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Contributed Paper

## Prospective Sorption Evaluation of Hydrothermally Carbonized *Lepironia articulata* (Grey sedge) for the Removal of Ni (II) from Aqueous Solution

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### ABSTRACT

As an alternate to pyrolysis, hydrothermal carbonization has been proposed as a promising technique for conversion of different wastes into biofuels, adsorbents and specific chemicals. Different types of biomass wastes were used for converting to adsorbent by researchers and their potential to adsorb heavy metals was reported to be excellent. This paper presents the efficiency of hydrochar produced from an alternate biomass *Lepironia articulata* (LA) through series of activation and carbonization methods for the removal of Ni (II) from aqueous solution, as well as proposed methods of improving hydrochar surface reactivity. Hydrochar produced at 200 °C with a maximum yield of 60% and with an improved surface functional group was selected as an adsorbent. The kinetic study, pH effect, an effect of Ni (II) initial concentration, and adsorbent dose were examined in batch experiments. Fourier Transform Infrared Spectroscopy (FT-IR) was employed to characterize the resulting lepironia articulata hydrochar (LAHC). The results of this characterization showed that after the hydrothermal carbonization, the functional groups from fresh biomass were preserved. Based on FT-IR results it can be concluded that the metal binding in biomass of LA takes place by the substitution of Ni (II) ions by an amine, nitro, and carboxylic functional groups. Furthermore, adsorption data for Ni (II) uptake by hydrochar were analyzed according to Langmuir and Freundlich adsorption models. It was noticed from results that maximum uptake percentage of Ni (II) was 72.77% at the initial concentration of 100 mg L<sup>-1</sup> and pH 6. The adsorption equilibrium was established in 180 minutes. The maximum adsorption capacity ( $q_m$ ) calculated is 12.2 mg g<sup>-1</sup>. Through above evident results it has been proved that the low-cost hydrochar prepared from LA has potential to adsorb Ni (II) from aqueous solution.

**Keywords:** pyrolysis, hydrothermal carbonization, adsorption, hydrochar

## 1. INTRODUCTION

Hydrothermal Carbonization (HTC) is a wet biomass conversion technology. It mimics the natural process of coal formation in the lab in just a few hours. During the HTC reaction, water, carbon dioxide, and other compounds are cleaved from the biomass. Subsequently, the energy density is raised significantly and the heating value is estimated to that of dry, high quality brown coal [1, 2]. At the same time, the macromolecular structure of the original biomass will be completely destroyed. This provides a porous, brittle and in part dust-like product that is considerably easier to dry and to be used as an efficient adsorbent in wastewater treatment applications. The HTC process is performed in high-pressure vessels by applying relatively high temperature (generally in the range 180-250 °C) and pressure (approximately 1000-5000 kPa) to biomass in liquid water for a few hours (0.5-8 h) in the absence of air [1]. The main products of HTC are the carbonaceous material hydrochar (HC), process liquid containing various inorganic and organic compounds, and no condensable gases [2]. The extra productive approach, cost effectiveness and efficient methodology for the production of HC has made this material a worth taking for the treatment of wastewater [3].

Although HC exhibits relatively undeveloped porous structure and surface chemistry with acidic properties, high O/C ratio of HC obtained at lower HTC temperatures indicate a greater abundance of surface organic functional groups (OFGs). Another advantage of the hydrothermal method is to allow carbonaceous sphere formation of nano and/or micro size. These carbonaceous spheres have a wide variety of surface functional groups such as -OH, C=O and -COOH [4]. Due to their

characteristic structure and abundance of oxygen- containing functional groups, HC represents suitable alternative lower-cost sorbent for removal of a wide spectrum of water contamination [5]. Therefore, the heavy metal adsorption ability of HC has been reported to be noteworthy [6-8].

Presently there is an exponential increment in the number of studies managing the utilization of various HC as adsorbent of heavy metals including nickel ions. In recent study, Han *et al.*, [9] from their study concluded that the high sorption capacity of HC obtained from animal manure for the removal of antimony (III) and cadmium (II). In another study Liu *et al.*, [6] have characterized and investigated Cu(II) adsorption properties of pinewood HC. The results indicated the existence of a large amount of OFGs on the HC surface responsible for removal of 4.46 mg g<sup>-1</sup> for Cu (II). Still, there are only a few studies for the removal of heavy metals using HC. In most of the previous studies, the HC prepared were only characterized for their surface and structures, further research studies on new biomass for their conversion to HC for the wastewater treatment application is still needed to be filled.

