

**Electro-assisted adsorption of heavy metals from aqueous solutions by biochar**

Author

Mahdi, Zainab, El Hanandeh, Ali, Jimmy Yu, Qiming

Published

2020

Journal Title

Water Science & Technology

Version

Accepted Manuscript (AM)

DOI

[10.2166/wst.2020.163](https://doi.org/10.2166/wst.2020.163)

Rights statement

© IWA Publishing 2020. This is the author-manuscript version of this paper. The definitive peer-reviewed and edited version of this article is published in Water Science and Technology 2020, 81 (4), pp. 801-812, <https://doi.org/10.2166/wst.2020.163> and is available at [www.iwapublishing.com](http://www.iwapublishing.com)

Downloaded from

<http://hdl.handle.net/10072/395547>

Griffith Research Online

<https://research-repository.griffith.edu.au>

# **Electro-assisted Adsorption of Heavy Metals from Aqueous Solutions by Biochar**

Zainab Mahdi <sup>a,\*</sup>

<sup>a</sup> School of Engineering and Built Environment, Nathan campus, Griffith University, Nathan QLD 4111, Australia

<sup>\*</sup>(Corresponding author) [Zainab.mahdi@griffithuni.edu.au](mailto:Zainab.mahdi@griffithuni.edu.au)

Ali El Hanandeh <sup>a</sup>

<sup>a</sup> School of Engineering and Built Environment, Nathan campus, Griffith University, Nathan QLD 4111, Australia

[a.elhanandeh@griffith.edu.au](mailto:a.elhanandeh@griffith.edu.au)

Qiming Jimmy Yu <sup>a</sup>

<sup>a</sup> School of Engineering and Built Environment, Nathan campus, Griffith University, Nathan QLD 4111, Australia

[jimmy.yu@griffith.edu.au](mailto:jimmy.yu@griffith.edu.au)

## **ABSTRACT**

Electro-assisted adsorption was investigated for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  removal using date seed biochar (DSB-Electro). Compared to pristine biochar, the results showed that DSB-Electro effectively increased the adsorption capacity of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  by 21% to 94%. Significant differences were observed between  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  adsorption compared to  $\text{Ni}^{2+}$  which could be explained based on ion polarizing power. Under the same voltage,  $\text{Ni}^{2+}$  solution shows the highest electric conductivity; thereby more  $\text{Ni}^{2+}$  being transported to the biochar anode and giving them greater chance to interact with the surface groups. Electro-assisted adsorption occurred rapidly as around 88% of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  adsorbed within the first 3h, while 96% of  $\text{Cu}^{2+}$  occurred within the first hour of contact. Reversing the polarity did not seem to cause significant desorption of the adsorbed ions as the amount released from reversing polarity was less than 38% indicating that only small fraction of the ions was held by the electrostatic charge introduced by the current. It was likely that the enhanced charge facilitated other adsorption mechanisms by bringing the ions in contact with the biochar initially via electrostatic force. Electro-assisted adsorption can improve the biochar economic feasibility for metals removal (particularly  $\text{Ni}^{2+}$ ) from industrial streams.

**Keywords:** adsorption; date seed biochar; electro-assisted; heavy metal; surface functionality.

## INTRODUCTION

Heavy metals cause serious environmental and health problems due to their toxic and nonbiodegradable nature. Lead, copper, and nickel are among the most commonly used metals. They are classified as toxic and carcinogenic heavy metals (Kaewsarn, 2000). Adsorption is known as an effective treatment method for heavy metal removal from contaminated aqueous solutions. Among various adsorbents, activated carbon (AC) is widely used for heavy metal adsorption. However, its high cost may impede its utilization (Ahmad et al. 2011). Other more novel adsorbents may also be un-economical for large scale applications and may require extensive use of chemicals to manufacture which may result in higher cost and adverse environmental impacts. Therefore, it is important to develop greener low-cost effective adsorbents.

Biochar is a promising green material that have been utilized successfully to remove contaminates such as heavy metal ions from wastewaters and aqueous solutions (Mohan et al. 2014). Biochar is prepared using pyrolysis without further chemical or physical activation. As a result, biochar in its pristine state may have a lower adsorption capacity for heavy metals than AC. Therefore, biochar might require further enhancement to promote its adsorption properties (Rajapaksha et al. 2016). Biochar modification to enhance its functionality and adsorption capacity is an emerging field of study.

Several modification methods have been used for biochar modifications including, but are not limited to, base and/or acid treatment, steam activation, magnetic modification, and impregnation with minerals. For example, surface modification of the biochar by a feasible chemical process like acid treatment further enhances its adsorption capacity by incorporating highly active  $-\text{COOH}$ ,  $\text{C}=\text{O}$ ,  $\text{C}-\text{O}$ , phenolic and alcoholic  $-\text{OH}$  functional groups on the biochar surface (Sarkar et al. 2019). However, most of the modification methods are complicated, time-consuming and requiring high chemical use. For instance, Sarkar et al.

(2019) prepared surface modified biochar using high concentration (8 M) of H<sub>2</sub>SO<sub>4</sub> with 6 h reaction time. In the study of Wu et al. (2017), chemically modified biochars were prepared by mixing the raw biochar with a 1:10 (w/v) ratio of (a) 5% ammonia (NH<sub>3</sub>) solution at 50 °C for 9 h; (b) 5% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution at 25 °C for 8 h; and (c) 2 M nitric acid (HNO<sub>3</sub>) shaken in a reciprocating shaker for 8 h. Furthermore, a special caution must be taken to minimize the effect of modification on the stability of biochar and to avoid the environmental contamination resulting from the modification processes (Rajapaksha et al., 2016).

Thus, a simple approach to upgrading the biochar properties and simultaneously enhancing its removal efficiency with simple operation that is less labour intensive in shorter time requirements is favourable. Mahdi et al. (2019) demonstrated in lab-scale experiments that modification with mild acid (1 M HCl) for 2 h can improve the adsorption capacity of biochar by 27%, 66%, and 98% for Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> respectively. Nevertheless, it is desirable to eliminate the chemical upgrading process.

Biochar is a highly stable porous carbonaceous material (Chen et al., 2011; Ahmad et al., 2012), with high surface area (up to 500 m<sup>2</sup> g<sup>-1</sup>) and high conductivity (up to 4.27 mS cm<sup>-1</sup>) (Usman et al. 2015). It has similar characteristics as activated carbon (AC). Grimm et al. (1998) reported that electro-adsorption of AC was the best for the removal for several kinds of contaminants and reported an enhancement in its adsorption capacity. Electro-adsorption is a kind of surface adsorption induced by electrical charges generated at low bias potential (Pirkarami et al. 2013). Ying et al. (2002) reported that electro-adsorption showed promising results for the heavy metal removal and desalination of dilute solutions. Haro et al. (2011) used a porous carbon gel electrode for the electro-assisted removal of ions from brackish water. They compared removal efficiency of the carbon gel electrode to the removal efficiency of AC and activated carbon cloth. They found that the carbon gel showed a better electrochemical performance than AC

and carbon cloth, both in terms of ionic removal efficiency, fast electro-adsorption kinetics and regenerability.

