

# Sequestering Divalent Nickel Ions from Aqueous Solution Using Activated Carbon of *Citrus limetta* Peel: Isothermic and Kinetic Studies

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## Abstract

The biochar (activated carbon) derived from *Citrus limetta* peel waste biomaterial, was tested for the removal of nickel (II) ions from aqueous solution. Batch experiments were conducted with nickel concentration, pH, and dosage to estimate the nickel ions sequestration from aqueous solution. Among the models employed, Langmuir Isotherm fit well with the adsorption data. The kinetic data analysed with Lagergren and Ho Models fit well with pseudo first-order. Maximum removal (99.8%) of Ni(II) was observed at pH 7, with 0.05 g adsorbent dosage of Ni(II) solution 100 mg L<sup>-1</sup>. The characterization of biochar carried out by using a scanning electron microscope (SEM), energy-dispersive x-ray spectrometer (EDX), and Fourier transform infrared spectrometer (FT-IR) revealed interaction with Ni(II) ions and the formation of isolated aggregates on the biosorbent surface. The results indicate that *Citrus limetta* peel biochar can effectively be used for the removal of nickel ions from aqueous solution.

**Keywords:** Nickel (II) ion adsorption, *Citrus limetta* peel biochar, isotherm and kinetic models, SEM and EDAX, FT-IR

## Introduction

Heavy metal ions like copper, nickel, zinc, cadmium, lead, chromium, and mercury have been documented as pollutants in the environment [1]. Nickel, a toxic heavy metal, is introduced into natural water systems mainly from many chemical industries viz., textile dyeing,

electroplating, and metal finishing. Nickel is reported to cause severe environmental hazards and public health issues. Even after carefully measuring discharged nickel(II) ions into the ecosystem, we still see serious threats of allergies, cardiovascular issues, gastrointestinal irritation, kidney disease, and lung fibrosis to [2]. The permissible discharge level of Ni(II) from industrial effluent into water bodies is 3 mg L<sup>-1</sup> and in drinking water for human consumption is less than 40 µg L<sup>-1</sup>. The main source of freshwater contamination can be attributed

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to the release of untreated sanitary and toxic industrial effluent and overflow from agricultural fields [3]. Thus it is necessary to remove the nickel before disposal of industrial waste. Although some known methods such as chemical precipitation, electro-coagulation, ion exchange, surface adsorption, and membrane filtration are already being used to remove heavy metals, these methods are cumbersome and costly [4]. In recent years, agricultural wastes have been extensively studied for their use in the removal of metal from water. These wastes comprise peat, wood, bark, husk, dust, peel, and leaves [5-7]. With this view, *Citrus limetta* peel, a plentiful waste material, was made into biochar (activated carbon) and then used here to study its adsorption ability of Ni(II) ions from aqueous solution. Thus, the purpose of the present study was to: (i) incorporate and characterize biochar from *Citrus limetta* peel, (ii) assess the potential of *Citrus limetta* peel biochar for the removal of Ni(II) from aqueous solution, (iii) evaluate the influence of experimental variables on Ni(II) adsorption onto *Citrus limetta* peel biochar, and (iv) analyze adsorption kinetics and isotherms to understand the mechanism of Ni(II) removal.

## Materials and Methods

### Biochar Preparation

The *Citrus limetta* peel was collected from various fruit shops in Coimbatore and was sun-dried before being kept in hot air oven at 100°C for 24 h. The dehydrated material was compressed and fed into a pyrolysis stove (Safire Scientific Company) at Tamil Nadu Agricultural University, Coimbatore. The charred (biochar) activated carbon sample was collected, and their significant characteristics were analyzed before conducting experiments.

### Characterization of *Citrus limetta* Peel Biochar

The biochar sample of *Citrus limetta* peel was sieved (<0.25 mm) and their water-holding capacity, zeta potential, and particle size were analyzed by standard methods [8]. Furthermore, proximate analyses of the *Citrus limetta* peel biochar were also carried out.