Therefore the objectives of this study were to prepare *Lepironia articulata* hydrochar (LAHC) using optimized HTC process. Further obtained LAHC was characterized according to its functional groups, cation exchange capacity (CEC) and yield to find out its significance for the removal of Ni (II) ions from aqueous solution. The responsible mechanisms for the removal of Ni (II) were elucidated at different pHs, doses, adsorbate initial concentrations and by means of batch adsorption isotherms.

## 2. MATERIALS AND METHODS

### 2.1 Material and Equipment

Type of biomass used in this study was *Lepironia articulata* (LA) obtained from Thalae Noi wetland area in Phatthalung, one of the southern provinces in Thailand. All other chemical reagents were used of analytical grade obtained from Sigma-Aldrich. To prepare stock solution analytical grade heavy metal salt  $\text{NiSO}_4 \times 6\text{H}_2\text{O}$  was used.

HTC experiments were carried out in a 1000 mL autoclave reactor equipped with an external resistance heater and internal sensor thermocouple. The internal temperature of the reactor was controlled using electric thermostats single display PID controller in a panel. A pressure gauge was also fitted at the top left of the reactor to monitor inside pressure and release pressure through safety valve if required.

### 2.2 Preparation of Hydrochar (HC)

The HC preparation method was obtained from [4]. LA obtained was first cut into small pieces of less than 2 cm and then washed several times with distilled water and dried by putting a sample into the heating oven under 80 °C for 3 hours or until the constant weight obtained. 30 gram of dried sample was dispersed into 300 mL distilled water (ratio 1:10) contained in a round bottom flask. 5 % (v/v) sulfuric acid was then mixed as a catalyst. The mixture was shaken vigorously to create a homogenous suspension. The suspension was put into the Teflon chamber which was then fixed into the reactor. Feed stock was heated at 200 °C for a residence time of 24 hours for all experiments [10]. After completing cycle the heater was turned off and the reactor was allowed to cool down to ambient condition. The solid material (HC) and liquid products were collected and subsequently separated by filtration using whatmann no.42 filter

paper. HC samples were washed thoroughly with warm distilled water and 0.1 M hydrochloric acid followed by washing with distilled water until neutral pH appeared. Filtered sample was dried in an oven at 105 °C for 3 hours. Dried samples were ground and sieved up to desired particle size and kept in airtight polyethylene bags for further experiments.

### 2.3 Physiochemical Characterization

Fourier transform infrared (FTIR) analysis of the biomass feed stock and HC were conducted using Bruker Vortex 70 spectrometer to analyze the modification in functional groups after hydrothermal carbonization. By the application of the standard Brunauer-Emmett-Teller (BET) adsorption-desorption isotherm method, the pore properties and BET surface area ( $S_{\text{BET}}$ ) were accessed using the micromeritics ASAP 2460 model analyzer. In which, the surface area was calculated based on adsorption data in the partial pressure (P/Po) range from 0.0095 to 0.9948 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore surface area and the micropore volume were obtained via t-plot analysis.

The ammonium acetate method was used to determine the cation exchange capacity (CEC).

The concentration of the Ni (II) in the aqueous solution was determined using Perkin Elmer AAnalyst 100 flame Atomic Absorption Spectrometer (AAS) by taking results through WinLab software at wavelength of 341.5 nm. A calibration curve was developed using standard Ni(II) solution in the concentration range of 7, 10, 20, 30, 50 and 100 mg L<sup>-1</sup>, respectively, for the quantification of Ni(II) after the adsorption processes.

## 2.4 Adsorption Experiments

Batch adsorption experiments were performed in a laboratory incubator shaker (Daihan WIS-20 Shaking Incubator) at 150 rpm under the controlled temperature. Experiments were carried out by allowing an accurately weighed amount of adsorbent (20 g L<sup>-1</sup>) into 50 mL Ni (II) solution of various initial concentrations ranging (50 - 500 mg L<sup>-1</sup>) in 250 mL conical flasks. A stock solution of 1000 mg L<sup>-1</sup> Ni (II) was initially prepared from analytical grade Nickel sulfate (NiSO<sub>4</sub>×6H<sub>2</sub>O) crystals using double distilled water. Experiments with variable pH, initial adsorbate concentration and contact time were initially conducted. pH of the sample solutions was adjusted using 0.1N HCl or 0.1N NaOH solution. To calculate the isotherm equilibrium data another set of experiment was performed by varying contact time under the controlled temperature of 303 K. All the above experiments were performed in triplicate.