Thus, few attempts have recently showed that biochar can be used to prepare a renewable electrode with a reliable adsorption capacity (Jung et al., 2015; Stephanie, 2017). For instance, Jung et al. (2015) fabricated chemically modified-biochar derived from marine macroalgae by applying  $MgCl_2$  as an electrolyte in aluminum-electrode based electro-modification system. They suggested that electro-assisted adsorption can offer dual advantages by reducing preparation time, and simultaneously enhancing the biochar physiochemical characteristics, resulting in significant adsorption uptake.

Unlike other conventional technologies such as ion exchange, evaporation, reverse osmosis and electrodialysis, electro-adsorption offers several advantages. Ying et al. (2002) and Zou et al. (2008) reported that electro-assisted adsorption provides several advantages by eliminating the need to use acids, bases, or salt solutions, thereby substantially reducing the amount of any potential secondary waste. Unlike evaporation process, electro-adsorption consumes less energy to achieve similar results as well as it has operational advantages over electrodialysis and reverse osmosis because no membranes are required (Ying et al. 2002).

Hence, such recent advances in the electro-assisted adsorption process have motivated the present study and make it possible to develop an innovative method for high adsorption of heavy metal removal onto biochar. The aim of this study is to develop an effective green adsorbent for heavy metal removal. This includes (1) develop a simple and an effective method for the preparation of biochar without using harsh chemicals (Greener process) to enhance its heavy metal adsorptive capacity; (2) assess the heavy metal removal ability of the biochars (electro-assisted) including an elaborative adsorption isotherm and kinetic studies; and (3) identify the interaction mechanisms governing the adsorption of heavy metal ions onto electro-assisted biochar adsorbents.

## **MATERILAS AND METHODS**

### **Chemicals**

All chemicals used in the experimental work were of analytical grade. A stock solution of 5.0 mM of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ni}^{2+}$  were prepared by dissolving specific quantity of each metal salt ( $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ , and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in 1.0 L deionized water. Then for adsorption experiments, working metal solutions of 0.3, 0.5, 1.0, 1.5, 3.0, 3.5, and 4.0 mM were prepared by diluting with deionized water to the required concentrations. The diluted solutions and standard solutions for atomic absorption spectroscopy analysis were freshly prepared before use and discarded after use. Deionized water was used in all chemical solution preparation and adsorption experiments. All the prepared solutions were stored in acid-washed glass containers at room temperature for further use.

### **Biochar Preparation**

The biochar preparation followed the procedure described in our earlier work [19]. Briefly, date seed biomass was collected after physical separation of the date flesh fruit. The seeds were washed several times with deionized water and then oven dried for 2 days at 50 °C before it was pyrolyzed at 550 °C for 3 h. The resultant biochar was gently crushed and sieved to particle size range of 0.6-1.4 mm. Biochar samples were washed with deionized water to remove fine particles and soluble salts. Then, the biochar samples were oven-dried at 105 °C for 2 h and stored in airtight containers. The pristine biochar was labelled according to its pyrolysis temperature and time as DSB550-3.

### **Electro-Assisted Adsorption of Biochar**

The electro-adsorption experiment was performed with a two-electrode configuration in a beaker cell. The schematic set up for electro-adsorption is shown in Fig. S1 (See supplementary data). For the electro-adsorption experiment, 1.0 g of the pristine biochar was formed as a working electrode (DSB-Electro). The biochar was placed inside a permeable tube and

connected by electrical wire. For reference electrode (Anode), a piece of an electrical copper wire was also used. Both electrical wires were attached to a DC power supply (GBC-30300G) to provide a constant voltage: 0.1 V for Pb<sup>2+</sup> and 0.2 V for both Cu<sup>2+</sup> and Ni<sup>2+</sup> to ensure that the metal ion was not oxidized or reduced during the electro-adsorption process and also ensure that the reference electrode would not be ionised. The beaker cell was filled with the metal solution and the initial pH of solution was adjusted to the required pH value of 6.0 using 0.1M HCl and NaOH solutions. The beaker was kept for 24 h to achieve equilibrium under an electrical field. Then, 1 mL samples were withdrawn at predetermined time intervals and the metal concentration was determined using atomic absorption spectroscopy (AAS) (Avanta-GBC, USA) operating with an air–acetylene flame.

Batch adsorption experiments were run at room temperature (23±2 °C) by mixing 0.1 g of each biochar sample in 10 mL of working solutions of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Ni<sup>2+</sup>. At the start of the experiment, initial pH was adjusted to pH 6.0 ± 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. And the samples were analysed using atomic absorption spectroscopy (AAS). The adsorption capacity of each metal ion adsorbed by the biochar were determined ( $q_e$ , mmol g<sup>-1</sup>) 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. To establish a reference for comparison, adsorption kinetics and isotherm experiments were also conducted without electro-assistance under the same laboratory conditions.







radius is, the larger the polarizing power is. In our case, soft Lewis acids such as  $\text{Ni}^{2+}$  shows smaller size (0.69 Å) with high polarizing power (2.89) (a large ratio of ionic charge to ionic radius) compared to  $\text{Cu}^{2+}$  (2.74) and  $\text{Pb}^{2+}$  (1.67) and consequently, it could form stronger bonds with soft Lewis bases (Reddad et al. 2002).

Furthermore, in electrolyte solutions, electricity is conducted by ions travelling between the cathode and anode. The conductivity of the solution depends on the solute and concentration. As such electrolyte with higher conductivity will have lower resistivity and in turn resistance to movement of the ions. Ohm's law indicates that current is proportionally related to voltage and inversely related to resistance. Therefore, under the same voltage, the solution that has the highest conductivity will involve the movement of more ions (higher current). In our case, the  $\text{Ni}^{2+}$  solution had the highest electric conductivity (165.12  $\text{mS cm}^{-1}$ ); thus, it involved more  $\text{Ni}^{2+}$  ions being transported to the biochar anode giving them greater chance to interact with the surface groups on the biochar. Copper electrolytes which has lower conductivity (19.85  $\text{mS cm}^{-1}$ ) than  $\text{Ni}^{2+}$  solutions while lead electrolytes shows a conductivity of (24.32  $\text{mS cm}^{-1}$ ).

$\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  adsorption onto electro-assisted adsorption biochar was statistically analyzed with the *t*-test and one-way ANOVA with a significance level of 0.05 ( $p < 0.05$ ). The results showed that the maximum adsorption capacities ( $q_{max}$ ) of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  onto DSB-Electro biochar was statistically and significantly higher than those onto DSB550-3 biochar ( $p < 0.05$ ).

