sample (0.1 g) was mixed with 10 ml of 1.0 mM metal solution and the adsorption equilibrium was attained by shaking the mixture at 30 rpm in a rotary shaker for 24 h. The final pH and residual Cu^{2+} and Ni^{2+} concentrations in the solutions were determined and the amount of each metal ion adsorbed (q_e , mmol g^{-1}) were calculated as given in Eq.(1).

2.4.3 Effect of particle size

The influence of particle size on Cu^{2+} and Ni^{2+} ion removal was investigated by varying the biochar particle size in the range of less than 0.3 to more than 2.0 mm. The initial pH of solutions was adjusted to the required value of 6. In these experiments, biochar sample (0.1 g) of particle sizes (<0.3, 0.3-0.6, 0.6-1.4, 1.4-2.0, and >2.0 mm) were placed into 10 ml solutions containing 0.5 mM of each metal solution and the adsorption equilibrium was attained by mixing for 24 h.

2.4.4 Effect of mineral composition

The amount of light metals including Na^+ , K^+ , Ca^{2+} , and Mg^{2+} released from the biochar into the solution during the adsorption experiment was measured [3,7]. For this experiment 0.1 g of biochar was mixed with 10 ml with initial metal solution of 0.5 mM and pH 6.0. As control, the release of cations after washing successively with deionized water at pH 6 was also measured. The values for cations released during adsorption of Cu^{2+} and Ni^{2+} (meq L^{-1}) were calculated as the difference between amount of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} cations released when rinsing with deionized water and amount of cations measured in the supernatant after Cu^{2+} and Ni^{2+} adsorption.

2.5 Adsorption isotherm, thermodynamic, and kinetics studies

Adsorption isotherms of Cu^{2+} and Ni^{2+} ions were determined by mixing 0.1 g of biochar in 10 mL solution containing different initial metal concentrations (0.3-4.0 mM). The mixtures were agitated at 30 rpm for 24 h and then, filtered to separate the supernatant solution for

analysis. Then the amount of each metal adsorbed (q_e , mmol g⁻¹) was calculated using Eq. (1).

The thermodynamic parameters related to the adsorption process of Cu²⁺ and Ni²⁺ including Gibb's free energy change (ΔG° , kJ mol⁻¹), entropy change (ΔS° , J mol⁻¹ K⁻¹), enthalpy change (ΔH° , kJ mol⁻¹) were obtained at 25 and 45 °C by the following equations [22]:

$$\Delta G^\circ = -RT \ln (K) \quad (2)$$

$$\ln(K) = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (3)$$

where T the absolute temperature (K), R the gas constant (8.314 J K⁻¹ mol⁻¹), K is the equilibrium adsorption constants of the isotherm fits obtained from the isotherm plots [23,24]. Liu [25] suggested that for heavy metal ions, the thermodynamic equilibrium constant would be adequately approximated by the Langmuir equilibrium constant (K_L). By plotting $\ln K$ as a function of $1/T$, the values of ΔH° and ΔS° can be obtained from the slope and intercept of the plot.

The adsorption kinetics of Cu²⁺ and Ni²⁺ uptake was evaluated by mixing 1.0 g of biochar with 100 mL of 1.5 mM metal solution in 250 mL glass vials. Filtrate samples were withdrawn at specific intervals from 2 to 1440 min. The amount of metal ion adsorbed on biochars at specific time interval (q_t , mmol g⁻¹) were each calculated as the difference between their initial and final concentrations at time as given in Eq.(1). All experiments were conducted at initial pH 6 and room temperature.

2.6 Control and reproducibility of data

Adsorption experiments were repeated at least three times and in cases where results were not conclusive further repetitions were conducted to ensure that effects seen were genuine. Fixed bed adsorption experiments were carried out in duplicates and the average value were reported. Control and preliminary experiments with no biochar were also performed for each system. Adsorption by the vials, filters material, and flask or interference with the analytical procedures were not detected. Solution pH was not controlled but adjusted at the beginning and recorded at the end of the equilibration.

2.7 Modelling of adsorption equilibrium and kinetics

The relationship between the amounts of metal adsorbed (q_e , mmol g⁻¹) and metal concentrations (C_e , mM) at equilibrium were modelled using Langmuir, Freundlich, and Sips isotherms. The Langmuir equation can be expressed as in Eq.(4):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

where K_L is the adsorption constant (L mmol⁻¹) related to energy of adsorption, q_m is the maximum adsorption capacity (mmol g⁻¹) and C_e metal concentration at equilibrium (mM).

The non-linear form of Freundlich equation is written as Eq.(5):

$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_F and n are Freundlich constants indicating the adsorption capacity and the adsorption intensity, respectively.

Sips isotherm, combination of Langmuir and Freundlich isotherms, is used for predicting the heterogeneous adsorption systems. When the metal concentrations is low, Sips effectively reduces to the Freundlich isotherm while at high metal concentrations, it approaches the Langmuir isotherm [26]. The Sips model is written as given in Eq.(6) [26]:

$$q_e = \frac{K_S C_e^{\beta_S}}{1 + a_S C_e^{\beta_S}} \quad (6)$$

where K_s is the Sips model isotherm constant ($L\ g^{-1}$); a_s the Sips model constant ($L\ mmol^{-1}$) and β_s the Sips model exponent.

