



## Assessment of cadmium ion adsorption capacity in water by biochar produced from pyrolysis of cow dung

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### ABSTRACT

Biochar production from cattle waste and the potential of biochar as an adsorbent for treating pollution are among the hot research topics in recent years. The goal of this study is to evaluate the ability to adsorption  $\text{Cd}^{2+}$  from water of biochar produced from cow dung at varying pyrolysis temperatures (300, 450, and 500°C). The study determined a number of surface-level chemical characteristics of the biochar samples such as total organic carbon (TOC), pH,  $\text{pH}_{\text{pzc}}$ , functional group  $\text{H}^+$ ,  $\text{OH}^-$ , and cation exchange capacity (CEC). Biochar samples were subjected to two different experiments: the first submerged the biochar in  $\text{Cd}^{2+}$  solutions at different concentration (0-132  $\text{mgCd}^{2+} \cdot \text{L}^{-1}$ ) for a fixed 12 h and the second submerged the biochar in  $\text{Cd}^{2+}$  solutions at a fixed concentration of 66  $\text{mgCd}^{2+} \cdot \text{L}^{-1}$  for a varying length of time. Adsorption kinetics and equilibrium analyses were conducted on the samples at the end of the experiments. The  $\text{Cd}^{2+}$  adsorption process of these biochar forms fit Langmuir and Freundlich adsorption models as well as a pseudo-second-order kinetic model. The study concluded that biochar produced from pyrolysis of cow dung could be employed as an adsorbent for the removal of  $\text{Cd}^{2+}$  from water.

**Key words** : adsorption kinetics, biochar,  $\text{Cd}^{2+}$ , equilibrium, cow dung

### 1. INTRODUCTION

The detrimental effect of heavy metals and their compounds on aquaculture and people is a great concern in environmental research circles in recent years[1]. Among these metals, Cd is an element commonly found in wastewater from mining, metallurgy, electro-coating, and oil-refining industries[2]. While extraneous in nature, Cd is a carcinogen to bioforms even at low concentrations and, therefore, an effective and economical solution to remove  $\text{Cd}^{2+}$  from water is of utmost urgency. A number of techniques have been developed to tackle this issue including chemical precipitation, membrane filtration, ion exchange and adsorption[3].

Among them, adsorption is a popular choice to remove  $\text{Cd}^{2+}$  from wastewater[2]. Furthermore, adsorption using biochar is considered advantageous in terms of environmental friendliness and cost as biochar is widely available in large quantities[2]. Biochar is produced from agricultural byproduct via anaerobic pyrolysis at

temperatures above 300°C. Studies into adsorption mechanics have shown that a number of surface-level characteristics heavily influenced the adsorption efficacy of biochar. These characteristics of biochar are heavily influenced by the conditions of the pyrolysis process such as temperature and processing duration[1]. Nowadays, researches on biochar originating from cow dung, a main ranching byproduct in Cu Chi District (Ho Chi Minh City), in this particular application remain few and far between. Therefore, the goal of this study is to survey the influence of pyrolysis temperature on the efficiency of biochar production and the influence of surface-level characteristics on the  $\text{Cd}^{2+}$  adsorption kinetics of biochar. In addition, the effects of the application of biochar to remove  $\text{Cd}^{2+}$  pollution in water were also assessed.

### 2. MATERIALS AND METHODS

#### Materials

Cow dung samples were taken in a cow farm in Cu Chi District, Ho Chi Minh City (Vietnam). The location of the sampling site is 10°58'17,8" N; 106°34'29,8" E. The samples were let to dry out and were cut into smaller portions under 5mm. They were then baked in an oven at 60°C for 24 h[4].

#### Chemicals

All chemicals used in the study were of analytical-grade (Merck) including  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , KCl,  $\text{HNO}_3$ , NaOH,  $\text{H}_2\text{O}_2$ . Aqueous solutions of  $\text{Cd}^{2+}$  were prepared as a stock solution at 1000  $\text{mg Cd}^{2+} \cdot \text{L}^{-1}$ . Distilled water used in the experiments was produced with an ultra-clean water purifier Model: EASYpure II RF from Thermo Scientific – USA.

#### Experiment procedure

The prepared cow dung samples underwent the pyrolysis in a Nabertherm P330 furnace with the following temperature settings: 300, 450, and 600°C (temperature is set depending on the running experiment). The heating rate was set to 10°C.min<sup>-1</sup>. Once the desired temperature was reached, the temperature was kept constant for 2 h and the samples were let to cool in the oven overnight. The biochar was then pressed through a plastic sieve (hole diameter of 1mm) to make homogeneous and were stored separately in polyethylene (PE) containers in dark at 4°C[5].

Analyses were conducted on these biochar samples to determine surface-level characteristics such as pH,  $pH_{pzc}$ [6]. Total organic carbon (TOC)[7], functional group  $H^+$ ,  $OH^-$  [8] and cation exchange capacity (CEC) based on [9]. These biochar samples were also employed in subsequent adsorption kinetics and adsorption equilibrium surveys.