### Zeta Potential Study

A nanoparticle analyzer (Horiba Scientific Nanopartica, Japan) was used to carry out the zeta potential (on the surface charge) of the *Citrus limetta* biochar. About 0.5 g of *Citrus limetta* peel biochar was suspended in 20 mL of solution with pH of 4, 5.5, 7, 8, and 9 was allowed to settle for about 30 minutes [9]. The samples were then tested three times, with five readings for each run. The output data were obtained in the form of mobility, zeta potential, and conductance.

### Fourier Transform Infrared Spectroscopic Analysis

The adsorption capacity of *Citrus limetta* peel biochar depends not only on porosity but also on chemical reactivity of functional groups at the surface of the adsorbent. The chemical reactivity creates an imbalance between forces at the exterior and inside the body of the adsorbent, thus resulting in Van der Waals force to create a molecular adsorption [10].

### Scanning Electron Microscopy and EDAX Analysis

Electron microscopy studies yield the interaction and non-interaction of logarithmic phase cells. Small pinches of *Citrus limetta* peel biochar powder were fixed on a 10 mm metal stub using carbon tape [10]. The samples were sputter-coated with gold under vacuum in an argon atmosphere and analyzed at 20 kV for the tungsten filament. The surface topography of the coated sample and the elemental analyses of non-interacted log phase biochar and Ni(II) interacted log phase biochar were carried out by Energy Dispersive X-ray spectroscopy (EDAX) using Quanta FEI 250 (Czechoslovakia) equipment.

### Adsorption Experiments

A stock solution of Ni (II) (1,000 mg L<sup>-1</sup>) was prepared by dissolving NiSO<sub>4</sub>·6H<sub>2</sub>O (E Merck) (procured from Himedia Laboratories India (Molecular weight 294.18, 99.9% Assay)) in deionized water. Desired concentrations of Nickel (II) solutions were prepared by diluting the stock solution. The pH of the solution was adjusted using 0.1 N HCl or 0.1 N NaOH solutions [11]. Other test concentrations between 50 and 250 mg L<sup>-1</sup> at an increment of 50 mg L<sup>-1</sup> were prepared from the stock solution.

Nickel concentration was determined by UV-spectrophotometer (Systronics visis, Canada; model No. 167) using the dimethyl glyoxime method. The adsorption of nickel (II) ion was determined by taking 0.05 g of *Citrus limetta* peel biochar in 250 ml Erlenmeyer flasks with 25 ml of initial concentrations (50-250 mg L<sup>-1</sup>) of nickel solution and were further agitated using a mechanical shaker (Orbit Shaker, Taiwan) at 150 rpm. After proper mixing, the resultant solution was allowed to equilibrate for a period of 120 min. The samples were filtered prior to analysis in order to minimize interference of the carbon fines. The wavelength of operation was kept at 470 nm. By standard calibration graph, the absorbance of the supernatant solution was measured to determine the residual Ni(II) concentration. All the investigations were carried out in triplicate and the mean values were reported to avoid any inconsistency in experimental results. The metal solution controls (check) were kept throughout the experiment. The adsorption capacity at equilibrium  $q_e$  was determined [12]. The percentage removal of divalent nickel was calculated for each run as follows.

$$\text{Removal capacity (\%)} = \frac{C_o - C_e}{C_o} * 100 \quad (1)$$

...where  $C_o$  and  $C_e$  represent the initial and equilibrium concentrations of nickel ion in aqueous solution. The adsorption capacity for each concentration of nickel (II) at equilibrium was determined by the following expression [13].

$$\text{Adsorption capacity} = q_e \frac{(mg)}{(g)} = \frac{C_o - C_e}{m} * V \quad (2)$$

...where  $V$  is the volume of solution in litres and  $m$  is the mass of the adsorbent used in grams.