Several models exist to describe the adsorption kinetics and rate-limiting step; the pseudo first and pseudo second order rate models are the most popular. Pseudo first order rate model can be expressed as follows Eq.(7) [27]:

$$q_t = q_e(1 - e^{-k_1 t}) \quad (7)$$

where q_t is the amount of metal ion adsorbed per unit mass ($mmol\ g^{-1}$) at time t and k_1 (min^{-1}) is the pseudo first order adsorption rate constant.

Non-linear form of pseudo second order model is expressed by Eq.(8) [27]:

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (8)$$

where k_2 is the equilibrium rate constant of pseudo second order adsorption ($g\ (mmol\ min)^{-1}$).

All parameters for the isotherm and kinetics models were obtained using the regression tool in MATLAB™.

2.8 Metal adsorption in a Fixed bed column system

The experimental setup of the fixed-bed column is schematically shown in Fig. 1. Pre-wetted biochar sample was packed to the depth of 5.0 cm in a glass column of 2.5 cm inner diameter fitted with a suction filter. Pre-wetted biochar was used to avoid air entrapment. A layer of glass spheres (2.0 mm) was placed at the top of the column to ensure homogenous distribution of the feeding solution. The metal solutions of 0.5 mM were pumped from a 1.0 L storage tank into the column. The metal solutions were fed into the column in a downward flow at $1.0\ mL\ min^{-1}$ flow rate using a peristaltic pump (Masterflex L/S–Cole/Palmer). The initial pH solution value in the storage tank was adjusted to 6.0 using a 0.1 M HCl and NaOH as required. Samples of the column effluent were collected from the bottom at pre-set time intervals and were analysed for heavy metals content. The column was operated until the bed

was saturated with metal, that is, the effluent concentration was 95% of the influent concentration.

The breakthrough time curve of Cu^{2+} and Ni^{2+} ions were determined and expressed in terms of the normalized concentration (C_t/C_o), as a function of time (t), where C_t is the metal effluent and C_o is the metal influent concentration (mM). The breakthrough point on the curve was selected at the point at which $C_t/C_o=0.05$. The time at which the breakthrough occurred is called the breakthrough time (t_b). The saturation time (t_s) was defined as the point when the effluent concentration reaches 0.95 of C_o .

Fig. 1 Fixed bed adsorption arrangement

The value of the total mass of metal adsorbed, q_t (mmol), can be calculated as shown in Eq.(9):

$$q_t = \frac{Q}{1000} \int_{t=0}^{t=t_s} (C_o - C_t) dt \quad (9)$$

The maximum capacity q_{eq} (mmol g^{-1}) in the column, also known as the equilibrium metal uptake, can be calculated by dividing the total mass absorbed (q_t) by the mass of adsorbent (m) as shown in the following Eq. (10):

$$q_{eq} = \frac{q_t}{m} \quad (10)$$

Total amount of metal ion entering the column (m_t) is calculated from the following Eq.(11):

$$m_t = \frac{C_o Q t_s}{1000} \quad (11)$$

and the removal percentage (R %) of metal ions can be obtained from Eq.(12):

$$R = \frac{q_t}{m_t} \times 100 \quad (12)$$

while MTZ% (mass transfer zone, where adsorption takes place) is determined as shown in Eq.(13):

$$MTZ \% = \frac{t_s - t_b}{t_s} \quad (13)$$

To predict breakthrough curves for Cu^{2+} and Ni^{2+} ions adsorption as a function of time, different mathematical models, namely Thomas and Adams-Bohart models were widely used to describe experimental data of the breakthrough curve. The linear form of Thomas model is given by Eq. (14):

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{K_{TH} q_o m}{Q} - K_{TH} C_o t \quad (14)$$

where, C_t is equilibrium concentration (mM) at time t (min); K_{TH} is Thomas constant ($\text{L min}^{-1} \text{mmol}^{-1}$); Q is volumetric flow rate (L min^{-1}); q_o is column capacity (mmol g^{-1}), determined by the Thomas model; m is mass of adsorbent (g).

Adams-Bohart model assumes that equilibrium is not instantaneous, and the adsorption rate is proportional to the adsorption capacity remaining on the adsorbent. Adams-Bohart model is given in the following Eq.(15):

$$t = \frac{N_o Z}{C_o v} - \ln\left(\left(\frac{C_o}{C_t}\right) - 1\right) \frac{1}{K_{AB} C_o} \quad (15)$$

where t is the breakthrough time (min); C_t the concentration at break through (mM); N_0 the adsorptive capacity of the adsorbent (mmol L^{-1}); Z the bed depth of column (cm); v the linear flow rate (cm min^{-1}); K_{AB} is the Adams–Bohart rate constant (L (mmol min)^{-1}). All required constants for Thomas and Adam-Bohart models were obtained using non-linear regression analysis (Curve fitting tool in Matlab).