The survey on the  $Cd^{2+}$  adsorption equilibrium of biochar was conducted based on a study of [10]. The experiment was performed in 60 mL polypropylene tubes containing a mixture of 0.25g biochar and 25mL diluted  $Cd^{2+}$  solution. The diluted  $Cd^{2+}$  solution was prepared by combining the  $Cd^{2+}$  stock solution ( $1000\text{ mg.L}^{-1}$ ) with KCl 0.01M solution. The concentration of the diluted  $Cd^{2+}$  solution varied between 0-132  $\text{mg.L}^{-1}$  depending on the running experiment. A GFL3015 shaker was employed to agitate the polypropylene tube at 100 rpm for 12 h, which is the time to reach  $Cd^{2+}$  adsorption equilibrium at room temperature based on preliminary experiments. The pH level was not adjusted during this experiment ranges from 5.0-5.5 during this experiment. The solid settlement was separated from the mixture by a DLAB DM0636 centrifuge at 4000 rpm for 15 min. Then, the remaining solution was filtered through a  $0.22\mu\text{m}$  filter and was immediately acidified to  $pH < 2$  using concentrated  $HNO_3$  in preparation for a  $Cd^{2+}$  analysis. by ICP-OES

**Calculation of biochar recovery efficiency %H:**

$$\%H = \frac{m_b}{m_0} * 100 \quad (1)$$

Where:

- $m_0$  (g): initial amount of cow dung before pyrolysis
- $m_b$  (g): amount of biochar recovered after pyrolysis

**Calculation of the biochar's  $pH_{pzc}$ :**

$$\Delta pH = (pH_f - pH_i) \quad (2)$$

Where:

- $pH_i$ : initial pH value
- $pH_f$ : pH value after biochar is added to the 0.01 M KCl solution
- The value  $pH_{pzc}$  was determined at the point where the plot  $\Delta pH.pH_i^{-1}$  intersected the line  $\Delta pH=0$ [6].

**Calculation of the maximum adsorption capacity at equilibrium  $q_0$ :**

$$q_i = \frac{(C_0 - C_i).V}{m} \quad (3)$$

Where:

- $C_0$  ( $\text{mg.L}^{-1}$ ): concentration of initial  $Cd^{2+}$  solution
- $C_i$  ( $\text{mg.L}^{-1}$ ): concentration of  $Cd^{2+}$  solution of sample i at equilibrium time
- V (L): volume of  $Cd^{2+}$  solution
- m (g): mass of biochar
- $q_i$  ( $\text{mg.g}^{-1}$ ):  $Cd^{2+}$  adsorption capacity at equilibrium of sample i

machine. Langmuir and Freundlich adsorption isotherms models were used in evaluating the suitability of experimental data [10].

The adsorption kinetics survey was similarly performed in 60 mL polypropylene tubes by mixing 0.25g biochar with 25 mL of 0.01M KCl solution containing  $66\text{mg.L}^{-1} Cd^{2+}$ . They were also agitated by GFL3015 shaker at around 100 rpm. But, instead of a fixed 12 h as in the adsorption equilibrium survey, the duration of the agitation was taken at different times depending on the running experiment. The rest of the procedure followed as in the previous survey with the solid settlement being separated from the mixture by a DLAB DM0636 centrifuge (4000 rpm, 15 min), the remaining solution being filtered through a  $0.22\mu\text{m}$  filter before being acidified ( $pH < 2$ ) using concentrated  $HNO_3$  in preparation for a  $Cd^{2+}$  analysis by ICP-OES. Pseudo first- and second-order kinetic models were used in evaluating the suitability of experimental data and calculating the kinetic constants [10].

**Calculation**

The important parameters for the subsequent analyses were determined from the above experiments based on the formula and calculations described in this section.

The adsorption capacity  $q_i$  above was then plugged into Langmuir adsorption isotherm equation in order to calculate the maximum adsorption capacity  $q_0$  [11]:

$$\frac{1}{q_i} = \frac{1}{K_L q_0} \frac{1}{C_i} + \frac{1}{q_0} \quad (4)$$

Where:

- $q_0$  ( $\text{mg.g}^{-1}$ ):  $Cd^{2+}$  maximum adsorption capacity at equilibrium
- $K_L$  ( $\text{L.mg}^{-1}$ ): Langmuir adsorption constant.

The above equation has the form of  $y = ax + b$  and therefore could be solved by curve fitting  $y = \frac{1}{q_i}$  and  $x = \frac{1}{C_i}$  to yield  $q_0$ .

The suitability of the adsorption isotherms was then evaluated by comparing the result of Langmuir's model to that of Freundlich adsorption isotherm equation [11]

$$q = y/m = K_F C_i^{\frac{1}{n_F}} \quad (5)$$

Or:

$$\text{Log } q_i = \frac{1}{n_F} \text{log } C_i + \text{log } K_F \quad (6)$$

Where:

- $n_F$ : Freundlich isotherm constant representing adsorption intensity of  $Cd^{2+}$ .
- $K_F$ : Freundlich adsorbent constant representing adsorption capacity of  $Cd^{2+}$ .