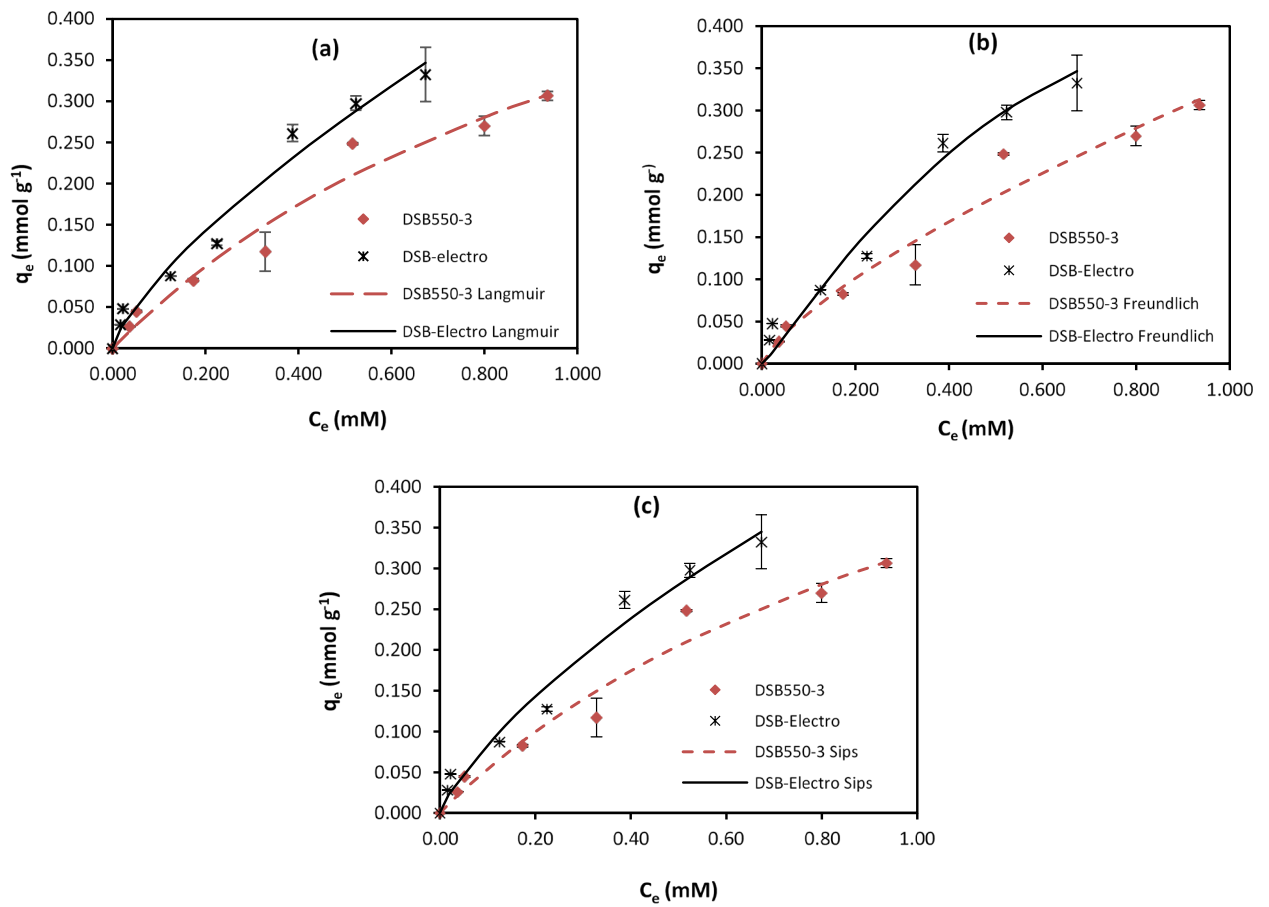


Figure 1. Electro-assisted adsorption of  $Pb^{2+}$  ion onto date seed biochar (biochar: solution =  $10\text{ g L}^{-1}$ ;  $C_0=0.3\text{-}4.0\text{ mM}$ ;  $\text{pH} = 6$ ; time = 24 h). Symbols represent experimental data. Solid and dashed lines represent isotherm models (a) Langmuir model; (b) Freundlich model; and (c) Sips model.

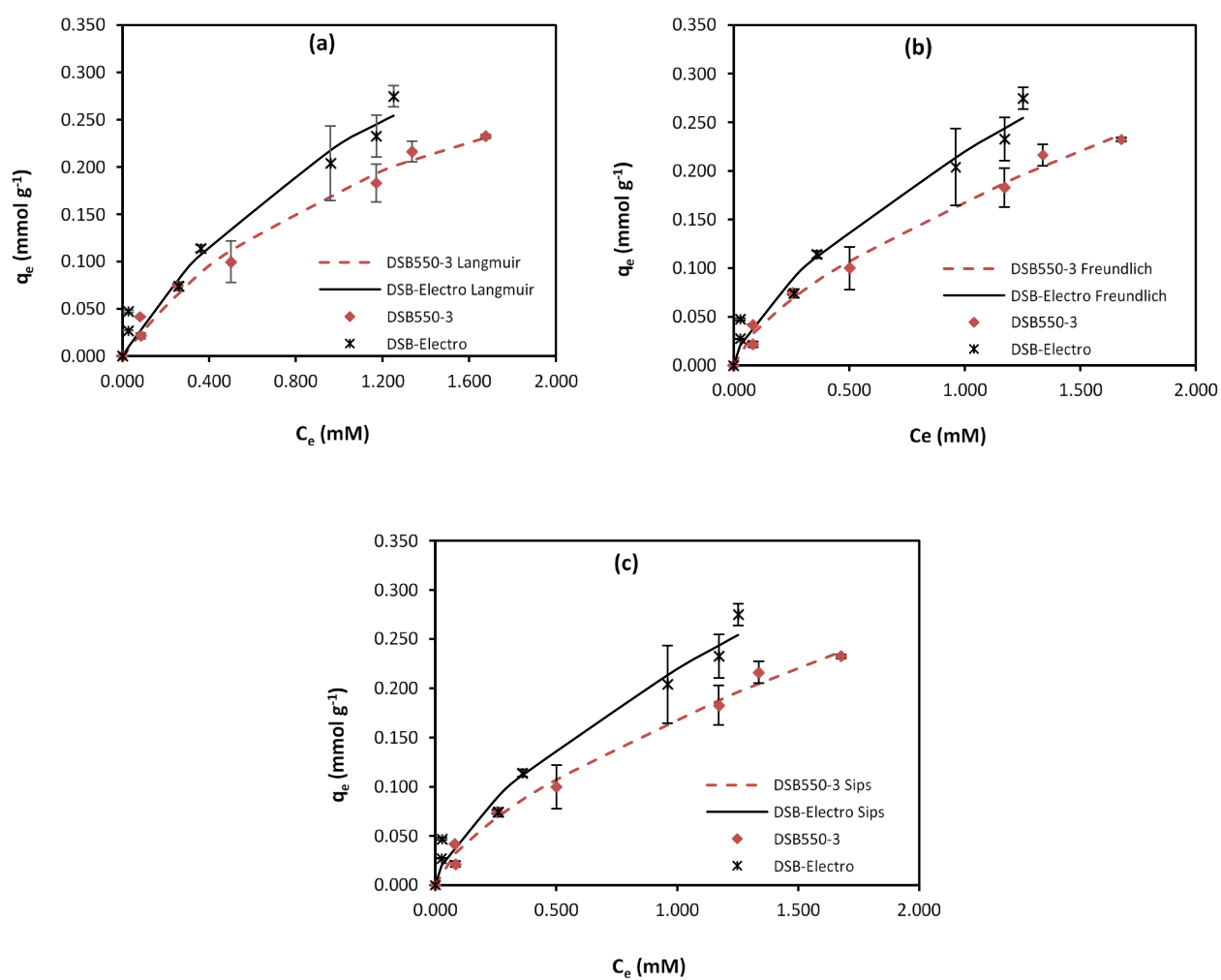


Figure 2. Electro-assisted adsorption of  $\text{Cu}^{2+}$  ion onto biochar. (biochar: solution =  $10 \text{ g L}^{-1}$ ;  $C_0 = 0.3\text{-}4.0 \text{ mM}$ ;  $\text{pH} = 6$ ; time = 24 h). Symbols represent experimental data. Solid and dashed lines represent isotherm models (a) Langmuir model; (b) Freundlich model; and (c) Sips model.