Adsorption capacity of the samples were measured using following equation (Eq. (1)).

$$q_e = \frac{V}{m} (C_0 - C_e) \quad (1)$$

Where  $q_e$  is the mass of Ni (II) ions adsorbed per mass of LAHC at equilibrium (mg g<sup>-1</sup>),  $v$  is the volume (L) of solution used for batch experiments,  $m$  is the mass (g) of adsorbent whereas  $C_0$  is the initial concentration (mg L<sup>-1</sup>) of Ni (II) ions in solution, and  $C_e$  is the equilibrium concentration of solution (mg L<sup>-1</sup>) when amount adsorbed equals to  $q_e$ .

## 2.5 Adsorption Isotherm

### 2.5.1 Adsorption Isotherm models

Adsorption equilibrium is the set of conditions at which the number of molecules arriving on the surface of the adsorbent equals the number of molecules that are

leaving. The relation between the amount of adsorbate adsorbed by an adsorbent (solid) and the concentration of the adsorbate at equilibrium and constant temperature is called adsorption isotherm [11].

Langmuir adsorption isotherm model equation (Eq. (2)) and Freundlich adsorption isotherm model equation (Eq. (3)) were used to fitting the sorption data.

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

$$q_e = K_f C_e^{1/n} \quad (3)$$

Where  $q_m$  (mg·g<sup>-1</sup>) is the Langmuir saturated adsorption capacity;  $K_L$  is a Langmuir constant (L mg<sup>-1</sup>);  $K_f$  (L g<sup>-1</sup>) is the Freundlich affinity coefficient, and  $n$  is the Freundlich exponential coefficient [12].

## 3. RESULTS AND DISCUSSION

### 3.1 Characteristics of Hydrochar (HC)

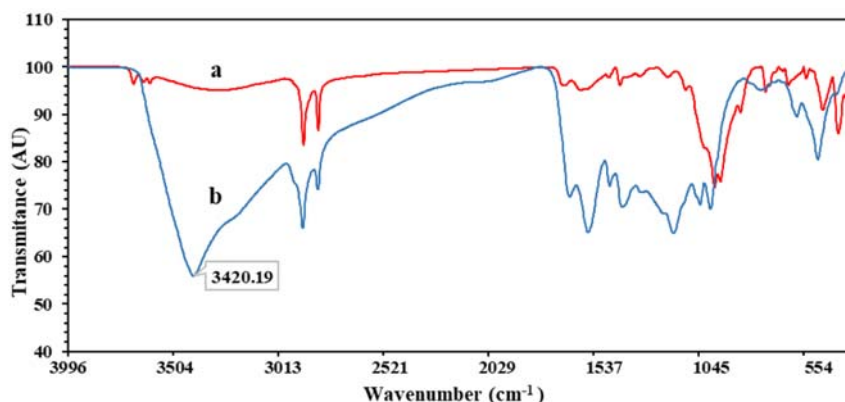
The prepared LAHC samples were characterized by measuring their surface functional groups, cation exchange capacity (CEC), and HC yield.

#### (A) Surface functional groups

Large surface area and well-developed porosity do not always indicate greater ability, in the adsorption, besides the structural morphology, surface functional groups perform essential role [13]. Oxygenated functional groups such as C-O, OH, and COOH are significant for improving hydrochar performance in various applications [14]. For example, surface OH and COOH groups can greatly enhance the adsorption capacity when HC is used as an adsorbent for heavy-metal removal. This is because such groups interact with the metals via hydrogen bonding and complexation [15]. Surface functional groups were improved during hydrothermal synthesis.