2.9 Desorption experiments

Laden biochar with Cu^{2+} and Ni^{2+} ions obtained from the earlier experiments were used to determine desorption potential of metal ions from laden biochar. The laden biochar was attained by elution using deionized water, 0.1 M HCl, 0.1 M CaCl_2 , and mixture (1:1) of 0.1 M HCl and 0.1 M CaCl_2 . The laden biochar was first collected and washed with deionized water (10 mL) to remove any unabsorbed metal ions and oven dried at 60°C for 24 h. The deionized water was collected and analysed for Cu^{2+} and Ni^{2+} ions concentrations. Then the dried biochar (0.1 g) was transferred to a clean flask containing 10 ml of desorption agents. The mixture was agitated in rotary shaker at 30 rpm for 24 h. After elution, biochar was filtered to measure concentration of Cu^{2+} and Ni^{2+} ion leached in the solution. The amount of Cu^{2+} and Ni^{2+} ions desorbed (mmol g^{-1}) of biochar was determined from the metal ion concentration in each solution.

2.10 FTIR and SEM analysis

Fourier transform infrared spectroscopy (FTIR) was employed to inspect the biochar surface chemistry of the biochar before and after Cu^{2+} and Ni^{2+} adsorption. FTIR analysis was performed by mixing biochar samples with small amount of KBr powder and ground in an agate mortar. FTIR absorbance data were obtained for wavenumbers in the range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution factor of 4 cm^{-1} using (Perkin Elmer Spectrum two). Electron microscopy (SEM) was performed using (JEOL JSM-6510) microscopy. SEM images were

detected to examine the biochar surface morphology as well as any structural changes that might have occurred after metal ion adsorption.

2.11 Statistical analysis

Regression analysis was used to investigate correlations between biochar adsorption uptake of Cu^{2+} and Ni^{2+} ions as function of pyrolysis temperature and heating time. The analysis was carried out using SPSS ver. 22. One-way ANOVA and Tukey Post-hoc (HSD) tests were also carried out to find the significance of the differences between the adsorption capacities of the biochars prepared at different pyrolysis temperatures and heating times. All the tests were conducted with significance level $\alpha=0.05$.

Apart from the correlation coefficient (R^2), the degree of the best-fit of a certain model to the experimental data was evaluated by the sum of square errors (SSE) and root mean square error (RMSE) as shown in Eq. (16) and Eq.(17):

$$SSE = \sum_{i=1}^N (q_{e,calc.} - q_{e,exp.})_i^2 \quad (16)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^N (q_{e,exp.} - q_{e,calc.})^2} \quad (17)$$

where $q_{e,exp}$ and $q_{e,calc}$ (mmol g^{-1}) are the experimental and predicted adsorption capacities of the metal ions onto adsorbent and N is the number of measurements.

3. Results and discussion

3.1 Selection of biochar

Fig. 2 shows the removal efficiency of Cu^{2+} and Ni^{2+} ions from the aqueous solutions by the different absorbents. The DSB550-3 showed the highest removal efficiency of Cu^{2+} and Ni^{2+} ions at 99.3% and 80.3%, respectively. The DBS450-3 was second best but not significantly different than the DBS550-3. Nevertheless, the DBS550-3 was significantly different to all other biochars. The results suggest that adsorption uptake is positively correlated with the pyrolysis temperature and heating time which are also correlated with the surface area of the

biochar [18]. These results are consistent with our earlier works on biochar prepared from date seed for MB removal [18]. This is also consistent with the literature where increased adsorption capacity of biochar with increased pyrolysis temperature has been reported [6,8,9]. This can be attributed to the effect of pyrolysis temperature on the biochar physiochemical characteristics including surface area, porous structure, and availability of surface functional groups. Furthermore, as presented in Fig. 2, there were no significant differences in Cu^{2+} removal among biochar samples. The results suggest that both pyrolysis temperature and heating time have lesser effect on Cu^{2+} adsorption compared to Ni^{2+} . This finding is supported by other investigators [28,29]. This difference may be explained on the basis of their covalent indices [Covalent index= (electronegativity)² (ionic radius+0.85)] [30]. A covalent index for Cu^{2+} is 5.703 which greater than Ni^{2+} (5.618) and consequently Cu^{2+} ion could form covalent bonds with different ligands onto biochar [30].

As DBS550-3 was the best performer, it was selected for all subsequent experiments in this study.

Fig. 2 Removal efficiency of date seed biomass as well as derived biochar for Cu^{2+} and Ni^{2+} removal (biochar: solution ratio=10 g L⁻¹; time=24 h; pH=6; room temperature; particle size=0.6-1.4 mm)

3.2 Effect of pH on metal adsorption

Fig. 3 shows the effect of pH on the adsorption of Cu^{2+} and Ni^{2+} onto DSB550-3. The figure shows that at lower pH, the adsorption of Cu^{2+} and Ni^{2+} onto the biochar was small and it increased until pH 6. Similar observations were reported that the highest adsorption of Cu^{2+} and Ni^{2+} ions was achieved within the pH range 5 to 6 [5,10,15]. At lower pH values the adsorption of metal ions are hindered by the abundance of H^+ ion due to competition for active sites.