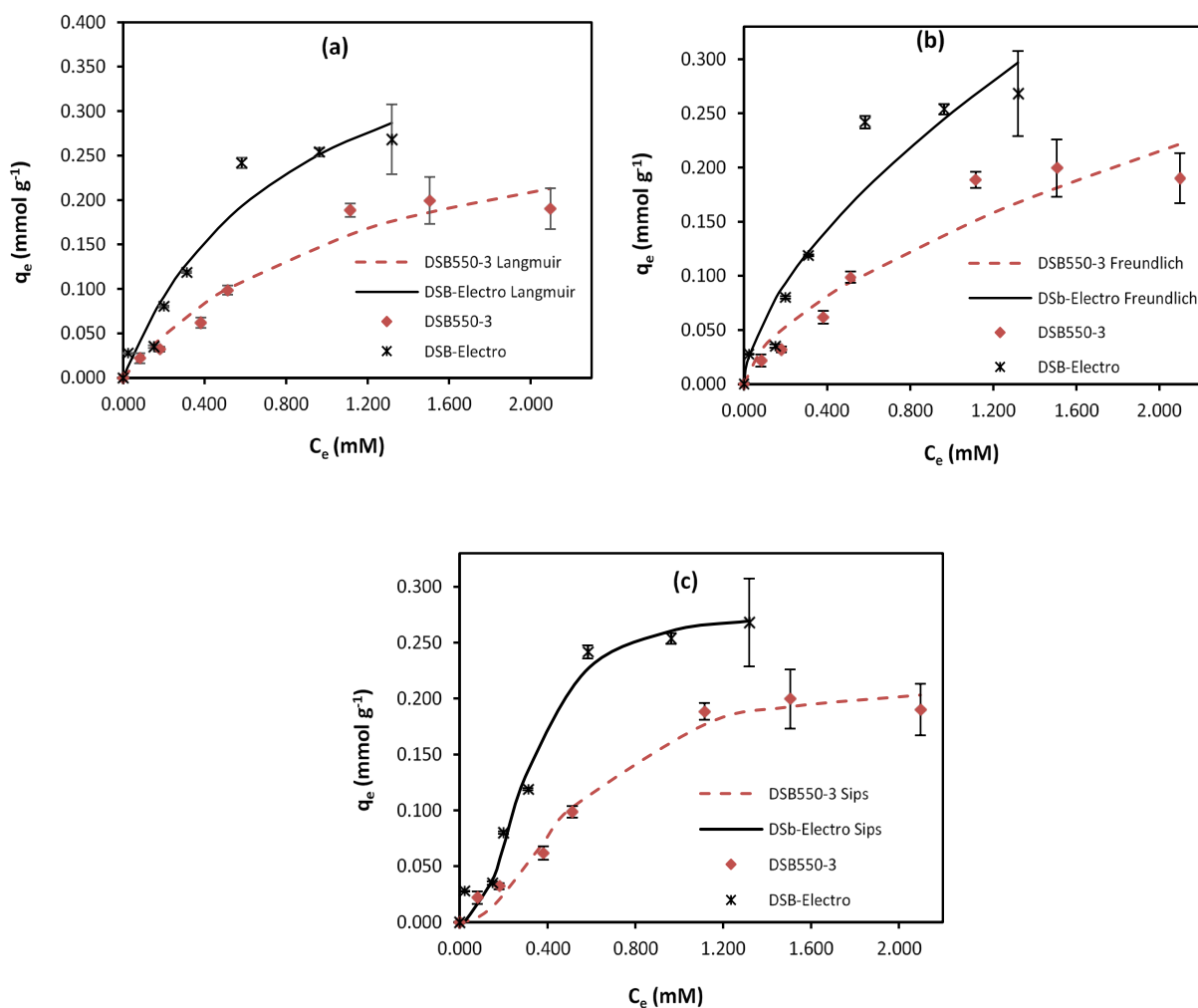


Figure 3. Electro- assisted adsorption of  $\text{Ni}^{2+}$  ion onto biochar. (biochar: solution =  $10 \text{ g L}^{-1}$ ;  $C_0 = 0.3\text{-}4.0 \text{ mM}$ ;  $\text{pH} = 6$ ; time = 24 h). Symbols represent experimental data. Solid and dashed lines represent isotherm models (a) Langmuir model; (b) Freundlich model; and (c) Sips model.

The adsorption isotherms of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  on the electro-assisted biochar were determined using the Langmuir, Sips and Freundlich isotherm models. The experimental results and fitting curves from the three isotherms are shown in Figures 1 to 3, and the estimated model parameters for the three models are listed in Table 1. The experimental data were better fitted by the Sips isotherm than Langmuir and Freundlich isotherms. The constant  $K_F$  ( $(\text{mmol g}^{-1}) (\text{L mmol}^{-1})^{1/n}$ ) obtained from the Freundlich isotherms for electro-assisted adsorption

(0.463, 0.219, and 0.250) were higher than DSB550-3 biochar (0.329, 0.169, and 0.141) for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$ , respectively. Furthermore, the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  by electro-assisted biochar was favourable in the studied concentration as the adsorption intensity obtained from the Freundlich isotherm ( $n$ ) was higher than 1.0 suggesting that an effective interaction process occurred between metal ions and the adsorbent (Table 1).

Table 1. Adsorption isotherm parameters for the adsorption of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions onto electro-assisted biochar (DSB-Electro)

<b>Isotherm</b>	<b>Pb<sup>2+</sup></b>	<b>Cu<sup>2+</sup></b>	<b>Ni<sup>2+</sup></b>
<b>Langmuir</b>			
$K_L$ (L mmol <sup>-1</sup> )	0.969	0.638	1.226
$q_{\max}$ (mmol g <sup>-1</sup> )	0.867	0.572	0.646
$R^2$	0.990	0.987	0.976
SSE	0.020	0.011	0.026
<b>Freundlich</b>			
$K_F$ (mmol g <sup>-1</sup> ) (L mmol <sup>-1</sup> ) <sup>1/n</sup>	0.463	0.219	0.250
$n$	1.363	1.513	1.629
$R^2$	0.987	0.987	0.950
SSE	0.022	0.018	0.033
<b>Sips</b>			
$a_s$ (L mmol <sup>-1</sup> )	0.234	0.001	16.50
$K_s$ (L g <sup>-1</sup> )	0.555	0.219	4.583
$\beta_s$	0.807	0.661	2.446
$R^2$	0.990	0.992	0.992
SE	0.020	0.011	0.011

The enhanced adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  during electro-assisted adsorption could be attributed to the electrostatic interaction. The working principle of electro-adsorption is based on imposing an external electric field in order to force charged species such as metal ions to move toward oppositely charged electrodes (Probstein and Hicks 1993). It was noticed that the solution pH at equilibrium decreased from 6.0 to value of  $\approx 5 \pm 0.1$  after  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  adsorption during the electro-assisted experiments. This could be explained by the release of  $\text{H}^+$  from the biochar surface where metal ions are adsorbed, consequently decreasing the solution pH. This phenomenon was also noted by Probstein and Hicks (Probstein and Hicks

1993).