A comparison of FTIR spectra of raw biomass and LAHC is illustrated in Figure 1. More oxygenated functional groups developed can be seen in Figure 1 shown on LAHC spectra line. Generally, LAHC is rich in functional groups containing oxygen and aromatic components which are containing C-O and C-C bands, which are the major components of LAHC. The absorption peak between  $3300\text{ cm}^{-1}$  and  $3600\text{ cm}^{-1}$  is assigned to O-H stretching vibrations, the peak between  $2850\text{ cm}^{-1}$  and  $2920\text{ cm}^{-1}$  represents C-H stretching vibrations [16], the band between  $1650\text{ cm}^{-1}$  and  $1735\text{ cm}^{-1}$  change is attributed to

represent C-O functional groups and aromatic C-O [5], the adsorption band observed at  $1512\text{ cm}^{-1}$  corresponds to aromatic C-C, and the peak between  $1000\text{ cm}^{-1}$  and  $1250\text{ cm}^{-1}$  represents C-O bending vibrations [17]. When comparing with raw biomass some newly formed peaks at  $3420\text{ cm}^{-1}$  in the spectra recorded for LAHC indicates hydroxyl groups which widely play role during the adsorption process. In the main, resulting findings indicate that in the removal of heavy metals, amount of the surface OFGs are closely correlated to the adsorption capacity of HC [13].



**Figure 1.** FTIR spectra of a) raw biomass lepironia articulata b) hydrochar after synthesis at  $200^{\circ}\text{C}$  and 24 hours residence time.

b) Surface area, pore size, and pore volume

The Surface area of the adsorbent used for the removal of heavy metals is another important parameter to be considered before adsorption process. Although in current study functional groups took major part in adsorption ion-exchange process, high surface area and pore volume have

also contributed towards the maximum capture of Ni (II) ions. The Surface area, pore volume and pore size of LAHC obtained were  $69.22\text{ m}^2\text{ g}^{-1}$ ,  $0.0800\text{ cm}^3\text{ g}^{-1}$  and  $4.623\text{ nm}$  respectively, which were found to be high when compared with previous research data (Table 1).

**Table 1.** Comparison of hydrochars by HTC process using different biomass feed stock.

Feed stock	Metal/ Organic	HTC Time	HTC Temperature (°C)	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Avg pore diameter (nm)	Yield (%)	CEC (cmol <sub>c</sub> kg <sup>-1</sup> )	qm (mg g <sup>-1</sup> )	Reference
Seafood waste	NA	1h	150	NA	NA	NA	38.12	NA	NA	[24]
Peanut hull	Ni(II), Pb(II)	5h	300	1.3	NA	NA	38	NA	6.47	[25]
Peels of Carya cathayensis sarg	NA	15	280	NA	NA	NA	44.9	NA	NA	[26]
Bamboo hydrochar	Congo red & 2- Naphthol	2h	200	17.94	0.03	3.83	65.7	NA	33.7	[27]
Fresh banana peels	Pb(II)	2h	230	45.27	NA	NA	39.59	NA	14.80	[28]
Municipal waste	PO4-P, NH4-N	NA	250	2	NA	NA	NA	44.5	1.14	[18]
Lepironia Articulata	Ni(II)	24h	200	69.22	0.0800	4.623	60	40	12.1	Current study

### c) Cation Exchange Capacity (CEC)

As CEC is said to be a function of surface area and functionality, an increase in hydrochar CEC suggests either the unblocking of pores increasing porosity and surface area or that a higher surface functionality is being revealed by removing tar. The effect of higher surface functionality is being revealed by removing tar may be more important as the surface area had negligible influence on char CEC, with HC possessing low surface areas ( $< 6 \text{ m}^2 \text{ g}^{-1}$ ) [18]. The development of carboxyl and other functional groups can improve CEC [19]. Current study revealed a high CEC value of ( $40 \text{ cmol}_c \text{ kg}^{-1}$ ) listed in Table 1 which is better when compared to HC from different biomass. Improvement in heavy metal removal efficiency in current study is the reason due to the development of negative functional groups on the surface of HC and higher CEC value.

### d) Hydrochar yield

Solid mass yield is one of the key characteristics for HC. It is very important to control parameters during hydrothermal treatment to increase the product yield and retaining its adsorption efficiency. Below equation (Eq. (4)) is used to calculate HC yield on dry basis

Yield of HC(%) =

$$\frac{\text{mass of hydrochar (dry basis)}}{\text{mass biomass before hydrolysis (dry basis)}} \times 100 \quad (4)$$

Yield and CEC along with  $q_m$  of the HC are listed in Table 1. Which clearly shows a good yield of 60% achieved in the current study. Low temperature with long retention time can also lead to high yield whereas high temperature may lead to decrease the yield. Long retention time is helpful to break down the hemicellulose complexes into

various functional groups.