### Optimization Studies of Ni(II) Adsorption

The batch adsorption studies with different parameters were analyzed by using known concentrations, dosages, and pH. Concentrations ranging from 50-250 mg L<sup>-1</sup> with pH from 3 to 8 and activated carbon dose of 0.01-0.05 g were used for optimization. Experiments were carried out for 120 minutes taking absorbance measurement in every 10-min interval. To fix the optimum concentration of Ni(II) ions, the pH and adsorbent dosage were kept at 7 and 0.05 g, respectively. Similarly, optimum dosage was determined by keeping pH 7 and concentration at 100 mg L<sup>-1</sup>. The optimum pH was determined by maintaining 0.05 g of the adsorbent and 100 mg L<sup>-1</sup> of nickel ion concentration. In every trial, after adsorption the sorbate was decanted and separated from the sorbent by centrifuge and the supernatant liquid was analyzed for the residual metal concentration and the residual carbon was used for further studies.

### Adsorption Isotherm Models

Adsorption isotherm explains the adsorbate interaction with adsorbents and therefore is significant in optimizing the use of adsorbents and it is necessary to create the most fitting correlation for the equilibrium curve [14]. Among several options, very important isotherm models (viz., Langmuir, Freundlich, and Temkin mathematical calculations) were selected to study the mode of interaction of Ni(II) ions with biochar at equilibrium. Langmuir, (Eq. 3), Freundlich, (Eq. 4), and Temkin (Eq. 5) isotherms were plotted by using standard straight-line equations and corresponding two parameters  $C_e$  and  $q_e$  for nickel ion.

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_{\text{ad}} * Q_{\max}} \quad (3)$$

$$\log q_e = \left[ \log K_f + \left\langle \frac{1}{n} \right\rangle \log C_e \right] \quad (4)$$

...where  $q_e$  (mg g<sup>-1</sup>) is the amount of metal adsorbed and  $C_e$  (mg L<sup>-1</sup>) is concentration at equilibrium.  $Q_{\max}$  (mg g<sup>-1</sup>),  $b$  (L mg<sup>-1</sup>) and  $K_{\text{ad}}$  (L mg<sup>-1</sup>) are Langmuir isotherm parameters [15-16].

$K_f$  and  $n$  are Freundlich isotherm parameters<sup>3</sup>.  $C_e$  (mg L<sup>-1</sup>) is the concentration of Ni(II) ions at equilibrium,  $q_e$  (mg g<sup>-1</sup>) is the equilibrium adsorption capacity and  $n$  is the heterogeneity factor.  $K_f$  and  $n$  can be determined from a linear plot of  $\log q_e$  against  $\log C_e$  [17-18].

The Temkin isotherm equation correlates the equilibrium metal concentration with the heat of adsorption due to adsorbent-adsorbate interactions.

$$q_e = B \ln A + B \ln C_e \quad (5)$$

...where  $B = RT/b$ ,  $b$  is the Temkin constant related to heat of adsorption (J mol<sup>-1</sup>),  $A$  is the Temkin isotherm constant (L g<sup>-1</sup>),  $R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>), and  $T$  is the absolute temperature (K) [19].

### Adsorption Kinetics

The adsorption kinetics of Ni(II) on *Citrus limetta* biochar was studied for its possible utilization in the treatment of industrial effluents. The first-order rate constant for adsorption of Ni(II) has been analyzed with the help of Lagergran's equation [20].

$$\text{Log}(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

...where  $q_e$  is the amount of metal adsorbed at equilibrium (mg/g), and  $q_t$  is the amount of metal adsorbed at time  $t$  (mg/g).

$k_1$  = rate constant of adsorption (per minute)

$t$  = Time (minute)

Pseudo second-order rate equation [21]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \frac{t}{q_e} \quad (7)$$

...where  $k_2$  is the second-order rate constant for adsorption (g mg<sup>-1</sup> min<sup>-1</sup>),  $q_e$  is the amount of metal adsorption at equilibrium (mg g<sup>-1</sup>), and  $q_t$  is the amount of metal adsorption in time  $t$  (min<sup>-1</sup>). The graphs  $\log (q_e - q_t)$  vs,  $t$  and  $t/q_t$  vs.  $t$  depict the metal sorption for first- and second-order rate kinetic models, respectively [22].