Table 2 shows that electro-assisted adsorption increases the adsorption capacities of biochar. The DSB-Electro biochar produced in this study showed a high adsorption potential for heavy metal ions compared to other modified biochars reported in the literature. For example, our results showed that DSB-Electro biochar exhibited higher adsorption capacity for  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Ni^{2+}$  than Hickory biochar treated with NaOH. However, it is hard to compare with each other adsorbents as the adsorption capacity is obtained under specific experimental conditions including type of modification method, method of preparation, solution pH, temperature, initial metal concentration, and particle size.

Table 2. Adsorption capacity of unmodified and modified biochars for heavy metal removal

Biochar	Pyrolysis temperature (°C)	pH	Ion	$q_{max}$ (mmol g <sup>-1</sup> )	References
Hickory treated with NaOH	600	5.0	$Pb^{2+}$	0.092	(Ding et al. 2016)
			$Cu^{2+}$	0.281	
			$Ni^{2+}$	0.015	
Peanut hull treated with H <sub>2</sub> O <sub>2</sub>	300	-	$Pb^{2+}$	0.110	(Xue et al. 2012)
Corn straw treated with MnOx	600	6.0	$Cu^{2+}$	0.291-2.526	(Song et al. 2014)
Switchgrass treated with KOH	300	5.0	$Cu^{2+}$	0.487	(Regmi et al. 2012)
Date seed biochar	550	6.0	$Pb^{2+}$	0.718	This study
			$Cu^{2+}$	0.421	
			$Ni^{2+}$	0.333	
DSB-Electro			$Pb^{2+}$	0.867	
			$Cu^{2+}$	0.572	
			$Ni^{2+}$	0.646	



## Adsorption Kinetics

Figures 4 to 6 show the time profiles of the adsorbed amount of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  as a function of contact time. As clearly presented, the metal ions adsorption onto electrode occurred rapidly, for example; around 88% of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  ions adsorbed within the first 3 h, while 96% of total adsorption of  $\text{Cu}^{2+}$  ion occurred at the first hour contact time. The fast adsorption at initial stage can be attributed to rapid external mass transfer and surface adsorption associated with the availability of large number of vacant surface sites for adsorption. Thus, the amount of adsorbate accumulated on the biochar surface rapidly increases. However, the subsequent gradual adsorption is due to the rate-limited intraparticle diffusion, associated with fewer metal ions that accumulated onto the adsorption sites.

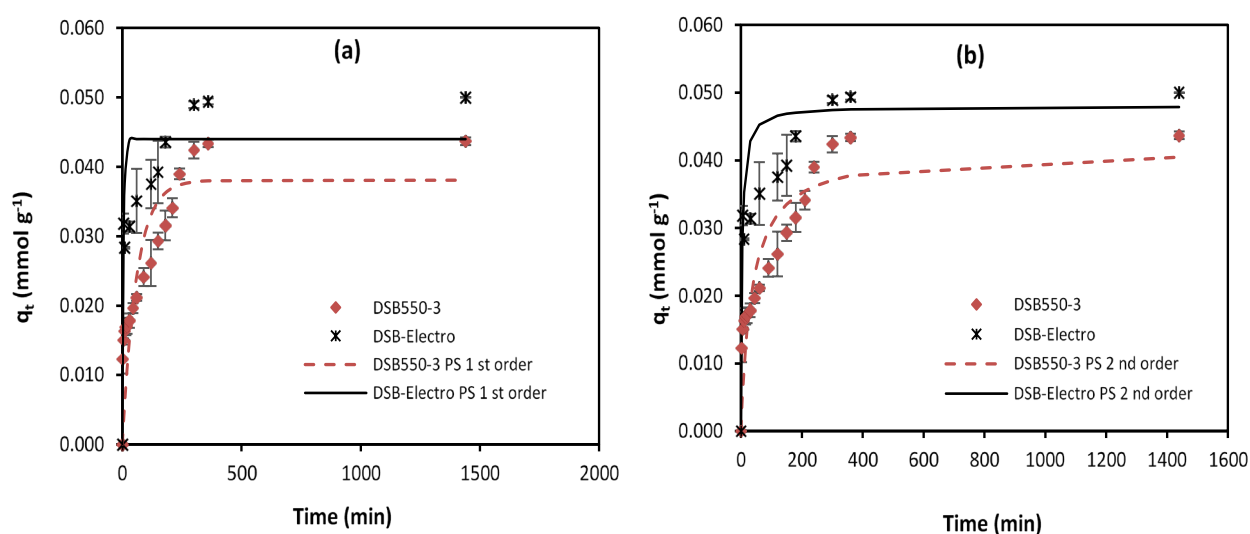


Figure 4. Electro-assisted adsorption kinetics of  $\text{Pb}^{2+}$  ion. Symbols represent experimental data while lines represent (a) Pseudo first order; (b) Pseudo second order.

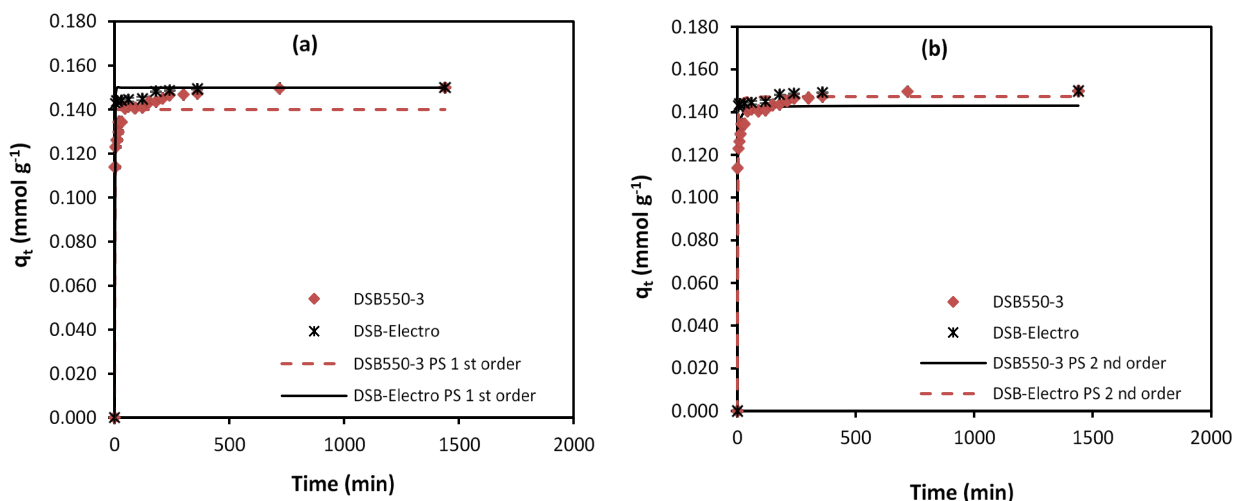


Figure 5. Electro-assisted adsorption kinetics of  $\text{Cu}^{2+}$  ion. Symbols represent experimental data while lines represent (a) Pseudo first order; (b) Pseudo second order.