This equation also has the form of  $y = ax + b$  and as all the parameters are known, the plot of  $\text{log } q_i$  against  $\text{log } C_i$  can be drawn. The shape of this plot is then compared to that drawn from experimental data.

**Calculation of adsorption kinetic coefficients:**

In order to evaluate the adsorption kinetic, the study employed pseudo first- and second-order models whose polynomial coefficients must be determined[11]. The models employed were the following:

Pseudo first-order kinetic equation:

$$\ln(q_e - q_t) - \ln q_e = -k_1 t \quad (7)$$

Or:

$$\ln(q_e - q_t) = -k_1 t + \ln q_e \quad (8)$$

Curve fitting  $y = \ln(q_e - q_t)$  and  $x = t$  yields the coefficients for this model.

Pseudo second-order kinetic equation:

$$\frac{1}{q_t} = \frac{1}{t} \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (9)$$

Where:

$q_e$ : adsorption capacity at equilibrium (mg.g<sup>-1</sup>)  
 $q_t$ : the adsorption capacity at time t (mg.g<sup>-1</sup>)  
 $k_1$  (min<sup>-1</sup>) và  $k_2$  (g.mg<sup>-1</sup>.min<sup>-1</sup>): constants of pseudo first-order and pseudo second-order kinetic  
 t (min): time adsorption.

Curve fitting  $y = \frac{1}{q_t}$  and  $x = \frac{1}{t}$  yields the necessary coefficients for this model.

**Statistical analysis**

Control and replicate samples (n=3) were employed in order to minimize error sources. The analysis evaluated the accuracy and precision of the parameters calculated using the methods described in the previous section. The statistical analysis software SPSS 20.0 was used for determining the fitness of data through correlation test and for constructing a mathematical model through curve-fitting / regression. In addition, homogeneity was also evaluated by Levene’s test, Tukey’s test post hoc (Sig.>0.05) and Tamhane’s T2 (Sig.<0.05)[12].

**3.RESULTS AND DISCUSSIONS**

**3.1.Effect of pyrolysis temperature on recovery efficiency and surface-level chemical characteristics of biochars**

The results showed that pyrolysis temperature has an effect on biochar recovery efficiency. Table 1 showed that when the temperature increases from 300 to 450 and 600°C, the recovery efficiency of biochars decreases to 63.0, 51.1, and 49.4%

respectively. This issue due to the reduction of volatile substances in biochar[13]. The results are consistent with those from Yavari et al. (2016) who had reported a decrease in recovery efficiency when pyrolysis temperature rises from 300 to 700°C[14]. In their study, the recovery efficiency at 300°C is 59.5% and 37.9% at 700°C[14], [15].

**Table1:** Recovery efficiency and surface-level characteristics of biochars by pyrolysis temperature

t °C	% H	pH	pHpzc	mmolH.g <sup>-1</sup>	mmolOH.g <sup>-1</sup>	%TOC	CEC. mmol.kg <sup>-1</sup>
300	63±1.7 <sup>b</sup>	7.91±0.03 <sup>a</sup>	7.4±0.1 <sup>a</sup>	5.1±0.1 <sup>b</sup>	11.3±0.1 <sup>a</sup>	36.7±5.3 <sup>b</sup>	113±12 <sup>a</sup>
450	51.1±0.6 <sup>a</sup>	9.34±0.03 <sup>b</sup>	8.8±0.1 <sup>b</sup>	4.4±0.3 <sup>ab</sup>	11.6±0.1 <sup>b</sup>	61.2±0.5 <sup>c</sup>	144±12 <sup>b</sup>
600	49.4±0.1 <sup>a</sup>	9.35±0.22 <sup>ab</sup>	9.1±0.1 <sup>c</sup>	3.7±0.2 <sup>a</sup>	12.4±0.2 <sup>c</sup>	16.6±1.8 <sup>a</sup>	188±12 <sup>c</sup>

*Different letters in a column show a statistically significant difference (p<0.05)*

The results in Table 1 showed that the total organic carbon (TOC) content increased from 36.7% at 300°C to 61.2% at 450°C. This is related to the production of organic acids and phenolic compounds due to thermal decomposition of cellulose and hemicelluloses compounds in the pyrolysis temperature range of the study Yavari et al., (2016)[14]. A sharp decrease of 16.6% was observed at 600°C and this is explained by products of the cellulose and lignin in biochar being completely decomposed in the temperature range of 280-500°C[14].

When the pyrolysis temperature increased from 300 to 450 and 600°C, the pH level of biochar also increased from 7.9 to 9.34 and 9.35, respectively. This is due to the partial transformation of organic matters into ashes, which releases alkali salts and increases the pH level of biochar[10].