## Results and Discussion

### Characterization of Biochar

The results on the proximate analyses of the *Citrus limetta* peel biochar sample are presented in Table 1 and the schematic representation of Ni(II) adsorption onto biochar in Fig. 1. The fixed carbon content of the sample was high, which indicates high carbonization. The pH was high, signifying the alkalinity of the biochar. The electrical conductivity of the biochar was 1.91. Zeta potential is a measure of charge stability that controls all particle-particle interaction within a suspension, and in this study the zeta potential of biochar was found to be -7.9 mV.

Table 1. Characteristics of *Citrus limetta* peel biochar.

| Characteristics        | Value                      |
|------------------------|----------------------------|
| pH                     | 10.0                       |
| EC                     | 1.91 (ds m <sup>-1</sup> ) |
| Water-holding capacity | 224.31 (%)                 |
| Moisture content       | 2.08 (%)                   |
| Volatile content       | 14 (%)                     |
| Fixed carbon content   | 70 (%)                     |
| Ash content            | 16 (%)                     |
| Zeta potential         | -7.9 (mV)                  |
| Particle size          |                            |
| SP Area ratio          | 1.00                       |
| Mean                   | 380.9 (nm)                 |
| Standard deviation     | 56.0 (nm)                  |
| Mode                   | 376.7 (nm)                 |

The characteristics of the *Citrus limetta* biochar had been discussed in detail in our previous study [9].

The stability behaviour of *Citrus limetta* biochar was found to be incipient unstable. The pH value is high, which may be due to the detachment of alkali metals such as Ca and Mg from the biochar. A similar conclusion was noted with the biochar generated from sugar cane bagasse [23]. The increase in adsorption capacity with increase in Ni(II) concentration may be due to the higher adsorption rate and consumption of all energetic sites available for adsorption at higher concentration or due to higher accessibility of Ni(II) ions in the solution for the adsorption [24]. This is mainly due to the greater availability of surface area and adsorption sites, which in turn brings about greater removal of Ni ions [25]. The increase in percentage of

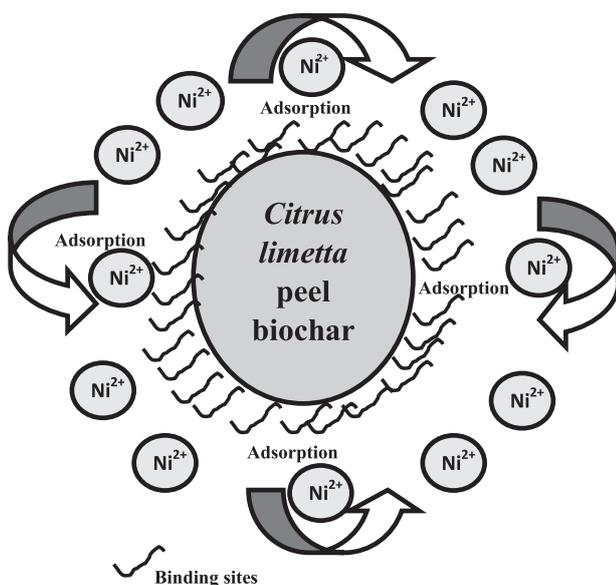


Fig. 1. Schematic representation of Ni (II) adsorption onto *Citrus limetta* peel biochar.

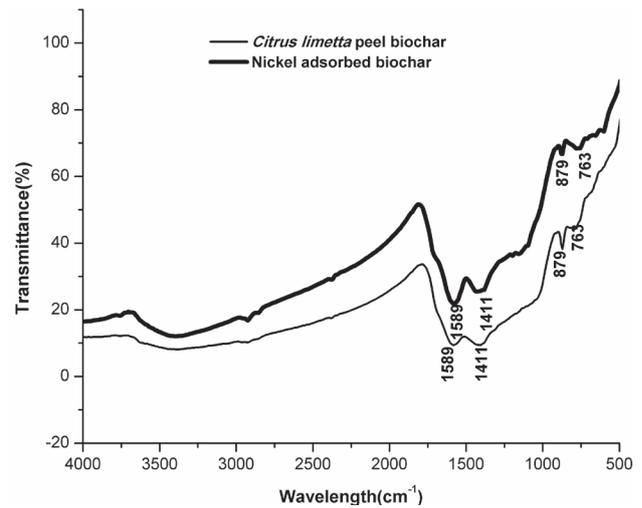


Fig. 2. FT-IR spectra of *Citrus limetta* peel biochar before and after Ni (II) adsorption.