The solution pH affects the surface charge of adsorbent as well as metal speciation in aqueous solution [5]. Furthermore, the pH significantly influences the amount of metal adsorbed due to its impacts on the complexation behaviour of the surface functional groups including carboxyl (COOH), amino (NH), and hydroxyl (OH) groups [7]. However, when the pH values exceed 6.0, there is a risk of forming insoluble metal hydroxides which then precipitate. To avoid the formation of precipitates, pH 6.0 was identified as the optimum value to maximize adsorption of Ni^{2+} and Cu^{2+} . This indicated that the adsorption capacity of the biochar is clearly pH dependent. Therefore, all subsequent adsorption experiments were performed at pH value of 6.

Fig. 3 Effect of pH on the adsorption of Cu^{2+} and Ni^{2+} onto biochar (room temperature; biochar: solution = 10 g L^{-1} ; $C_0 = 1.0 \text{ mM}$)

3.3 Effect of particle size on metal adsorption

The effect of particle size on the uptake of Cu^{2+} and Ni^{2+} ions is presented in Fig. 4. As shown in Fig. 4, the removal efficiency increased with particle size until it reached its maximum in the particle range (0.60-1.40 mm) after which removal efficiency declined. The effect of particle size was more prominent on the Ni^{2+} removal efficiency. However, the finding of this study is contrary to the findings of Zheng et al. [31] who found that the removal efficiency of atrazine increased with decreasing biochar particle size from < 0.25 to < 0.053 mm. They attributed the increase of removal efficiency to the increase of specific surface area available for adsorption. This apparent contradiction may be attributed to the difference between the adsorption mechanisms governing heavy metal removal and those of organic pollutants. In general, several studies implied that particle size and surface area of biochar are important parameters that allow biochar easy access to metal ions [10,32]. However, Ding et al. [33] reported that oxygen containing functional groups are more important factors for metal adsorption than surface area. This was also observed in this study and is discussed later in the mechanisms section.

From an operational point of view, using extremely fine particles might be difficult to implement due to the difficulty of separating the adsorbents from the solution and the high requirements of labour for centrifugation and filtration [34]. Furthermore, the lower particle size may lead to flocculation thus; removal of metal ions may be reduced. Therefore, very fine particles might be unfavourable to be used for biochar adsorption. Similarly, large particle size (> 2.0 mm) was also avoided in the current study due to the possibility of the higher diffusion resistance suggesting that most of the internal surface of the particles may not be utilized for adsorption. Therefore, biochar with particle size range from 0.6-1.4 mm was used in this study.

Fig. 4 Effect of biochar particle size on the adsorption of Cu^{2+} and Ni^{2+} (room temperature; biochar: solution = 10 g L^{-1} ; $C_0 = 0.5 \text{ mM}$)

3.4 Adsorption isotherms

The adsorption isotherms for Cu^{2+} and Ni^{2+} ions onto DSB550-3 at a solution pH of 6.0 containing different initial metal concentrations (0.3-4.0 mM) were investigated. The results showed that the adsorption uptake increases with increasing metal concentration until the equilibrium was reached. This can be attributed to the increase in the driving force for mass transfer, which is the concentration gradient [5]. Isotherms including Langmuir, Freundlich, and Sips isotherms were used to represent the experimental data for Cu^{2+} and Ni^{2+} adsorption onto DSB550-3. The parameters for the three isotherm models are given in Table 2. The experimental data adequately described by Sips isotherm model with high correlation coefficients ($R^2=0.99$) and ($R^2=0.98$) for Cu^{2+} and Ni^{2+} , respectively. Judging by the adsorption intensity (n) obtained from the Freundlich isotherms, the adsorption of Cu^{2+} and Ni^{2+} ions by date seed biochar is favourable in the studied concentration range.

Table 2Adsorption isotherms constants for the adsorption of Ni^{2+} and Cu^{2+} ions date seed biochar

Model	Cu^{2+} ion	Ni^{2+} ion
Langmuir isotherm		
K_L (L mmol^{-1})	0.725	0.837
q_m , mmol g^{-1}	0.421	0.333
R^2	0.98	0.96
SSE	0.0008	0.002
RMSE	0.011	0.018
Freundlich isotherm		
K_F (mmol g^{-1}) (L mmol^{-1}) $^{1/n}$	0.169	0.141
n	1.523	1.647
R^2	0.99	0.93
SSE	0.0005	0.003
RMSE	0.009	0.023
Sips model		
a_s (L mmol^{-1})	0.010	3.617
K_s (L g^{-1})	0.171	0.779
β_s	0.662	2.066
R^2	0.99	0.98
SSE	0.0005	0.001
RMSE	0.009	0.015

Comparison of q_m values in mmol g^{-1} for different solutes are found to be in the following order $\text{Cu}^{2+} > \text{Ni}^{2+}$ ions. The difference in adsorption capacities between Cu^{2+} and Ni^{2+} under the same environmental conditions could be attributed to different ionic characteristics of the metal ions including electronegativity, ionic radii and hydrated radii size. Anirudhan and Sreedhar [35] reported that the amount of metal adsorbed increases with decreasing hydrated radius because ions with larger hydrated radii increases the swelling pressure within the adsorbent and therefore decreases the metal affinity. This may be one possible explanation of the higher affinity of DSB550-3 biochar to Cu^{2+} compared to Ni^{2+} ion, as Cu^{2+} has smaller hydrated radius ($4.04\text{\AA}$) and bigger ionic radii ($0.73\text{\AA}$) than Ni^{2+} (hydrated radius $4.19\text{\AA}$ and ionic radii $0.69\text{\AA}$).