### 3.2 Effect of pH

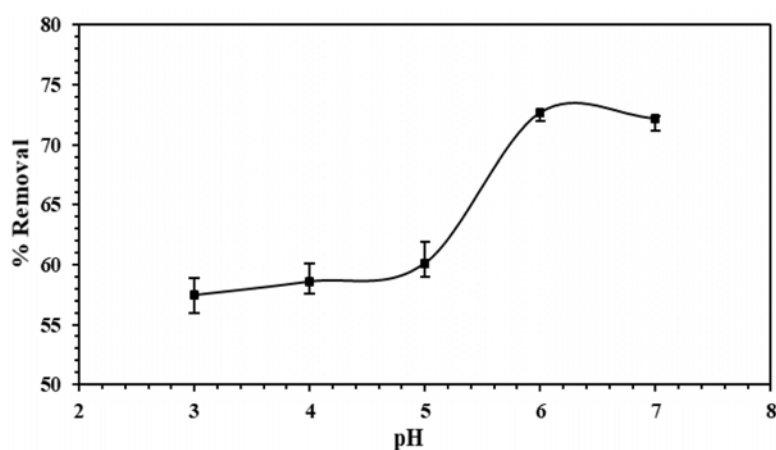
The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate [20]. Figure 2 shows the similar trend as percentage removal of Ni (II) as a function of pH at a heavy metal concentration of  $50 \text{ mg L}^{-1}$  and a HC dosage of  $20 \text{ g L}^{-1}$ . Removal efficiency of Ni (II) increases with increase in pH of the solution to 6. After that, a small decrease was observed to pH 7. The percent adsorption of metal ion decreased with the decrease in pH below 5, because protons compete with metal ions for sorption sites on the adsorbent surface and because the contaminant decreases the negative charge of the same surface[21]. On the other hand at higher pH values above 6, the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) may become significant mechanisms in the metal removal process. In practice the precipitation can be very small in size sometimes and, upon the neutralization of the wastewater the solubility of the metal ion increases, which leads to re-contamination of the treated water. Therefore the pH of the solution was kept at 6 for rest of the experiments.

### 3.3 Effect of Initial Concentration of Adsorbate

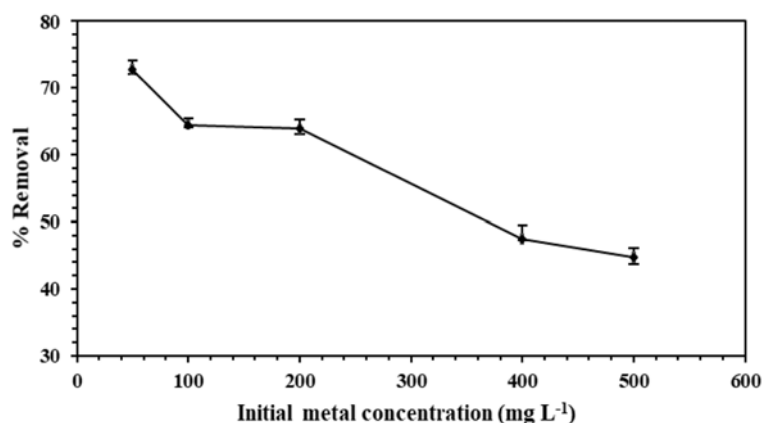
The Initial concentration of adsorbate is one of the effective factors on adsorption efficiency. To calculate the removal efficiency of Ni(II) by varying initial adsorbate concentration, experiments were done with variable initial Ni(II) concentration ( $50, 100, 200, 400$  and  $500 \text{ mg L}^{-1}$ ) and constant temperature ( $303 \text{ K}$ ), pH (6),

agitation speed (150 rpm), contact time (2 h) and adsorbent dose ( $20 \text{ g L}^{-1}$ ). The experimental results of the effect of initial Ni (II) concentration on removal efficiency were presented in Figure 3. The trend line shown in Figure 3 illustrates a decrease in removal efficiency of Ni (II) from aqueous solution with an increase in initial adsorbate concentration. In case the low concentration of Ni (II) the fractional

adsorption become independent of initial Ni (II) ions due to the fact that the ratio of initial number of moles of adsorbate ions to the available surface area of LAHC is large. However, at higher concentration, the uptake rate becomes slower which ultimately decreases the removal efficiency of adsorbent overall, it is likely due to most of the sites on adsorbent are already occupied when the concentration is high.