metal ion removal with the increase in pH can be explained on the basis of a decrease in competition between proton and Ni(II) ions for the same functional group, and by a decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. A decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes [26]. More than 80% removal of Ni(II) by *Brassera oleracea* at pH 5 was also reported [7]. Increasing pH from 5 resulted in reductions in adsorption. But the present study contradicts the earlier works and demonstrates that pH 7 as the best suitable condition for *Citrus limetta* peel biochar.

#### FT-IR, SEM, and EDAX Analyses

It is evident from the FT-IR, SEM, and EDAX studies that the adsorption of Ni(II) on to *Citrus limetta* peel biochar with due reasons. The FT-IR spectrum of nickel-loaded *Citrus limetta* peel biochar showed a noticeable difference from the FT-IR spectrum of *Citrus limetta* peel biochar. The FT-IR spectra of *Citrus limetta* peel biochar before and after adsorption of nickel were used to establish the vibration frequency of the functional groups in the adsorbents. In general, the biochar is a residual complex of organic compounds containing groups such as carboxylic acid, hydroxyl, ketones, aromatic moieties, and unsaturated compounds. Both the spectra of *Citrus limetta* peel biochar were measured in the range between 4,000 and 400 cm<sup>-1</sup>. The spectra were plotted using the same scale on the transmittance axis for the adsorbent before and after adsorption (Fig. 2). The results suggest that FT-IR spectrum of *Citrus limetta* biochar (before adsorption) had a broad band at 1,589 cm<sup>-1</sup> associated with the CO<sub>2</sub> stretching vibration, and the peak at 879 cm<sup>-1</sup> may be due to C-H bending of the alkyl group. The band at 1,411 cm<sup>-1</sup> is attributed to aromatic C-C stretching vibration. The frequency at 779 cm<sup>-1</sup> before adsorption shifted to 763 cm<sup>-1</sup> after adsorption. This is due to the

formation of a weak bond between Ni and the ketonic group of the biochar [27].

SEM analysis is useful in understanding the porous structure of the biochar. There are holes and openings which are permeable structures, and heterogeneous rough surface with crater-like pores in *Citrus limetta* peel biochar that definitely increase the surface area available for adsorption (Fig. 3). Asymmetrical shape and the surface exhibit a micro-rough texture, which can support the adherence of heavy metals on to biosorbents [28-29]. It is very clear from the image that the porous surface has adsorbed nickel ions, confirming the sequestering process. Moreover, the EDAX spectra of preferred region of biochar before and after adsorption were recorded to investigate the chemical constituents in the biochar sample, further confirming the adsorption of Ni(II) ions (Fig. 4). EDAX analysis also identifies the presence of potassium, calcium, and phosphorus in both control and test samples. In short, the *Citrus limetta* peel biochar both by physical and chemical means is capable of adsorbing the nickel up to 99% from aqueous solution.