Numerous types of adsorbents have been employed for their adsorption ability to remove Cu^{2+} and Ni^{2+} ions from contaminated solution (Table 3). Although, comparisons must be carried with caution as the adsorption capacities are considered as an example of adsorbent effectiveness under specific experimental conditions including solution pH, temperature,

metal concentration, particle size, and adsorbent properties, the results suggest that DSB550-3 has high adsorption potential compared to other adsorbents reported in the literature (Table 3).

Table 3
Adsorption capacities of Cu^{2+} and Ni^{2+} on various adsorbents

Adsorbent	Pyrolysis temperature, ($^{\circ}\text{C}$)	pH	Ion	q_m , (mmol g^{-1})	References
Hard wood char	450	5.0	Cu^{2+}	0.107	[10]
Corn straw char	600			0.197	
Softwood biochar	500	4.8	Cu^{2+}	0.099	[8]
	700			0.174	
hardwood biochar	500			0.006	
	700			0.111	
Switchgrass biochar	500			0.082	
	700			0.048	
Pinewood biochar	300	6.2	Cu^{2+}	0.070	[35]
	700			0.043	
Rice husk biochar	300	5.0	Cu^{2+}	0.072	[5]
	600			0.004	
Dried olive pomace	300			0.081	
	600			0.010	
Orange waste	300			0.077	
	600			0.007	
Compost	300			0.125	
	600			0.053	
Almond husk AC	700	5	Ni^{2+}	0.524	[37]
Non-activated date-pits	700	5	Cu^{2+}	0.150	[38]
AC fibres	-	-	Ni^{2+}	0.152	[39]
Almond shell biochar	650	7	Ni^{2+}	0.340	[15]
Date seed biochar	550	6.0	Cu^{2+}	0.421	This study
	550		Ni^{2+}	0.333	

3.5 Effect of contact time and adsorption kinetics

The effect of contact time on Cu^{2+} and Ni^{2+} adsorption onto DSB550-3 biochar is presented in Fig. 5. As shown in Fig. 5, the amount of Cu^{2+} and Ni^{2+} adsorbed increased with contact time until equilibrium was reached. Nearly 95% of the Cu^{2+} ion was adsorbed within the first hour of contact then followed by a slower adsorption stage until equilibrium state was reached after 4 h. The faster first stage can be attributed to the abundance of vacant sites on the biochar, whereas as adsorption continued, a progressive saturation of these active sites with time occurred [5]. These results were consistent with kinetics models which assume

higher adsorption stage at the start followed by slower stage as the system approaches equilibrium.

In the case of Ni^{2+} adsorption, unlike Cu^{2+} a multi-stage adsorption was observed as shown in Fig. 5. The first stage lasted 45 min and accounted for 52% of the total adsorption capacity, after which adsorption nearly plateaued for 105 min before a second rapid stage (but slower than the first) started and lasted for 210 min and accounted for nearly 42% of the total amount adsorbed, then finally adsorption plateaued for the remaining of the 24 h. It can be hypothesized that the adsorption rate pattern Ni^{2+} by the studied biochar could be attributed to the mass transfer of Ni^{2+} ion to the unoccupied binding sites as well as diffusion of metal ion into pores which continued until saturation of the active sites [40]. Moreover, it is also assumed that some of the very small pores might be inaccessible to Ni^{2+} ions and thus diffusion problems can be a limiting factor.

Fig. 5 Adsorption kinetics onto biochar of Cu^{2+} and Ni^{2+} ions

Significant differences were observed between the adsorption rates of Cu^{2+} and Ni^{2+} as shown in Fig. 5. Quantitatively, the removal kinetic of Cu^{2+} was faster than Ni^{2+} ion. This might be related to the strength of Cu^{2+} binding with surface functional groups such as carboxyl groups

[41]. Furthermore, the preference of DSB550-3 biochar for Cu^{2+} ion could be due to metal ionic characteristic such as electronegativity and geometrical coordination [42]. For example, soft Lewis acids such as Cu^{2+} have high polarizing power (a large ratio of ionic charge to ionic radius) compared to Ni^{2+} and consequently, it forms stronger bonds with soft Lewis bases [41].

Adsorption kinetics models including pseudo first order and pseudo second order models were used to describe the Cu^{2+} and Ni^{2+} adsorption. The results showed that the pseudo second order model had good agreement with the experimental values ($R^2 > 0.98$) for both metals (Ni^{2+} and Cu^{2+}) than the pseudo first order model (Table 4).