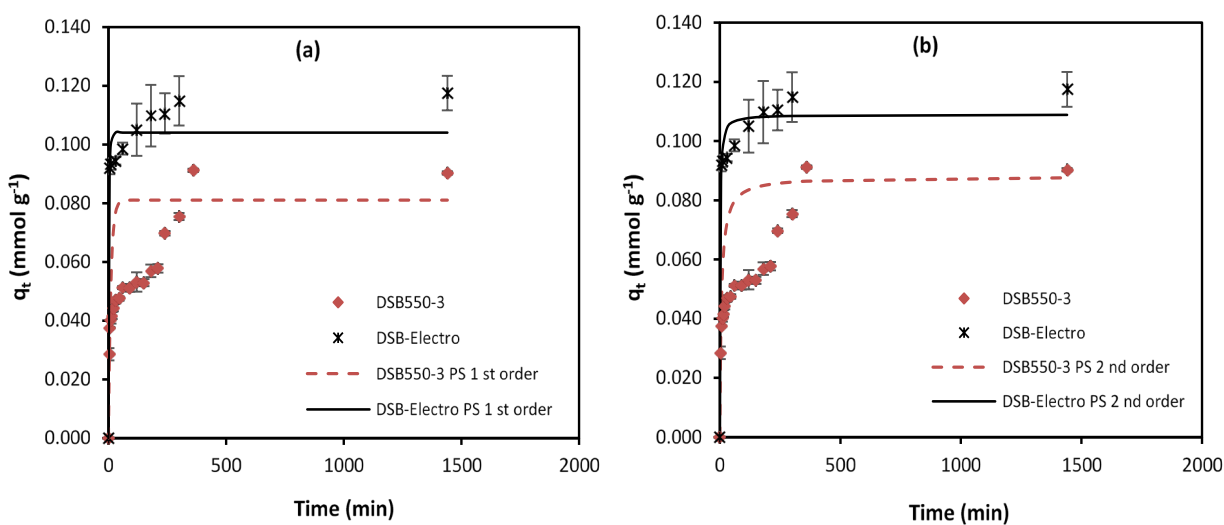


Figure 6. Electro-assisted adsorption kinetics of  $\text{Ni}^{2+}$  ion. Symbols represent experimental data while lines represent (a) Pseudo first order; (b) Pseudo second order.

The adsorption kinetic data were determined using pseudo first order and pseudo second order models. Pseudo second order model gives a better fit ( $R^2 \geq 0.93$ ) for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  than pseudo first order model (Table 3). Furthermore, the calculated  $q_{calc}$  value (mmol  $\text{g}^{-1}$ ) obtained from pseudo second order was considerably close to the experimental  $q_{exp}$  value (mmol  $\text{g}^{-1}$ ) as

seen in Table 3. Pseudo second order model also confirms the observed behaviour of faster adsorption as the parameter  $k_2$ , adsorption rate constant, for the DSB-Electro biochar (5.733, 33.78, and 7.098 g mmol<sup>-1</sup> min<sup>-1</sup>) is much higher than for DSB550-3 (0.676, 10.35, and 0.232 g mmol<sup>-1</sup> min<sup>-1</sup>) for Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> implying faster adsorption rate. Haro et al. (2011) reported that the fast-electro-assisted ion adsorption kinetics of the carbon-based electrode might be due to the combination of an interconnected micro/mesoporous matrix. Faster adsorption rate might be also due to the increased concentration of metal ions near the anode which increases the drive force for diffusion.

Table 3. Kinetics parameters of heavy metal removal onto DSB-Electro biochar

Model	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Ni <sup>2+</sup>
<b>Pseudo first order (PS 1st)</b>			
q <sub>exp</sub> (mmol g <sup>-1</sup> )	0.050	0.148	0.177
q <sub>calc</sub> (mmol g <sup>-1</sup> )	0.042	0.149	0.104
k <sub>1</sub> (min <sup>-1</sup> )	0.194	0.717	2.871
R <sup>2</sup>	0.900	0.980	0.960
SE	0.007	0.002	0.010
<b>Pseudo second order (PS 2nd)</b>			
q <sub>exp</sub> (mmol g <sup>-1</sup> )	0.050	0.148	0.117
q <sub>calc</sub> (mmol g <sup>-1</sup> )	0.044	0.149	0.109
k <sub>2</sub> (g mmol <sup>-1</sup> min <sup>-1</sup> )	5.773	33.78	7.098
R <sup>2</sup>	0.930	1.000	0.980
SE	0.006	0.002	0.006

### Spectroscopy Analysis of Electro-assisted Biochar Surface

SEM images of DSB550-3 before electro-assisted and after electro-assisted metal ions adsorption were analysed. As can be seen from Figure 7, the SEM image of the DSB550-3 biochar (non-electro assisted) (Figure 7 a) shows less apparent pores on the surface in comparison to DSB-Electro one (after electro-adsorption) (Figure 7 b, c, and d). The surface

morphological structure of DSB-Electro biochar showed a rough and porous structure which can provide channels for the adsorbates to reach the active adsorption sites and promote the rapid adsorption to reach equilibrium faster. The increasing in pores structure might be attributed to the effect of the electric current which caused some of the negatively charged impurities to repel thus opening the pores which were blocked by the impurities (ash and minerals). SEM images confirm that biochar electrode is highly porous material and thus physical adsorption is considered as one of the mechanisms responsible for heavy metal adsorption onto the biochar electrode (Haro et al. 2011). This can be seen in images after adsorption (Figure 7 b, c, and d SEM) which show the pores of biochar packed with metal ions.