The results also showed that pHpzc is proportional to pyrolysis temperature. pHpzc plays an important role

in the choice of optimal pH level for adsorption experiments and reveals the adsorption kinetics. When the pH level in the test solution falls below pHpzc, the electrical potential on the surface of biochar becomes positive due to the protonization of acidic functional groups. This inhibits the adsorption of metals due to the pushing interactions between ions and functional groups[3]. On the other hand, precipitation takes place when the pH level rises above pHpzc. As the biochar samples produced from cow dung had pH level >pHpzc, they possessed negative electrical potential and heightened reactivity with metal ions[16].

**Table2:** Cross-correlation analysis of surface-level characteristics in biochar

	t°C	pH	pHpzc	mmolH <sup>+</sup> .g <sup>-1</sup>	mmolOH <sup>-</sup> .g <sup>-1</sup>	% H	% TOC	CEC. mmol.kg <sup>-1</sup>
t°C	1	0.860**	0.920**	-0.953**	0.942**	-0.908**	-0.445	0.946**
pH	0.860**	1	0.979**	-0.815**	0.666	-0.973**	0.057	0.745*
pHpzc	0.920**	0.979**	1	-0.905**	0.744*	-0.992**	-0.066	0.820**
mmolH <sup>+</sup> .g <sup>-1</sup>	-0.953**	-0.815**	-0.905**	1	-0.865**	0.885**	0.384	-0.867**
mmolOH <sup>-</sup> .g <sup>-1</sup>	0.942**	0.666	0.744*	-0.865**	1	-0.725*	-0.689*	0.933**
% H	-0.908**	-0.973**	-0.992**	0.885**	-0.725*	1	0.068	-0.806**
% TOC	-0.445	0.057	-0.066	0.384	-0.689*	0.068	1	-0.514
CEC(mmol.kg <sup>-1</sup> )	0.946**	0.745*	0.820**	-0.867**	0.933**	-0.806**	-0.514	1

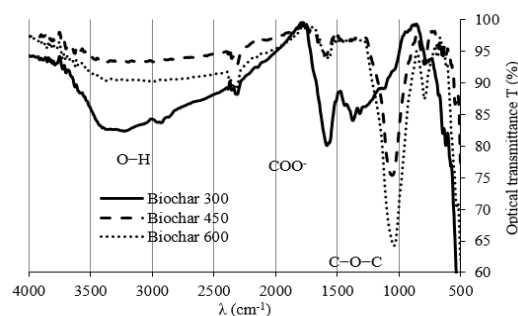
\*\* The correlation is significant at 0.01; \*The correlation is significant at 0.05

In other words, as the pyrolysis temperature increases, the number of H<sup>+</sup> on the biochar's surface decreases correspondingly to the range of 5.1-3.7 mmolH<sup>+</sup>.g<sup>-1</sup>. The decrease in mmolH<sup>+</sup>.g<sup>-1</sup> was statistically significant at 300 and 600°C while the increase in mmolOH<sup>-</sup> was significant at all three temperatures. This observation matched the conclusion reached by Mukherjee *et al.*(2011) [17] and Yang *et al.*(2019)[18] in regard to biochar originating from plant. The CEC of biochar increased to 113-188 mmol.kg<sup>-1</sup> when the pyrolysis temperature increased.

Correlation analysis showed that pyrolysis temperature is proportional and strongly correlated to surface-level chemical characteristics of the biochar samples such as mmol OH<sup>-</sup>, pH<sub>pzc</sub>, and pH (Table 2). Moreover, it also showed that the inverse proportionality between pyrolysis temperature and mmol H<sup>+</sup> (as well as recovery efficiency) is strongly correlated while that between temperature and TOC is weakly correlated. TOC has almost no correlation with other factors except for a moderate downhill relationship with OH<sup>-</sup>. Meanwhile, CEC has a positive relationship with pyrolysis temperature.

FTIR spectroscopy was used to determine functional groups in biochar samples. The results from the analysis on a FT/IR-4700 type A spectrometer (Figure 1), showed a peak at 3500-3000 cm<sup>-1</sup> for biochar produced at 300°C. This suggests the presence of a large -OH functional groups[19]. -OH group gradually decreases for

biochar produced at 450 and 600°C. The peak at 1590-1520 cm<sup>-1</sup> happened due to COO<sup>-</sup> bonds. The spectra's intensity here is reduced when the temperature increases. The peak at 1160-1020 cm<sup>-1</sup> is speculated to be caused by the vibration of C-O-C bonds of polysaccharide or carbonate (CO<sub>3</sub><sup>2-</sup>) compounds[16]. These bonds are formed when the temperature increases. Figure 1 matches the conclusion of a previous study, which suggests that biochar produced at high pyrolysis temperatures are characterized by strong carbon-carbon bonds and have high stability as a result of their aromatic hydrocarbons qualities[20]. The appearance of the peak at 2311 cm<sup>-1</sup> in biochar produced at 450 and 600°C is speculated to be caused by the vibration of C≡C bonds or by carbon dioxide.