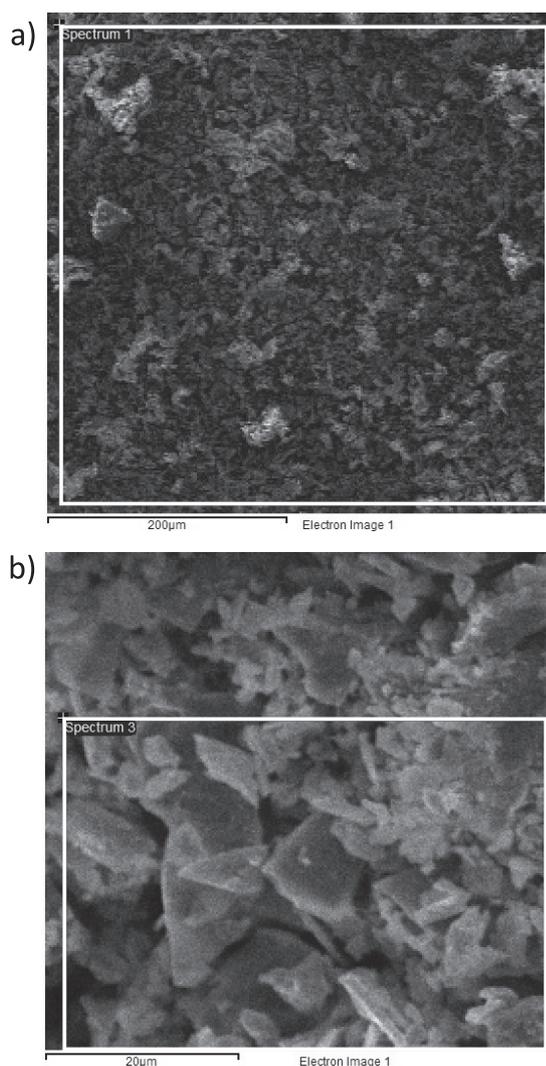


Fig. 3. SEM micrograph of *Citrus limetta* peel biochar before a) and after b) Ni(II) adsorption.

## Optimization of Ni(II) Adsorption

The uptake of Ni(II) from aqueous solution by *Citrus limetta* biochar increased with time and attained equilibrium in 120 min for all the concentrations studied (Fig. 5a). The concentration of the solution varied from 50 to 250 mg L<sup>-1</sup> with a dosage 0.05 g and at pH 7 [30]. The equilibrium time was independent of initial Ni(II) concentration. When the concentration was 100 mg L<sup>-1</sup>, the percent removal of Ni(II) was 99.8% by the *Citrus limetta* biochar. Fig. 5b) represents the effect of the dosage of biochar on the removal of Ni(II). The dosage amount increased from 0.01 to 0.05 g and equilibrated for 120 min with the Ni(II) concentration of 100 mg L<sup>-1</sup> and at pH 7. The percentage removal was 99.41 at 0.05 g dose. This study corroborates with previous adsorption studies of Cr(VI) onto biochar [9, 31]. The most significant controlling parameter in the adsorption process is pH. The level of removal of Ni(II) ions was investigated by changing the pH from 2 to 8, and the results are shown in Fig. 5c). It was noticed that with the increase in the pH of the solution, the amount of Ni(II) ion removal also increased. Maximum adsorption was observed at pH 7 [32].

## Adsorption Isotherms

An adsorption isotherm describes the stability relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given