**Figure 2.** Effect of pH on the percent removal of Nickel: initial metal Concentration of  $50 \text{ mg L}^{-1}$  and hydrochar dosage of  $20 \text{ g L}^{-1}$ .



**Figure 3.** Removal efficiency of Ni(II) with variable initial Concentration of adsorbate ( $\text{mg L}^{-1}$ ).



### 3.4 Effect of Contact Time on Removal Efficiency

Adsorption of Ni (II) was examined against contact time (min). A 20 g L<sup>-1</sup> fixed amount of adsorbent was mixed with 50 mL of the sample solution in a 250 mL conical flask and were shaken with a different interval of time. From Figure 4 a trend of increase in removal efficiency is observed against time 15, 30, 60, 90, 120, and 180 min respectively, the plot illustrates that the percent nickel removal is higher at the start; this is possibly due to a larger surface area of the LAHC being accessible at the beginning for the adsorption of nickel. As soon as the

adsorption sites become exhausted, the uptake rate is minimized and controlled by the rate of adsorbate ions which are transported from exterior to the interior available sites of the adsorbent. The maximum percentage removal of Ni (II) was achieved after 120 min of contact time and thereafter no further increment in removal efficiency was observed. From above observations, it was concluded that the maximum time required for the removal of Ni (II) from aqueous solution was 120 min whereas the adsorption of Ni (II) took place immediately after 15 min of starting a process.

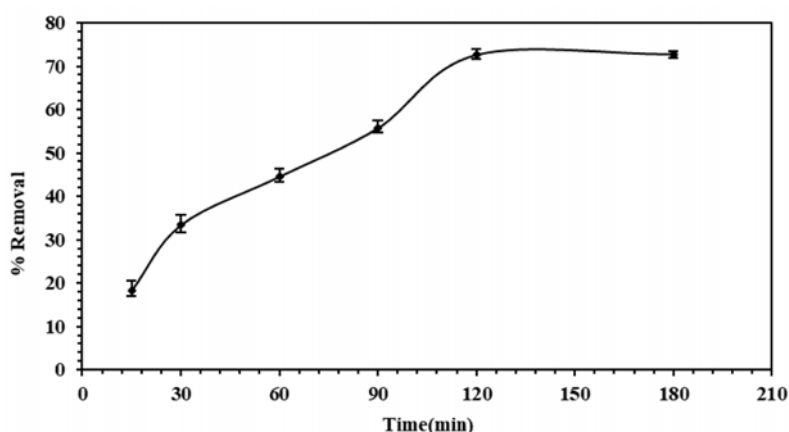
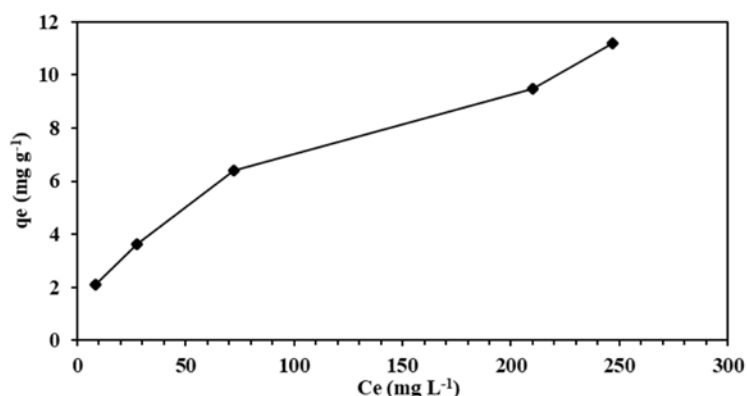


Figure 4. Removal efficiency of Ni(II) against contact time (min) of adsorption process.