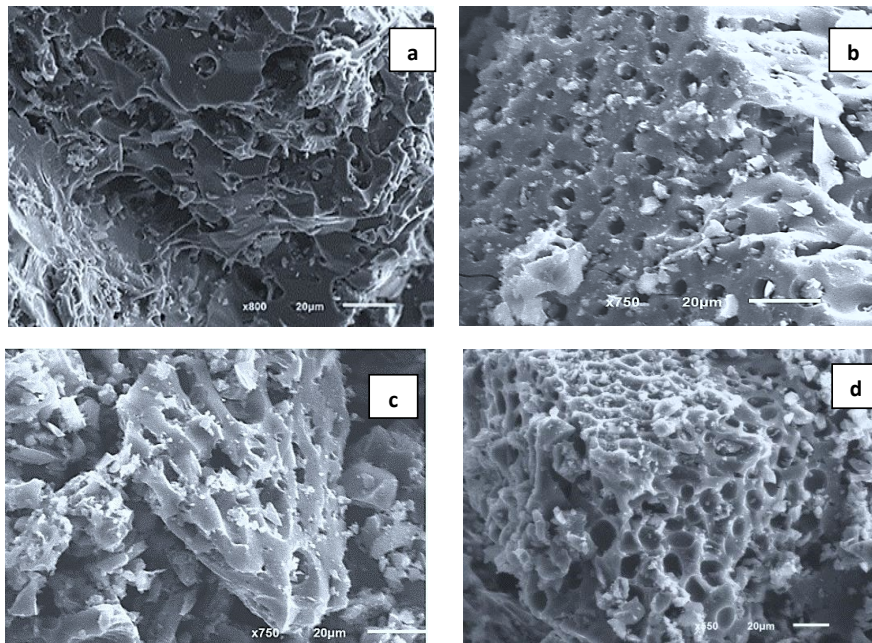


Figure 7. SEM images of biochar before adsorption (non-electro) and after (DBS-Electro) (a) before adsorption (DSB550-3); (b) after Cu<sup>2+</sup> adsorption; (c) after Ni<sup>2+</sup> adsorption; (d) after Pb<sup>2+</sup> adsorption.

The enhanced adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Ni<sup>2+</sup> during electro-assisted adsorption can be also related to the surface functional groups presented onto biochar surface as indicated by the FTIR spectra (Figure 8). The spectral analysis of the DSB-Electro biochar after Pb<sup>2+</sup> adsorption (Figure 8) shows various surface functional groups. For instance, significant differences at the

peaks 2325, 2652.37, 1979.97 were observed for both biochars after  $Pb^{2+}$  adsorption confirming that functional groups such as  $C\equiv C$ ,  $O-H$ ,  $C=O$  participated in binding ions onto the biochar. The peaks at 1564.4, 1127, and  $1070.83\text{ cm}^{-1}$  in both biochars after  $Pb^{2+}$  adsorption was also observed confirming that functional groups such as  $C-O$ ,  $N-O$ ,  $O-H$  and  $COO^-$  groups were involved in binding ions onto the biochar.

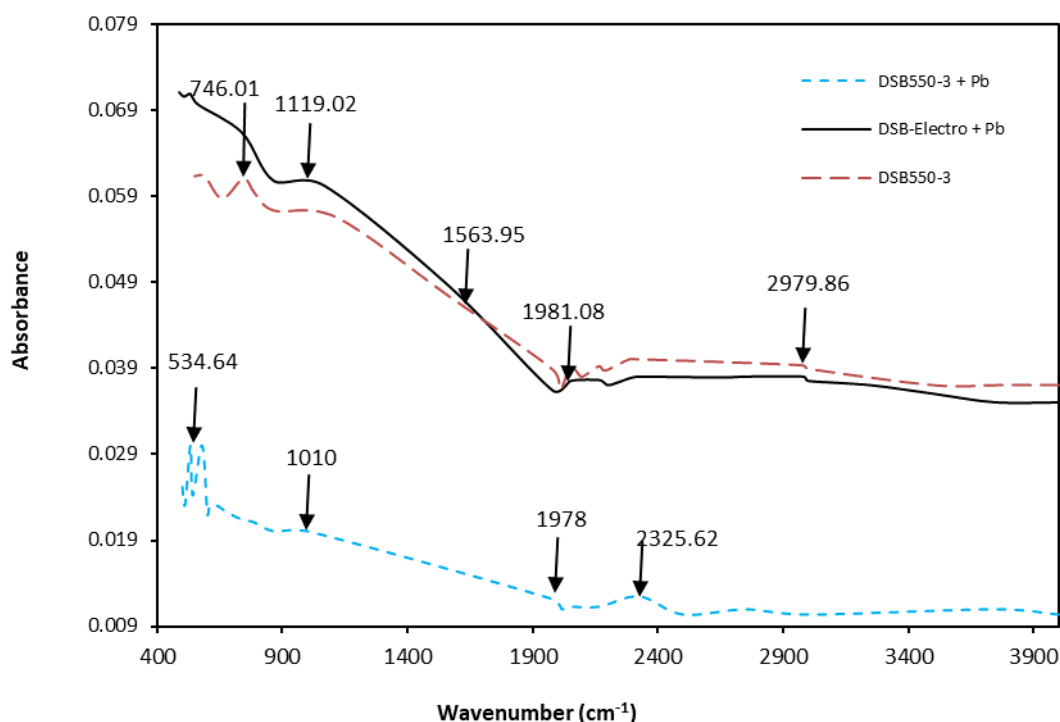


Figure 8. FTIR spectra of before and after  $Pb^{2+}$  adsorption onto DSB550-3 biochar and electro-assisted biochar (DSB-Electro).

### Desorption of Electro-assisted Laden Biochar

In order to investigate the potential reversibility of electro-assisted biochar (i.e. desorption) for the metal ions retained at the electrode under an external electric field, adsorption–desorption reversibility of the electrode was investigated with reversing the external electric field. First, the electro-assisted adsorption experiment was conducted by setting the biochar electrode as the anode as described earlier. After 24 h the electric field was disconnected, and samples were

obtained to determine the amount of metals adsorbed on the biochar. Second, the electric field was reversed by reversing the polarity (setting the biochar electrode as the cathode) for 24 h. Finally, samples were collected to determine the amount of metals released to the solution. Reversing the polarity did not seem to cause significant desorption of the adsorbed metals from the biochar. The amount released from reversing polarity of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  were 28.5%, 37%, and 34%, respectively.

As the electro-assisted adsorption process relies on electrostatic attraction, it would be expected that the process could be a fully reversible (Haro et al. 2011). However, the experimental results showed that a fraction of the metal ions is not leached out upon the reversing of the polarization and remained inside the porous structure of the biochar electrode. This indicates that only a fraction of the ions was held by the electrostatic charge introduced by the current. It is likely that the enhanced charged facilitated other adsorption mechanisms by bringing the ions in contact with biochar initially via electrostatic force. Additionally, as electrical potential is only playing an "assistant" role and it is only one of the aspects in the adsorption process, we probably cannot expect a full recovery, rather the extra amount adsorbed maybe fully recoverable by reversing the polarity.

## **CONCLUSION**

For any adsorption system, the adsorption rate and capacity are two important factors affecting the performance of the process. This work investigates electro-adsorption of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  from aqueous solutions by biochar. Biochar has been introduced to be an ideal material for an electrode because of its low electrical resistivity and its porous structure with high surface area. The results confirmed that electro-assisted adsorption enhanced the adsorption rate as well as capacity of biochar for heavy metals. The adsorption capacity of DSB-Electro biochar increased by 21%, 36% and 94% for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  respectively. Metal ion adsorption onto electrode occurred rapidly, for example; around 88% of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  adsorbed

within the first 3 h, while 96% of total adsorption of  $\text{Cu}^{2+}$  occurred within the first hour of contact. The enhanced adsorption of aqueous  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  during electro-assisted adsorption can be attributed to bringing the ions to closer contact with the biochar and increasing the surface charge density on the surface of the biochar which were subsequently held by, other mechanisms such as electrostatic interaction, surface complexation, and physical surface adsorption. Electro-assisted adsorption can improve the biochar economic feasibility for metals removal (particularly  $\text{Ni}^{2+}$ ) from industrial streams by increasing the capacity and reducing the quantities of waste. It is further recommended to investigate the cost effectiveness of electro-assisted biochar application as well as the reusability of biochar from a life cycle perspective.