Table 4

Adsorption kinetics parameters for of Cu^{2+} and Ni^{2+} on onto DSB550-3 biochar

Metal ion	Pseudo first order model		Pseudo second order model	
Cu^{2+}	$k_1 (\text{min}^{-1})$	0.007	$k_2 (\text{g mmol}^{-1} \text{min}^{-1})$	1.614
	R^2	0.84	R^2	0.99
	$q_{e, \text{exp}} (\text{mmol g}^{-1})$	0.149	$q_{e, \text{exp}} (\text{mmol g}^{-1})$	0.149
	$q_{e, \text{calc}} (\text{mmol g}^{-1})$	0.024	$q_{e, \text{calc}} (\text{mmol g}^{-1})$	0.150
Ni^{2+}	$k_1 (\text{min}^{-1})$	0.004	$k_2 (\text{g mmol}^{-1} \text{min}^{-1})$	0.232
	R^2	0.81	R^2	0.98
	$q_{e, \text{exp}} (\text{mmol g}^{-1})$	0.057	$q_{e, \text{exp}} (\text{mmol g}^{-1})$	0.090
	$q_{e, \text{calc}} (\text{mmol g}^{-1})$	0.090	$q_{e, \text{calc}} (\text{mmol g}^{-1})$	0.089

3.6 Mechanisms of heavy metal adsorption by biochar

The adsorption of heavy metal ions onto biochar can be explained by the two types of adsorption processes: physical and chemical adsorption. The underlying mechanisms primarily involve surface complexation, metal precipitation, ion exchange, electrostatic interaction, and physical adsorption. In the following sections, these mechanisms are explored in further detail.

3.6.1 Ion exchange

Ion exchange mechanism represents one of the most predominant mechanisms involved in heavy metal adsorption from aqueous solutions [7]. The ion exchange mechanism by biochar

in this work was investigated by measuring the stoichiometric release of Na^+ , K^+ , Ca^{2+} , and Mg^{2+} from adsorbent after the adsorption of Cu^{2+} and Ni^{2+} . The release of cations from the blank solution, consisting of the adsorbent and deionized water, was also measured (Table 4). As shown in Table 5, the amount of Cu^{2+} adsorbed was 0.791 meq L^{-1} and the amount of the released cations was 0.545 meq L^{-1} , thus suggesting that ion exchange accounted for about 69% of the total adsorption of Cu^{2+} . Comparing the amount of Ni^{2+} adsorbed (0.688 meq L^{-1}) with the amount of ions released (0.493 meq L^{-1}) it could be concluded that ion exchange accounted for 72% of the total adsorption process. Similar observations were reported by other researchers [3,43]. Furthermore, DSB550-3 biochar exhibits a high ash content (12.67 %) with CEC of 1.897 meq L^{-1} [19] suggesting that the biochar may exhibit a high tendency to adsorb Cu^{2+} and Ni^{2+} by releasing other cations such as K^+ , Ca^{2+} , and Mg^{2+} .

Table 5

Release amount of earth cations due to adsorption of Cu^{2+} and Ni^{2+} onto DSB550-3

System	Total metal ion adsorbed (meq L^{-1})		Amount of cation released (meq L^{-1})				R %
	Cu^{2+}	Ni^{2+}	Na^+	K^+	Ca^{2+}	Mg^{2+}	
Control ^b	-	-	0.065	0.420	0.051	0.068	-
$\text{Cu}^{2+ \text{a}}$	0.791	-	0.055	0.021	0.374	0.094	69
$\text{Ni}^{2+ \text{a}}$	-	0.688	0.051	0.013	0.366	0.063	73

^a Difference between metal released by system and that by the control.

^b Biochar and deionized water.

3.6.2 Spectroscopy analysis of biochar surface

To identify the surface functional groups responsible for Cu^{2+} and Ni^{2+} ions adsorption, FTIR analysis was performed before and after metal adsorption. The FTIR scans are shown in Fig. 6. FTIR spectra display several absorption peaks, indicating the complex nature of the adsorbent examined. The broad bands at 3300 cm^{-1} could be attributed to stretching of the the O-H functional groups. The observed peaks in the range of 2920 cm^{-1} and 2850 cm^{-1} could be attributed to aliphatic C-H stretching groups. The bands in the range of $2000\text{--}1000 \text{ cm}^{-1}$ indicated C=C stretching within the aromatic rings, whereas the peaks between 1000 and 400 cm^{-1} indicated C-H stretching within the aromatic rings [44].

Comparing the FTIR spectra of metal (Cu^{2+} and Ni^{2+})-laden biochar to that of the pristine biochar (Fig. 6), the peaks at 1100, 1320, 1563, 1620 cm^{-1} were shifted after adsorption, indicating that functional groups such as C–O, C=O, O–H and COO^- groups were involved in the adsorption process of Cu^{2+} and Ni^{2+} . These shifts suggest that surface functional groups such as carboxyl and hydroxyl are predominant contributors in heavy metal ion adsorption.

SEM images of biochar before and after metal ion adsorption was carried out to obtain visual clues of the active adsorptive areas on the biochar surface as shown in Fig. 7. Based on SEM images, the biochar has highly heterogeneous pores and well-defined structures. After adsorption, the pores were packed with metal ions. Comparing SEM images before (Fig. 7a) and after (Fig. 7 b and c) the adsorption experiments revealed metal deposition on the biochar particles. Particularly, the deposition occurred in the mesopores which can provide channels for the adsorbates to reach the active adsorption sites and promote the rapid adsorption to reach equilibrium [45].

