Single Component Adsorption of Copper (II) and Nickel (II) from Aqueous Solution using Biochar Derived from Date Seed biomass

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Abstract

Biochar has received increasing attention as a potential cost-effective and eco-friendly adsorbent to treat metal-contaminated wastewater. The purpose of this study was to investigate the removal of Cu^{2+} and Ni^{2+} ions from single component aqueous solutions by adsorption onto biochar derived from date seed biomass (DSB). The biochar was prepared through slow pyrolysis process at 550 °C and a heating time of 3 h. Batch experiments were conducted to study the effects of solution pH, contact time, and initial metal ions concentration. Adsorption removal of the heavy metals was found to be pH dependent and the maximum adsorption capacities were achieved at pH 6. The maximum adsorption capacities for single ions were 0.292 and 0.228 mmol/g for Cu^{2+} and Ni^{2+} ions, respectively. Adsorption equilibrium data fitted adequately to the Freundlich isotherm model. The kinetic experimental data were well fitted by the pseudo second-order kinetic model with R^2 values of 0.98 and 0.99 for Cu^{2+} and Ni^{2+} systems, respectively; thus, indicating chemisorption process involving valence forces through the sharing or exchange of electrons. The results showed that date seed derived biochar may be an effective and low-cost adsorbent for the removal of Cu^{2+} and Ni^{2+} ions from aqueous systems.

Keywords: Adsorption, biochar, heavy metal, isotherms, kinetics.

1. INTRODUCTION

Water contamination with heavy metals has received considerable attention worldwide because of their high toxicity and non-biodegradability (Gautam et al. 2014). Considering the harmful effects of heavy metals on human health and the environment, it is important to reduce their concentrations in effluents to limits suitable to the receiving environment. Adsorption is the most adopted method due to its simplicity and convenience (Mohan and Singh 2002). Nevertheless, traditional adsorbents such as activated carbon (AC) are expensive.

Recently, biochar received attention as a cost-effective material for heavy metal adsorption (Pellera et al. 2012; Chen et al. 2011; Tong et al. 2015; Kılıc et al. 2013). Several studies demonstrated that biochars exhibited high adsorption capacity towards heavy metal ions. Tong et al. (2015) found that some biochars were more effective than commercial activated carbon for the removal of Cu^{2+}. Wide ranges of existing literature cover adsorption of different heavy metals onto various biochars (Inyang et al. 2016; Tan et al. 2015). However, to minimize the cost and environmental impacts of biochar production, biochar should be produced from locally available materials such as agricultural waste.

Date palm (*Phoenix dactylifera* L.) is a tropical and subtropical tree that grows in hot and arid regions of the world. In 2014, the total world production of date fruit was 8.897 billion tons (FAO 2014). Seed represents about 10-15% of total date fruit weight (Abu-Jrai et al. 2017). Date seeds are often discarded as a waste material which becomes a burden to the environment in date producing countries. Nevertheless, the chemical constituents of the date seed make it a suitable candidate for the production of high quality biochar (Ahmad et al. 2012). Therefore, the production of biochar may offer a new way to manage and valorize this waste stream. The aim of this study was to evaluate the adsorption behavior of date seed derived biochar at 550 ^oC and heating time of 3 h for Cu^{2+} and Ni^{2+} removal from aqueous phase.

2. MATERIALS AND METHODS

2.1 Biochar preparation and characterization

Date seed biomass was collected from local markets, Brisbane, Australia. Seeds were washed several times with deionized water and dried in an oven at 50 ^oC for 24 h. The dried biomass was placed in covered crucible and purged with N_2 gas and pyrolyzed at temperature of 550^oC for 3h. Further details on biochar preparation and characterization were discussed in our previous works (Mahdi et al. 2015; Mahdi et al. 2016). The biochar produced was gently crushed and sieved to particle size range of 0.6-1.4 mm. Date seed biochar was washed with deionized water to remove impurities (e.g., ash), then oven-dried (105^oC) for 2h, and sealed in airtight container.