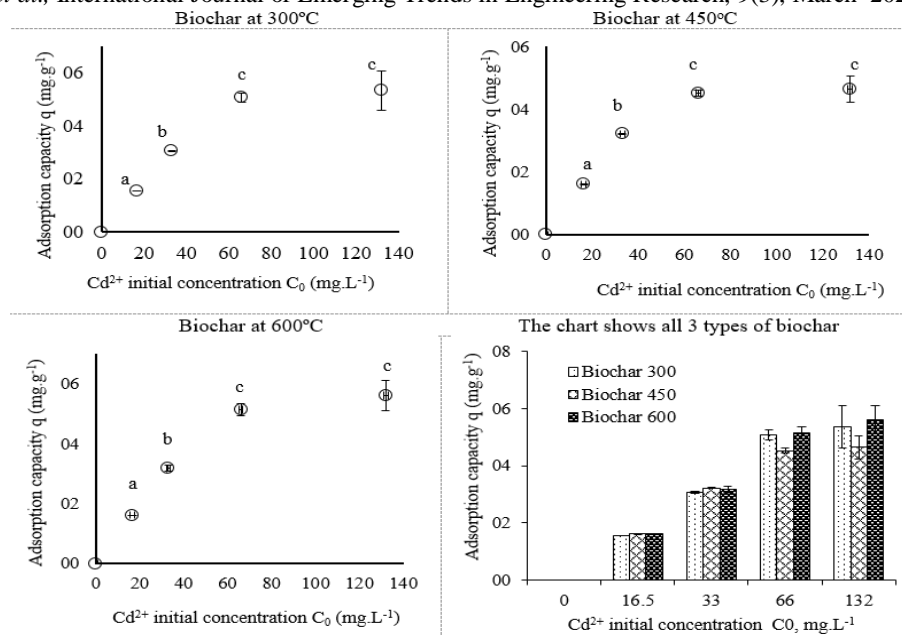


**Figure 1:** FTIR spectra of biochar produced from pyrolysis at 300, 450 and 600°C

**3.2.Effect of pyrolysis temperature on Cd<sup>2+</sup> adsorption equilibrium of biochar**

The investigation of Cd<sup>2+</sup> adsorption equilibrium of three biochar samples produced at different pyrolysis temperatures (300, 450 and 600°C) showed that the adsorption capacity rises in proportion to the initial

concentration C<sub>0</sub> of Cd<sup>2+</sup> regardless of the pyrolysis temperature. In specific, when C<sub>0</sub> increases from 0 to 132 mgCd<sup>2+</sup>.L<sup>-1</sup>, the adsorption capacity rises to 5.3, 4.6, 5.6 mg.g<sup>-1</sup>, respectively and has reached saturated adsorption state (Figure 2).



**Figure 1:** Adsorption capacity Cd<sup>2+</sup> (mg.g<sup>-1</sup>) vs C<sub>0</sub> (mg.L<sup>-1</sup>) at different pyrolytic temperatures. Different letters represent statistically significant differences

The calculated parameters for an adsorption isotherm equation yielded a good fit for Langmuir's model with the Chi-square R<sup>2</sup> values 0.99, 0.93, and 0.96 respectively. The maximum adsorption capacity was calculated to be 5.81, 5.12 and 5.88 mg.g<sup>-1</sup> respectively and these values approximated the data gathered from experiments. The result indicated that the Cd<sup>2+</sup> adsorption on the biochar's surface is homogeneous in terms of energy. Experimental data also matched Freundlich's model with the Chi-square correlation value R<sup>2</sup> ranged from 0.83 to 0.91 (Table 3). In addition, the Freundlich isotherm constant n<sub>F</sub> representing adsorption intensity (also known as surface heterogeneity) and the degree of adsorption in this study are calculated to be greater than 1, with the values of 3.86, 6.25, 4.67 respectively for the three biochar samples. As n<sub>F</sub> > 1 indicates high adsorption[21], this means these three samples are highly adsorptive of Cd<sup>2+</sup> given the experiment's conditions. According to Xu et al. (2013), the adsorption of metal ions in solutions are influenced by surface-level chemical characteristics and precipitation-inducing reactions. Furthermore, a study by Han et al. (2017)[22] suggested that the presence of electrostatic adsorption and functional groups might also be a factor in Cd<sup>2+</sup> adsorption. The experimental results in this study indicated the presence of functional groups such as -COOH and -OH on the surface of biochar samples (Table 1 and Figure 1) and, as these functional groups can interact with Cd<sup>2+</sup> to create complex or precipitation on the

surface, they might indeed play a role in Cd<sup>2+</sup> adsorption equilibrium.