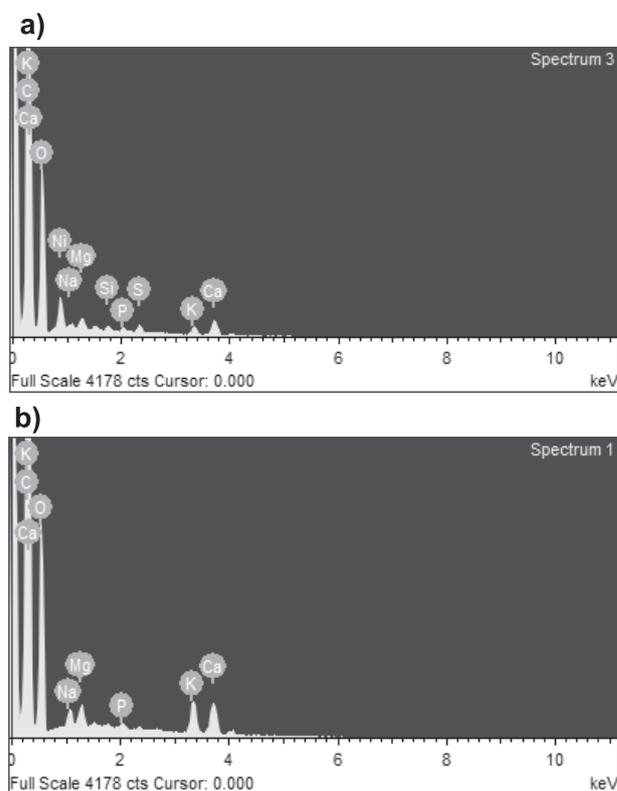


Fig. 4. Energy dispersive spectrum of *Citrus limetta* peel biochar before a) and after b) Ni(II) adsorption.

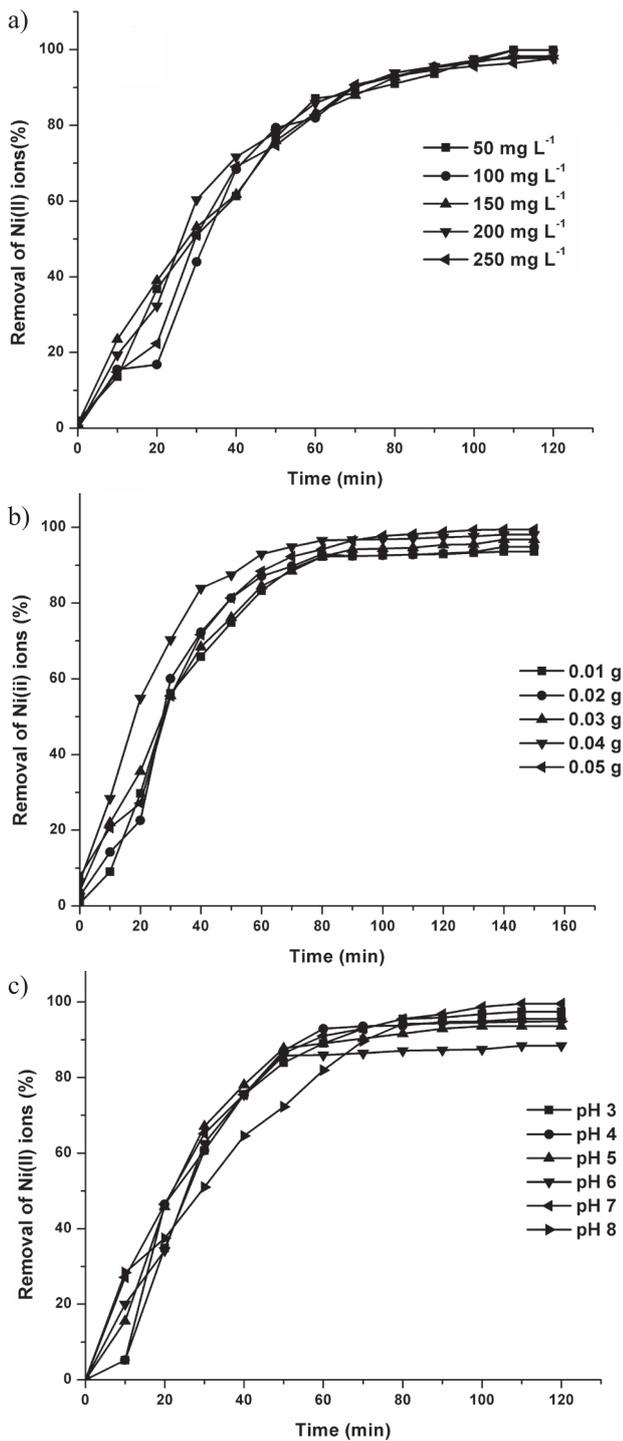


Fig. 5. Effect of concentration a), dosage b) and pH c) on the removal of Ni (II) by Citrus limetta peel biochar where, a = effect of concentration at pH 7, adsorbent dose 0.05 g and contact time 120 mins; b = effect of Dosage at pH 7, concentration 100 mg L<sup>-1</sup> and contact time 120 mins; and c = Effect of pH at concentration 100 mg L<sup>-1</sup>, contact time 120 mins and dosage 0.05 g.