Fig. 6 FTIR spectra of DSB550-3 biochar before and after Cu^{2+} and Ni^{2+} ion adsorption

Fig. 7 SEM images of biochar before and after adsorption (a) DSB550-3; (b) Ni-DSB550-3; (c) Cu-DSB550-3

3.6.3 Electrostatic attraction

Electrostatic attraction is dependent on the solution pH and biochar point of zero charge (pH_{PZC}) [8]. The pH_{PZC} value of the DSB550-3 biochar was approximately 6.35 [18], indicating that basic groups were dominant on the biochar surface [28]. Basically, when the solution pH is $< \text{pH}_{\text{PZC}}$, the biochar surface is positively charged and electrostatic repulsion between metal ions and functional groups might occur. As illustrated previously, ion exchange mechanism is the primary adsorption mechanisms accounting 69% and 73% of Cu^{2+} and Ni^{2+} removal. However, when pH solution $< \text{pH}_{\text{PZC}}$ of biochar, the Cu^{2+} and Ni^{2+} adsorption on biochar still occurs with the optimal initial pH value of 6.0 (Fig. 3) suggesting that electrostatic attraction plays a negligible role in the Cu^{2+} and Ni^{2+} adsorption onto the biochar. Similar observations have been reported by previous studies [28,46].

3.6.4 Other potential adsorption mechanisms

Divalent metal cations such as Cu^{2+} and Ni^{2+} tend to be hydrated in aqueous solutions and the hydration is pH dependent [47]. Several studies suggested that precipitation can be also one of the potential removal mechanisms for heavy metal ions from aqueous solution. For

example, the metal species M(II) are present in deionized water as M^{2+} , $M(OH)^+$, $M(OH)_{2(aq)}$, $M(OH)_{2(s)}$ [48]. Srivastava et al. [48] reported that at solution pH 6.0, the solubility of the $M(OH)_{2(s)}$ is high, therefore; the M^{2+} becomes the main metal species. However, at higher pH (> 6), metal hydroxide which has lower solubility than other metal species tend to form and thus increasing the form of precipitation [48,13]. To determine whether or not a precipitate will form or not, the solubility product constant Q_{sp} of $M(OH)_{2(s)}$ was measured and compared with the value of K_{sp} of metal hydroxide. The results revealed that the solubility product (Q_{sp}) were 1.122×10^{-23} and 2.951×10^{-23} for Cu^{2+} and Ni^{2+} hydroxides, respectively which are less than their corresponding K_{sp} values (4.8×10^{-20} and 5.48×10^{-16}). The results suggested that no evidence for precipitation mechanisms. Although Liu et al. [36] reported that chemical precipitation of copper ion as $Cu(OH)_{2(s)}$ was occurred at a pH values above 6.2. However, as the pH of DSB550-3 biochar is high (8.58) [18], some localised surface precipitation in the form of $M(OH)_2$ might have taken place particularly inside the biochar pores due to the potential buffering of pH to more than 6.

In short, ion-exchange was the main adsorption mechanism accounting to more than two thirds of the metal ions removal. The other mechanisms (complexation, electrostatic attraction, and micro-precipitation) also combined accounted for less than a third of the metal ions removed. However, it was not possible to quantify the exact contribution each of these mechanism.

3.7 Fixed bed column adsorption

Fig. 8 shows the breakthrough curves obtained from the column experiments expressed in C_t/C_0 as a function of time. It can be seen from Fig. 8 that the breakthrough point (t_b) and time required to attain the total capacity of the column (t_s) were reached approximately within 120 and 440 min for Cu^{2+} and 130 and 450 min for Ni^{2+} , respectively. From the breakthrough curves, the total removal (R%), mass transfer zone (MTZ%), and total adsorption capacity

(q_t , mmol) were found to be 70.34-56%, 70.45-73.33%, 0.158-0.125 mmol for Cu^{2+} and Ni^{2+} ions, respectively.

The adsorption capacities for Cu^{2+} and Ni^{2+} uptake onto the biochar from the breakthrough curves were less than those from the batch adsorption (Table 1). This could be attributed to the insufficient contact time of the solution to diffuse into biochar particles. Therefore, the adsorption process could be still ongoing and adsorption equilibrium had not been reached yet. This was consistent with the kinetics results (Fig. 5) where the required time to reach equilibrium was 4 h and 6 h for Cu^{2+} and Ni^{2+} , respectively. Moreover, the high initial metal concentration which contributed to the abundance of ions might cause saturation of the available sites and therefore, the metal solution leaves the column before equilibrium occurs [49].

Comparison of Adams-Bohart and Thomas kinetic models with the experimental results was performed and the kinetic model parameters were calculated by linear regression analysis for Cu^{2+} and Ni^{2+} adsorption under experimental conditions. The experimental data fit well with Adams-Bohart model predicate good performance of fixed bed column for Cu^{2+} and Ni^{2+} with the correlation coefficients ($R^2=0.92$ and $R^2=0.94$) for Cu^{2+} and Ni^{2+} , respectively. The maximum adsorption capacity (N_o) in the fixed bed column was found to be $0.246 \text{ mmol L}^{-1}$ for Cu^{2+} and $0.213 \text{ mmol L}^{-1}$ for Ni^{2+} which are more than the values obtained from the batch experiments. This might suggest that in the column study, besides adsorption other additional removal mechanism such as surface precipitation may be involved [50]. The pH profile (Fig. 8) shows that the pH has fluctuated and at times was higher than 6 increasing the chances of precipitation.