### **CRedit author statement**

Zainab Mahdi: Writing-original draft preparation; Writing-editing& revision; conceptualization; methods; software; investigation; data analysis; data curation.

Ali El Hanandeh: Writing-original draft preparation; Writing-editing & revision; conceptualization; supervision, resources.

Jimmy Yu: Writing-editing & revision; supervision; resources.

### **REFERENCES**

- AHMAD, M., LEE, S. S., DOU, X., MOHAN, D., SUNG, J. K., YANG, J. E. & OK, Y. S. 2012. Effects of pyrolysis temperature on soybean stover- and peanut shell-derived biochar properties and TCE adsorption in water. *Bioresour Technol*, 118, 536-44.
- AHMAD, T., RAFATULLAH, M., GHAZALI, A., SULAIMAN, O. & HASHIM, R. 2011. Oil Palm Biomass-Based Adsorbents for the Removal of Water Pollutants—A Review. *Journal of Environmental Science and Health, Part C*, 29, 177-222.
- CHEN, B., CHEN, Z. & LV, S. 2011. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. *Bioresour Technol*, 102, 716-23.
- DING, Z., HU, X., WAN, Y., WANG, S. & GAO, B. 2016. Removal of lead, copper, cadmium, zinc, and nickel from aqueous solutions by alkali-modified biochar: Batch and column tests. *Journal of Industrial and Engineering Chemistry*, 33, 239-245.
- GRIMM, J., BESSARABOV, D. & SANDERSON, R. 1998. Review of electro-assisted methods for water purification. *Desalination*, 115, 285-294.
- HAN, Y., QUAN, X., CHEN, S., ZHAO, H., CUI, C. & ZHAO, Y. 2006. Electrochemically enhanced adsorption of phenol on activated carbon fibers in basic aqueous solution. *Journal of colloid and interface science*, 299, 766-771.

- HARO, M., RASINES, G., MACIAS, C. & ANIA, C. O. 2011. Stability of a carbon gel electrode when used for the electro-assisted removal of ions from brackish water. *Carbon*, 49, 3723-3730.
- JUNG, K.-W., JEONG, T.-U., HWANG, M.-J., KIM, K. & AHN, K.-H. 2015. Phosphate adsorption ability of biochar/Mg–Al assembled nanocomposites prepared by aluminum-electrode based electro-assisted modification method with MgCl<sub>2</sub> as electrolyte. *Bioresource Technology*, 198, 603-610.
- KAEWSARN, P. 2000. *Single and multi-component biosorption of heavy metal ions by biosorbents from marine alga Durvillaea Potatarum*. Doctor of Philosophy, Griffith university.
- MAHDI, Z., EL HANANDEH, A. & YU, Q. J. 2019. Preparation, characterization and application of surface modified biochar from date seed for improved lead, copper, and nickel removal from aqueous solutions. *Journal of Environmental Chemical Engineering*, 7, 103379.
- MOHAN, D., SARSWAT, A., OK, Y. S. & PITTMAN, C. U. 2014. Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. *Bioresource Technology*, 160, 191-202.
- PIRKARAMI, A., OLYA, M. E. & YOUSEFI LIMAEI, N. 2013. Decolorization of azo dyes by photo electro adsorption process using polyaniline coated electrode. *Progress in Organic Coatings*, 76, 682-688.
- PROBSTEIN, R. F. & HICKS, R. E. 1993. Removal of contaminants from soils by electric fields. *Science*, 260, 498-503.
- RAJAPAKSHA, A. U., CHEN, S. S., TSANG, D. C. W., ZHANG, M., VITHANAGE, M., MANDAL, S., GAO, B., BOLAN, N. S. & OK, Y. S. 2016. Engineered/designer biochar for contaminant removal/immobilization from soil and water: Potential and implication of biochar modification. *Chemosphere*, 148, 276-291.
- REDDAD, Z., GERENTE, C., ANDRES, Y. & LE CLOIREC, P. 2002. Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies. *Environmental science & technology*, 36, 2067-2073.
- REGMI, P., GARCIA MOSCOSO, J. L., KUMAR, S., CAO, X., MAO, J. & SCHAFFRAN, G. 2012. Removal of copper and cadmium from aqueous solution using switchgrass biochar produced via hydrothermal carbonization process. *Journal of Environmental Management*, 109, 61-69.
- SARKAR, A., RANJAN, A. & PAUL, B. 2019. Synthesis, characterization and application of surface-modified biochar synthesized from rice husk, an agro-industrial waste for the removal of hexavalent chromium from drinking water at near-neutral pH. *Clean Technologies and Environmental Policy*, 21, 447-462.
- SONG, Z., LIAN, F., YU, Z., ZHU, L., XING, B. & QIU, W. 2014. Synthesis and characterization of a novel MnO<sub>x</sub>-loaded biochar and its adsorption properties for Cu<sup>2+</sup> in aqueous solution. *Chemical Engineering Journal*, 242, 36-42.
- STEPHANIE, H. 2017. *Using Biochar Electrodes for Brackish Water Desalination*. 10606138 M.S., Mississippi State University.
- USMAN, A. R. A., ABDULJABBAR, A., VITHANAGE, M., OK, Y. S., AHMAD, M., AHMAD, M., ELFAKI, J., ABDULAZEEM, S. S. & AL-WABEL, M. I. 2015. Biochar production from date palm waste: Charring temperature induced changes in composition and surface chemistry. *Journal of Analytical and Applied Pyrolysis*, 115, 392-400.
- WU, W., LI, J., LAN, T., MÜLLER, K., NIAZI, N. K., CHEN, X., XU, S., ZHENG, L., CHU, Y. & LI, J. 2017. Unraveling sorption of lead in aqueous solutions by chemically modified biochar derived from coconut fiber: a microscopic and spectroscopic investigation. *Science of the Total Environment*, 576, 766-774.
- XUE, Y., GAO, B., YAO, Y., INYANG, M., ZHANG, M., ZIMMERMAN, A. R. & RO, K. S. 2012. Hydrogen peroxide modification enhances the ability of biochar (hydrochar) produced from hydrothermal carbonization of peanut hull to remove aqueous heavy metals: Batch and column tests. *Chemical Engineering Journal*, 200-202, 673-680.



- YING, T.-Y., YANG, K.-L., YIACOUMI, S. & TSOURIS, C. 2002. Electrosorption of ions from aqueous solutions by nanostructured carbon aerogel. *Journal of colloid and interface science*, 250, 18-27.
- ZOU, L., MORRIS, G. & QI, D. 2008. Using activated carbon electrode in electrosorptive deionisation of brackish water. *Desalination*, 225, 329-340.