### 3.5 Adsorption Isotherm Models

Modelling of experimental data from adsorption processes is a very important means of predicting the mechanisms of various adsorption systems [21]. Various adsorption isotherm models are being used to identify the adsorption process in detail. To identify the model which best fits the experimental data linearized equations are used to calculate adsorption rate, capacity, and mechanism. Initial values in terms

of equilibrium adsorption capacity and adsorbate ion concentration were first calculated before plotting to isotherm model. Adsorption capacity or maximum rate of adsorption can be found in Figure 5. Which shows the linear trend of equilibrium adsorption capacity  $q_e$  (mg g<sup>-1</sup>) against Ni (II) ion concentration in the solution at equilibrium adsorbate concentration in solution  $C_e$  (mg L<sup>-1</sup>).



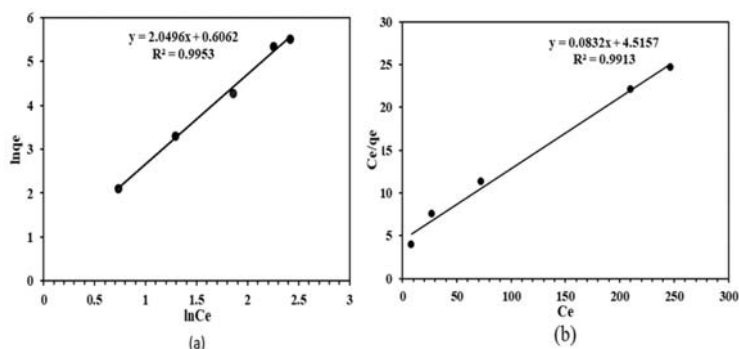
**Figure 5.** Adsorption capacity  $q_e$ (mg g<sup>-1</sup>) Against Equilibrium adsorbate concentration in solution  $C_e$ (mg L<sup>-1</sup>).

Langmuir and Freundlich isotherm models were studied in this research. Both models were used to identify the surface mechanism of adsorption of Ni (II) onto LAHC.

Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is opened while desorption is proportional to the fraction of the adsorbent surface that is covered [22]. Freundlich isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies [23].

Figure 6 (a) and (b) shows that both Langmuir and Freundlich isotherm models fit the experimental data. Still, the trend is

better in case of Freundlich isotherm model. The results clearly demonstrate that the adsorption is favorable in terms of higher adsorption capacity with equal distribution of metal ions amongst the active sites of adsorbent. Table 2 Further illustrates the correlation coefficients and constants used in both isotherm models. Value of  $K_L$  is 0.0183 which characterizes the ability of LAHC surface to adsorb Ni (II) from the aqueous solution at equilibrium concentration in surface monolayer. Whereas the value of  $1/n$  from Freundlich model smaller than 1 represents favorable adsorption condition, and a smaller  $1/n$  value indicates an easier adsorption process [22]. In the current study the value of  $1/n$  is 0.4856 which is well under 1 and satisfies favorable adsorption process.



**Figure 6.** (a) Freundlich adsorption isotherm, (b) Langmuir adsorption isotherm.

**Table 2.** Langmuir and freundlich isotherm parameters for the sorption Ni(II) ions onto hydrochar.

Isotherm	Parameter	Value
Langmuir	$q_m$ (mg g <sup>-1</sup> )	12.1
	$K_L$	0.0183
	$R^2$	0.9913
Freundlich	1/n	0.4856
	$K_f$	1.33
	$R^2$	0.9953

#### 4. CONCLUSION

The hydrothermal synthesis process for the preparation of HC from *Lepironia Articulata* was found inexpensive and productive. Equilibrium data obtained for LAHC were plotted using Langmuir and Freundlich isotherm linear equations, the later one exhibited the best fit with 1/n calculated 0.4856 and  $R^2 = 0.9953$ . The maximum removal efficiency obtained was 72.77% with pH 6 and 100 mg L<sup>-1</sup> Initial metal concentration. Product yield was calculated to be 60% and was found excellent when compared with different HC obtained from various biomass materials. It was concluded that synthesizing of biomass at 200 °C and 24 h residence time in the presence of a catalyst can lead to highest yield and could help in the development of negative functional groups on the surface of HC, which is helpful in the removal of cationic heavy metal. Environmental issues concerning to high-temperature pyrolysis methods could be reduced up to a maximum extent, as this process does not allow the gaseous product to release into the open atmosphere and the remaining liquor can be further processed to obtain various other useful products. It is therefore suggested LAHC can be utilized to remove various

contaminants in wastewater and the removal efficiency and adsorption capacity of the adsorbent can be enhanced by applying further modification on the structure of HC.

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