In addition to adsorption by electrostatic interactions, adsorption by O-H bonds was also confirmed by FT/IR-4700 type A spectrometer (Figure 1) analyses. Specifically, biochar produced at 300°C exhibited this form of adsorption the strongest as the O-H bonds that create complexes within the solution are converted to weaker C-O bonds at 450°C. As C-O-C bonds are weaker, the maximum adsorption capacity q<sub>0</sub> is also reduced accordingly Xu et al., (2013)[10]. However, the adsorption capacity increased again with biochar produced at 600°C. This is consistent with q of experiment of the study by Kolodynska et al. (2012)[11], which found biochar originating from cow dung has better Cd<sup>2+</sup> adsorption when produced at 600°C than when produced at 400°C. It is speculated that this increase was caused by the increase in pH level, which in turn promotes precipitation on the biochar's surface (Figure 1). It is shown in this study that the maximum Cd<sup>2+</sup> adsorption capacity of these three biochar samples ranged from 5.12 to 5.88 mg.g<sup>-1</sup>. This is much lower than the result of Kolodynska et al. (2012), in which the value ranged from 49.06 to 51.28 mg.g<sup>-1</sup>. This can be explained by the lower initial concentration in this study (0-132 mg.L<sup>-1</sup>) compared to the study of Kolodynska et al. (2012) (112-2800 mg.L<sup>-1</sup>) where hydrolytic precipitation processes had occurred and changed the adsorption capacity[11]

**Table3:**Parameters of Cd<sup>2+</sup>adsorption isotherm models

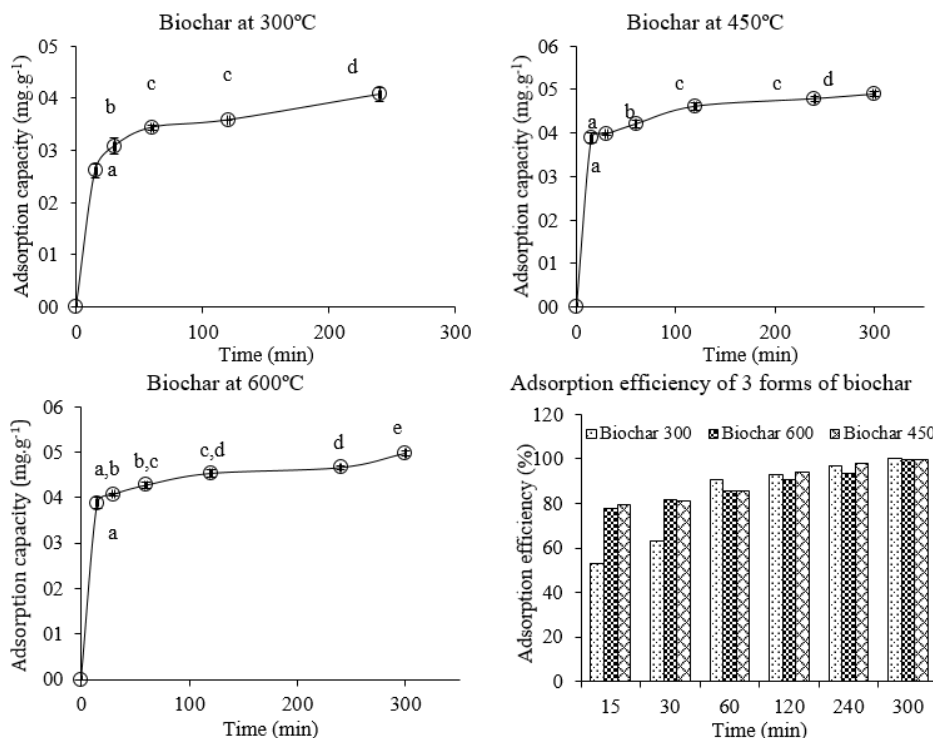
Models	Pyrolytic temperature	Parameters		R <sup>2</sup>	Q <sub>max</sub> of experiment, mg.g <sup>-1</sup>
Langmuir	Biochar 300°C	q <sub>0</sub> (mg.g <sup>-1</sup> )=5.81	K <sub>L</sub> =0.44	0.99	5.3
	Biochar 450°C	q <sub>0</sub> (mg.g <sup>-1</sup> )=5.12	K <sub>L</sub> =1.67	0.93	4.6
	Biochar 600°C	q <sub>0</sub> (mg.g <sup>-1</sup> )=5.88	K <sub>L</sub> =1.46	0.96	5.6
Freundlich	Biochar 300°C	n <sub>F</sub> =3.86	K <sub>F</sub> =2.05	0.83	5.3
	Biochar 450°C	n <sub>F</sub> =6.25	K <sub>F</sub> =2.54	0.91	4.6
	Biochar 600°C	n <sub>F</sub> =4.67	K <sub>F</sub> =2.55	0.89	5.6

**3.3.Effect of pyrolysis temperature on Cd<sup>2+</sup> adsorption kinetic of biochar**

Cd<sup>2+</sup> adsorption increased sharply in a first hour for all three biochar samples produced at 300, 450, 600°C (Figure 3). After that, the adsorption process slowed down and reached equilibrium after 2 h from the start of the experiment. The adsorption capacity q<sub>t</sub> reached 53.2, 79.2, and 77.7% in the first 15 min and the adsorption capacity at equilibrium q<sub>e</sub> is achieved at 93.1, 94.1, and 90.7% in 2 h respectively. In addition, the variance of Cd<sup>2+</sup> adsorption capacities at equilibrium after 2 h indicated no statistical significance between the three biochar samples (Figure 3).