2.2 Adsorbate solution

All chemicals used in this study were of analytical grade. The $Cu(NO_3)_2$ $2.5H_2O$ (Ajax Chemical) and $Ni(NO_3)_2$ $6H_2O$ (Scharlau Chemicals) were used to prepare stock solution of 5.0 mM. Then, metal solutions of (0.3-4.0 mM) were prepared by successive dilutions with deionized water. The standard solutions for atomic absorption spectroscopy analysis were freshly prepared before use.

2.3 Batch adsorption isotherm studies

Batch experiments were conducted by mixing 0.1 g of biochar in 10 mL of working solution containing different metal concentrations (0.3-4.0 mM) in 50 ml glass containers. The solution was agitated at 30 rpm and kept at 23 ± 2°C for 24 h. Initial pH was adjusted to pH 6 using 0.1 M NaOH or HCl. Then, the solution was filtered using 0.45 µm Millipore filters. Final metal concentrations of Cu^{2+} and Ni^{2+} were analyzed using Atomic Absorption Spectroscopy (AVANTA-GBC). All adsorption experiments were conducted in triplicate and the average values were reported. The amount of each metal ion adsorbed on the biochar (q_e, mmol/g) was calculated as given in Eq.(1):

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

where, C_o and C_e are initial and equilibrium metal concentrations (mM), V is volume of metal solution (L), and W is amount of biochar (g). The experimental results were fitted using Langmuir and Freundlich isotherms. The non-linear form of the Langmuir equation can be expressed as in Eq.(2):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where C_e is the equilibrium concentration (mM), q_e is the amount of metal ion adsorbed at equilibrium, K_L is the adsorption constant (L/mmol) related to energy of adsorption, q_m is the maximum adsorption capacity (mmol/g). Freundlich isotherm is an empirical model based on adsorption on heterogeneous surface. It can be written as shown in Eq.(3):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

where K_F and n are Freundlich constants, indicating the adsorption capacity and the adsorption intensity, respectively. K_F and n are, respectively, determined from the linear form of Freundlich model using the intercept and slope of plotting lnq_e *vs* lnC_e.

2.3.2 Effect of solution pH

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 the solution was adjusted to the required values by using 0.1 M HCl or NaOH. Briefly, biochar (0.1 g) was placed into 10 mL solution containing 1.0 mM of metal solution and the adsorption equilibrium was attained by shaking mixture at 30 rpm in a shaker for 24 h. The final pH and residual Cu^{2+} and Ni^{2+} in the solutions were determined. The amount of each metal adsorbed (q_e, mmol/g) was determined using Eq.(1). In this experiment, pH values higher than 6 were excluded to avoid precipitation of metal.

2.3.3 Adsorption kinetics

The rate of adsorption of Cu^{2+} and Ni^{2+} uptake was evaluated by mixing 1.0 g of biochar with 100 ml of 1.5 mM metal solution in 250 ml glass vials and the initial pH solution was adjusted to 6. Filtrate samples were withdrawn at specific intervals from 2 to 1440 min for analysis. The amount of metal ion adsorbed on biochars at specific time interval (q_t, mmol/g) was calculated as the difference between their initial and final concentrations as given in Eq.(1). Both pseudo first and second order rate models were used to study the adsorption kinetics. Pseudo first order rate is expressed as follows Eq.(4):

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

where, q_e and q_t are the amount of metal ion adsorbed (mmol/g) at equilibrium and at time, t respectively. k_1 (min^{-1}) is the pseudo first order constant. The values of k_1 and q_e are obtained from the slopes and intercepts of the linear plot of $ln(q_e$ - $q_t)$ against t. A linear pseudo second order kinetic model is expressed by Eq.(5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_t} \quad (5)$$

where k_2 is the equilibrium rate constant of pseudo second order (g (mmol/min). The pseudo-second-order rate constants are obtained from the intercept and the slope of the plot t/q_t versus t.

3. RESULTS AND DISCUSSION

3.1 Effect of solution pH on adsorption

Figure 1 shows the effect of solution pH on Cu^{2+} and Ni^{2+} adsorption onto the biochar. As shown in Figure 1, the highest metal uptake was achieved at pH of 6. Solution pH is a significant factor influencing metal adsorption onto biochar surface due to the effect of pH on surface charge of adsorbent and metal speciation in aqueous solution (Wang et al. 2015). The lower metal uptake at lower pH can be attributed to the higher competition with H^+ ions for adsorption sites. Similar observations were reported for Cu^{2+} and Ni^{2+} ions (Tong et al. 2011; Chen et al. 2011; Pellera et al. 2012). Therefore, subsequent adsorption experiments were performed at pH value of 6.