Moreover, the pH profile for Cu^{2+} and Ni^{2+} ions during fixed bed adsorption are shown in Fig. 8. It can be seen from the figure that at the early part of the adsorption process, there was a sudden increase in pH value and then the pH tends to decrease as the time ongoing and

eventually reached nearly the initial pH of the influent. Several explanations have been proposed to explain pH fluctuation in the fixed bed adsorption. Vijayaraghavan et al. [51] suggested that formation of complexes between surface function groups and metal ions may be responsible for increasing pH value in the initial stages but as these functional groups become occupied with the saturation of the bed, the pH values decrease [51]. In this study, ion exchange has been identified as the major mechanism responsible for Cu^{2+} and Ni^{2+} removal displacing alkaline light metals such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} which can increase the pH value initially and then decrease as the adsorbent bed gets saturated [52]. Issabayeva et al. [53] proposed that the changes in pH during fixed bed adsorption was attributed to the adsorption of H^+ ion from the solution, and dissolution of some impurities from the adsorbent as well as the release of hydroxyl ions from adsorbent into aqueous phase is possible due to hydrolysis reaction.

Fig. 8 Breakthrough curve and pH profile of fixed bed adsorption of Cu^{2+} and Ni^{2+} ions

3.8 Adsorption thermodynamics

Thermodynamic parameters related to the adsorption process of Cu^{2+} and Ni^{2+} (ΔG° , ΔS° , and ΔH°) were obtained to further understand the adsorption mechanisms evaluated for the Cu^{2+} and Ni^{2+} adsorption process. The values of the standard Gibbs free energy (ΔG° , kJ mol^{-1}) at 25 and 45 °C were negative values of (-16.72 and -18.69) and (-14.20 and -16.27) for Cu^{2+} and Ni^{2+} , respectively. This indicated that the Cu^{2+} and Ni^{2+} adsorption on DSB550-3 was thermodynamically feasible and spontaneous [22,39,6]. Moreover, the positive value of

enthalpy changes ΔH° for Cu^{2+} and Ni^{2+} at 25 and 45 °C were 31.46 and 32.99 kJ mol⁻¹, indicated an endothermic process [23]. Furthermore, the positive value of entropy change ΔS° for Cu^{2+} and Ni^{2+} at 25 and 45 °C were 0.162 and 0.158 kJ mol⁻¹ K⁻¹ confirmed an increase in the degree of disorder during the adsorption process at the solid-liquid interface [6].

3.9 Desorption studies

After adsorption, laden biochar with heavy metal ions has the potential to create another environmental problem. This problem may be overcome by the recovery of the heavy metal ions and recycling of the adsorbent for subsequent uses [54]. Desorption studies of laden biochar with metal ions was carried out by mixing metal-laden biochar with an eluent solution. Desorption efficiencies for Cu^{2+} and Ni^{2+} is shown in Fig. 9. Deionized water as eluent resulted in small amount of metal ion desorption (<15%) while HCl showed the maximum desorption efficiency of 57.3% for Cu^{2+} and 68.8% for Ni^{2+} . The results suggested that HCl has the potential to recover copper and nickel ions from biochar adsorption. The same observation was also noticed by other researchers [55].

Fig. 9 Desorption studies of laden biochar DSB550-3 with Cu^{2+} and Ni^{2+} ions

4. Conclusions

The adsorption capacity, kinetics and mechanisms of Ni^{2+} and Cu^{2+} by date seed derived biochar were investigated. The adsorption capacity increased with the pyrolysis temperature and heating time. Optimal adsorption was achieved using biochar prepared at 550 °C and 3 h heating time with particle size range 0.6-1.4 mm at pH 6 and room temperature. Ion exchange accounted for 69% and 72% of the Cu^{2+} and Ni^{2+} ion removal by biochar, respectively. Interaction between the metal ions and the carboxyl and hydroxyl groups on the biochar surface also played important role in the metal ion adsorption. Thermodynamic experiments showed that the adsorption of the metal ions onto the biochar was spontaneous. Column experiments results showed that the biochar had higher adsorption capacity than what was calculated from the batch experiments; this is likely due to surface precipitation resulting from changes in the pH profile during the experiment. Desorption experiments suggested that the biochar can be regenerated, and copper and nickel can be recovered using HCl as elution agent. Compared to biochars prepared from other agricultural waste and woody biomass, date seed derived biochar showed higher capacity for Ni^{2+} and Cu^{2+} adsorption making it a promising low-cost alternative to activated carbon for wastewater treatment.

Based on our results, additional works are still required and recommended to investigate: biochar adsorption/desorption cycles and regeneration; biochar adsorption under dynamic conditions and the cost effectiveness of biochar applications.

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