One-way ANOVA on the adsorption kinetic using a pseudo first-order model (Table 4) showed that the correlation coefficients R<sup>2</sup> fell in the range from 0.83 to 0.99. However, the calculated q<sub>e</sub> did not match the experimental value; the calculated q<sub>e</sub> values for the three biochar samples were 1.84, 1.98, and 0.94 mg.g<sup>-1</sup> while the experimental values were found to

be 4.8, 4.9, and 5.0 mg.g<sup>-1</sup>, respectively. Therefore, it is safe to conclude that the pseudo first-order model was not suitable for explaining the Cd<sup>2+</sup> adsorption kinetic of the biochars in this research. This result was identical to that of Kolodynska *et al.* (2012), which also demonstrated that the pseudo first-order model was not suitable due to the difference between the calculated and experimental values [11]. On the other hand, one-way ANOVA on the adsorption kinetic using a pseudo second-order model (Table 4) yielded a strong correlation (R<sup>2</sup> coefficients 0.8-0.95) and the calculated q<sub>e</sub> matched that from the experiments. Hence, it was concluded that the pseudo second-order kinetic model appropriately explained Cd<sup>2+</sup> adsorption kinetic of the biochar samples in this research. That means the kinetic process is influenced by the chemical adsorption [11],[23]. The value of k<sub>2</sub> increased slightly from 0.013 to 0.072 g.mg<sup>-1</sup>.min<sup>-1</sup> when the pyrolysis temperature increased from 300 to 600°C, indicating a faster adsorption rate [11].



**Figure2:** Effect of the contact time on Cd<sup>2+</sup> adsorption of the biochar forms. Different letters represent statistically significant differences

**Table4:**Parameters of Cd<sup>2+</sup> adsorption kinetic on biochar

Models	Pyrolytic temperature	q <sub>e</sub> (mg.g <sup>-1</sup> )	Kinetic constant	q <sub>e</sub> of experiment. mg.g <sup>-1</sup>	R <sup>2</sup>
Pseudo first-order	Biochar 300°C	1.84	k <sub>1</sub> (1.min <sup>-1</sup> )= 0.012	4.8	0.83
	Biochar 450°C	1.58	k <sub>1</sub> (1.min <sup>-1</sup> )= 0.015	4.9	0.91
	Biochar 600°C	0.94	k <sub>1</sub> (1.min <sup>-1</sup> )=0.013	5.0	0.99
Pseudo second-order	Biochar 300°C	5.11	k <sub>2</sub> (g.mg <sup>-1</sup> .min <sup>-1</sup> )= 0.013	4.8	0.95
	Biochar 450°C	4.73	k <sub>2</sub> (g.mg <sup>-1</sup> .min <sup>-1</sup> )= 0.055	4.9	0.8
	Biochar 600°C	4.60	k <sub>2</sub> (g.mg <sup>-1</sup> .min <sup>-1</sup> )= 0.072	5.0	0.9

#### 4.CONCLUSION

In general, the temperature at which the biochar was pyrolyzed has a strong proportional correlation with the biochar's surface-level chemical characteristics such as mmolOH, pH<sub>pzc</sub>, pH, CEC and a weak proportional correlation with TOC. The maximum Cd<sup>2+</sup> adsorption capacities at pyrolysis temperatures 300, 450 and 600°C were determined to be as follows: 5.81, 5.12, 5.88 mg.g<sup>-1</sup>. Both Langmuir and

Freundlich adsorption isotherm models matched the observed Cd<sup>2+</sup> adsorption process in the experiments. A pseudo second-order model is sufficient in representing the Cd<sup>2+</sup> adsorption process. Based on the aforementioned results, the biochar produced from cow dung is viable as an adsorbent for Cd<sup>2+</sup> removal from water and the pyrolysis temperature of the biochar production has a negligible impact on the adsorption capacity of biochar.