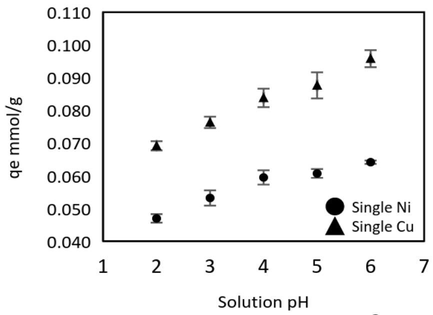

Figure 1. Effect of solution pH on the adsorption of Cu^{2+} and Ni^{2+} onto biochar (room temperature; biochar: solution = 10 g/L; C_o= 1.0 mM)

3.3 Adsorption isotherms

The effect of initial metal concentration (Cu^{2+} and Ni^{2+}) on the amount of metal ion adsorbed by biochar was studied as shown in Figure 2. It was found that the amount of metal ion adsorbed (q_e, mmol g^{-1}) increased with the increasing initial concentration. Similar results were obtained in the systems described in the literature (Liu and Zhang 2009; Zheng et al. 2008; Pellera et al. 2012). The results were fitted to Freundlich and Langmuir isotherms as shown in Figure 2. The Freundlich isotherm fits very well with the experimental data (R^2 = 0.95) and (R^2= 0.96) for Cu^{2+} and Ni^{2+}, respectively. Freundlich and Langmuir isotherms parameters are presented in Table 1. The maximum adsorption capacities of Cu^{2+} and Ni^{2+} ions by biochar were calculated according to Langmuir isotherm to be 0.292 and 0.228 mmol/g, respectively.

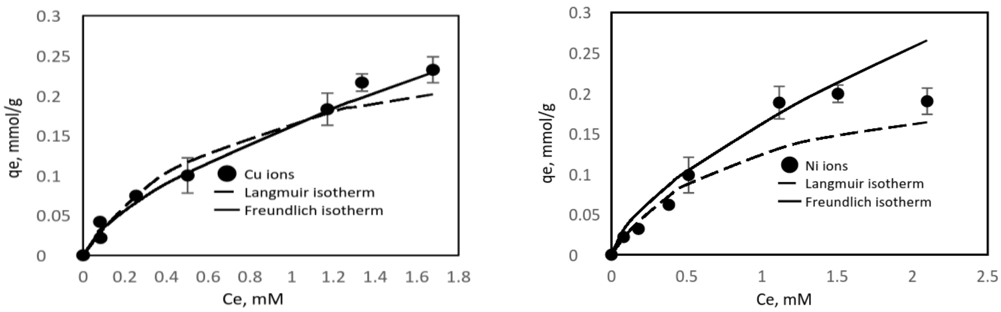

Figure 2. Adsorption isotherms of Cu^{2+} and Ni^{2+} onto date seed biochar

Table 1. Langmuir and Freundlich isotherm constants for the adsorption of Cu^{2+} and Ni^{2+} ions on biochar derived from date seed

Metal	Langmuir isotherm			Freundlich isotherm		
	K_L (L/ mmol)	q_m, (mmol/g)	R^2	K_F (mmol/g) (L/ mmol)$^{1/n}$	n	R^2
Cu^{2+}	1.325	0.292	0.80	0.169	1.475	0.95
Ni^{2+}	1.222	0.228	0.95	0.139	1.326	0.96

Values of the adsorption capacity of Cu^{2+} and Ni^{2+} ion using other adsorbents from the literature are given in Table 2 for comparison. However, this comparison must be treated with caution because of differences in physiochemical properties of adsorbent as well as variation in the experimental conditions. Nevertheless, date seed derived biochar showed high Cu^{2+} and Ni^{2+} uptake compared to other adsorbents as shown in Table 2.

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

Adsorbent	Pyrolysis temperature, (°C)	pH	Ion	q_m (mmol/g)	References
Hard wood char	450	5.0	Cu^{2+}	0.107	Chen et al. (2011)
Pinewood biochar	300 700	6.2	Cu^{2+}	0.070 0.043	Liu et al. (2010)
Almond husk AC	700	5.0	Ni^{2+}	0.524	Hasar (2003)
AC fibres	-	-	Ni^{2+}	0.152	Kadirvelu et al. (2000)
Date seed biochar	550	6.0	Cu^{2+} Ni^{2+}	0.292 0.228	This study

3.5 Adsorption kinetics

Figure 3 shows the adsorption rate of Cu^{2+} and Ni^{2+} onto DSB biochar. It can be seen from the figure that more than 99% saturation was attained within two-hour from the start of the reaction in the case of Cu^{2+}. The reaction rate then slowed down until it reached equilibrium state. This can be attributed to the availability of vacant active adsorption sites which were saturated as the reaction progressed. On the other hand, for Ni^{2+} ions, it was found that more than 33% of saturation was attained within the first hour of reaction. Similar findings were reported by Pellera et al. (2012); Zheng et al. (2008) and El-Ashtoukhy et al. (2008). Adsorption kinetics of Cu^{2+} and Ni^{2+} onto DSB biochar was fitted using pseudo-first order and pseudo-second order models as shown in Figure 3.

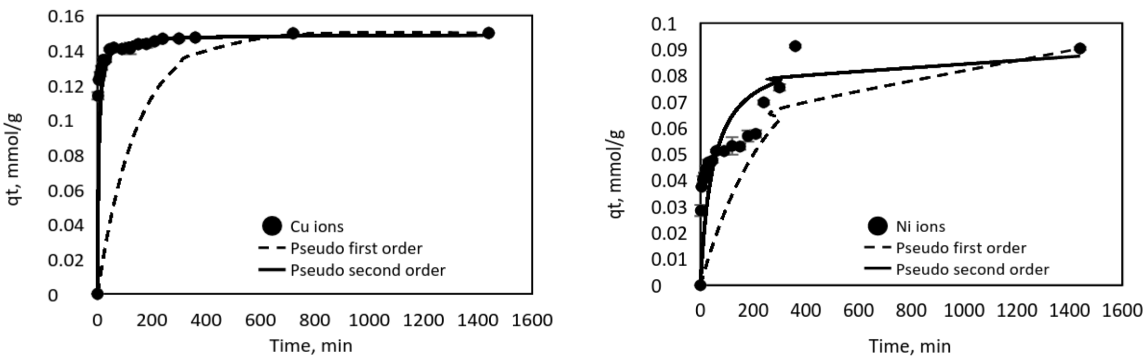

Figure 3. Adsorption kinetics of Cu^{2+} and Ni^{2+} ions onto date seed biochar

The values of calculated q_e, k_1, k_2 and the coefficient of determination R^2 are presented in Table 3. The results showed that pseudo second order model was in good agreement with the experimental values as shown in Table 3. This gives indication that Cu^{2+} and Ni^{2+} ions adsorption by biochar is chemisorption.

Table 3. Adsorption kinetics parameters for of Cu^{2+} and Ni^{2+} onto DSB biochar

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

4. CONCLUSIONS

In this study biochar, date seed derived biochar was evaluated as an alternative low-cost adsorbent for the removal of Cu^{2+} and Ni^{2+} from aqueous solution. Optimum adsorption conditions were determined as a function of solution pH, initial metal ion concentration, and contact time for Cu^{2+} and Ni^{2+} removal. Adsorption equilibrium data fitted very well to the Freundlich isotherm model. The monolayer adsorption capacity of DSB biochar was found to be 0.293 and 0.228 mmol/g for Cu^{2+} and Ni^{2+} ions, respectively. The kinetic of Cu^{2+} and Ni^{2+} ions adsorption on the biochar indicated that the experimental data fitted well to the pseudo second-order kinetic model indicating chemisorption due to valence forces, through the sharing or exchange of electrons. It can be concluded that date seed biochar is an effective, alternative, and low-cost adsorbent precursor for the removal of heavy metals from aqueous solutions.

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