#### REFERENCES

- [1] Z. Zhou, Z. Xu, Q. Feng, D. Yao and J. Yu, "Effect of pyrolysis condition on the adsorption mechanism of lead, cadmium and copper on tobacco stem biochar," *Journal of Cleaner Production*, vol. 187, pp. 1-26, 2018.
- [2] Chen, Z., Zhang, J., Huang, L., Yuan, Z., Li, Z., Liu, M., "Removal of Cd and Pb with biochar made from dairy manure at low temperature," *Journal of Integrative Agriculture*, vol. 18(, no. 1, pp. 201-210. [https://doi.org/10.1016/S2095-3119\(18\)61987-2](https://doi.org/10.1016/S2095-3119(18)61987-2), 2019.
- [3] H. N. Tran, S.-J. You and H.-P. Chao, "Effect of pyrolysis temperatures and times on the adsorption of cadmium onto orange peel derived biochar," *Waste Management & Research*, vol. 34, no. 2, p. 129–138, 2016.
- [4] N. V. Phuong, N. T. C. Nhung and L. T. M. Ngoc, "Equilibrium and kinetic of copper adsorption on livestock waste derived biochar," *Journal of Food Science and Technology*, vol. 18, no. 2, pp. 78-88, 2019.
- [5] G. Yoo, H. Kim, J. Chen and Y. Kim, "Effects of Biochar Addition on Nitrogen Leaching and Soil Structure following Fertilizer Application to Rice Paddy Soil," *Soil Science Society of America Journal*, vol. 78, no. 3, pp. 852-861, 2014.
- [6] T. T. Tu, "Physical and chemical characterization of biochar derived from rice husk," *Journal of Science - Hue university*, vol. 120, no. 6, pp. 233-247, 2016.
- [7] TCVN 8941, "Soil quality - Determination of total organic carbon - Walkley Black method," Ministry of natural resource and environment, 2011.
- [8] W. Cheung, S. Lau, S. Leung, A. Ip and G. McKay, "Characteristics of Chemical Modified Activated Carbons from Bamboo Scaffolding," *Chinese Journal of Chemical Engineering*, vol. 20, no. 3, pp. 515-523, 2012.
- [9] ISO 11260, "Soil quality - Determination of effective cation exchange capacity and base saturation level using barium chloride solution.," ISO, 1994.
- [10] X. Xu, X. Cao, L. Zhao and H. Wang, "Removal of Cu, Zn, and Cd from aqueous solutions by the dairy manure-derived biochar," *Environ Sci Pollut Res*, vol. 20, p. 358–368, 2013.
- [11] D. Kolodynska, R. Wnetrzak, J. Leahy, H. M.H.B., W. Kwapinski and Z. Hubicki, "Kinetic and adsorptive characterization of biochar in metal ions removal," *Chemical Engineering Journal*, vol. 197, p. 295–305, 2012.
- [12] J. Xie, X. Sun, D. Yang and R. Cao, "Combined toxicity of cadmium and lead on early life stages of the Pacific oyster, *Crassostrea gigas*," *ISJ - Invertebrate Survival Journal*, vol. 14, pp. 210-220, 2017.
- [13] S. Joseph, C. Peacocke, J. Lehmann and P. Munroe, **Biochar for Environmental Management: Science and Technology**, J. Lehmann and S. Joseph, Eds., London: Earthscan, 2009.
- [14] S. Yavari, A. Malakahmad and N. B. Sapari, "Effects of production conditions on yield and physicochemical properties of biochars produced from rice husk and oil palm empty fruit bunches," *Environmental*

- Science and Pollution Research*, vol. 23, no. 18, pp. 1-13, 2016.
- [15] M.-E. Lee, J. H. Park and J. W. Chungg, "**Adsorption of Pb(II) and Cu(II) by Ginkgo-Leaf-Derived Biochar Produced under Various Carbonization Temperatures and Times,**" *Int J Environ Res Public Health*, vol. 12, p. 14, 2017.
- [16] Y. Ding, Y. Liu, S.liu, Z. Li, X. Tan, X. Huang, G. Zeng, Y. Zhou, B. Zheng and X. Cai, "**Competitive removal of Cd (II) and Pb (II) by biochars produced from water hyacinths: performance and mechanism,**" *RSC Advances*, pp. 1-28, 2016.
- [17] Mukherjee, A., Zimmerman, A.R., Harris, W., "Surface chemistry variations among a series of laboratory-produced biochars," *Geoderma*, pp. 163(3-4), 247-255., 2011.
- [18] X. Yang, S. Zhang, M. Ju and L. Liu, "**Preparation and Modification of Biochar Materials and their Application in Soil Remediation,**" *Applied Sciences*, pp. 2-25, 2019.
- [19] Y. K. Kiran, A. Barkat, C. Xiao-qiang, F. Ying, P. Feng-shan, T. Lin and Y. X. -e, "**Cow manure and cow manure-derived biochar application as a soil amendment for reducing cadmium availability and accumulation by Brassicachinensis L. in acidic red soil,**" *Journal of Integrative Agriculture*, vol. 16, no. 3, p. 725–734, 2017.
- [20] B. Singh, M. C. Arbestain and J. Lehmann, **Biochar : a guide to analytical methods**, B. Singh, M. Camps-Arbestain and J. Lehmann, Eds., CRC Press/Taylor and Francis Group, LLC, 2017.
- [21] A. Khalil, N. Sergeevich and V. Borisova, "**Removal of ammonium from fish farms by biochar obtained from rice straw: Isotherm and kinetic studies for ammonium adsorption,**" *Adsorption Science & Technology*, vol. 36, no. 5-6, pp. 1294-1309, 2018.
- [22] L. Han, H. Sun, K. S. Ro, K. Sun and J. A. Libra, "**Removal of antimony (III) and cadmium (II) from aqueous solution using animal manure-derived hydrochars and pyrochars,**" *Bioresource Technology*, vol. 234, pp. 77-85, 2017.
- [23] X. Cui, Y. Yao, S. Fang and T. Li, "**Potential mechanisms of cadmium removal from aqueous solution by Canna indica derived biochar,**" *Science of The Total Environment*, vol. 562, no. 15, pp. 517-525, 2016.