condition. Among several options, Freundlich, Langmuir, and Temkin isotherm models were used here to describe the equilibrium relationship. The Langmuir isotherm model explains the sorption phenomena and suggests that uptake occurs on a homogeneous surface by monolayer

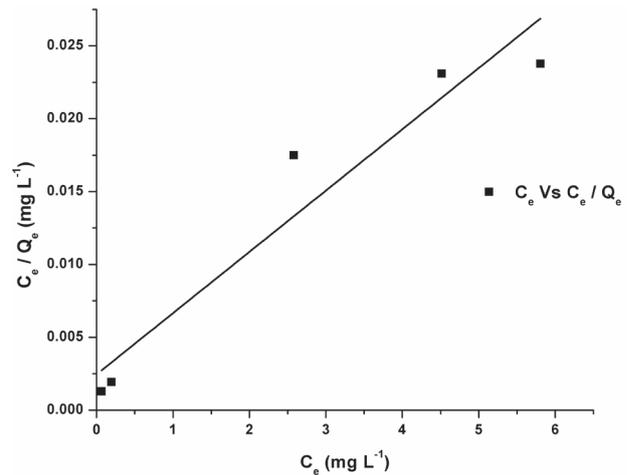


Fig. 6. Langmuir isotherm of Ni (II) adsorption by *Citrus limetta* peel biochar at pH 7, dosage 0.05 g and contact time 120 mins.

sorption. The plots of specific sorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ) for nickel(II) are shown in Fig. 6 and the linear isotherm parameters,  $Q_e$ ,  $b$ , and the coefficient of determinations are found in Table 2. We observed that the Langmuir adsorption isotherm was the best fitting model for the sorption of nickel(II) from aqueous solution using *Citrus limetta* peel biochar, which has correlation coefficient ( $R^2$ ) of 0.9312, indicating favourable adsorption [7]. In the batch adsorption process the Langmuir Isotherm can be used to express whether a sorption system is favourable or not. The necessary features of the isotherm can be expressed in terms of separation factor (RL), which can be explained by the following relationship. The values of RL reflect the type of Langmuir isotherm. RL value can be calculated by the formula,  $RL = 1/(1+b \cdot C_0)$ . When the RL value is zero, the adsorption process is irreversible. When RL value is between 0 and 1 the process is favourable, and if it is greater than 1 the process is unfavourable (Table 2). The RL values in the present study are found to be between 0.002 and 0.01, which indicate that the isotherm is a favourable one. The present study suggests that it has high  $Q_{max}$  values. Mao et al. (2010) reported that the adsorbent with high  $Q_{max}$  values is usually advantageous for the wastewater treatment process [33]. High Kf values also indicate that the saturation time for adsorption of metal ions was attained quickly due to high affinity of activated bioadsorbent towards adsorbate, while low Kf values indicate low adsorption rate of metal ions [34].

In the Freundlich isotherm the magnitude of constant  $1/n$  gives an indication of the favourability of adsorption. The value of  $n > 1$  represents favourable adsorption conditions (or) if the value of  $1/n$  lies in the range of 1 to 10, the adsorption is favourable. The values of  $1/n$  were low for nickel ions in this study (Table 2), revealing that the  $1/n$  and Kf values in Freundlich isotherm are not found to fit this adsorption data. The Temkin adsorption isotherm model was preferred to assess the adsorption potentials of the adsorbent for the adsorbates. The Temkin

Table 2. Langmuir, Freundlich, and Temkin isotherm constants for nickel ion adsorption by *Citrus limetta* peel biochar.

| <i>Citrus limetta</i> peel biochar | Langmuir isotherm                |                         |                | Freundlich isotherm         |                         |                | Temkin isotherm        |                          |                |
|------------------------------------|----------------------------------|-------------------------|----------------|-----------------------------|-------------------------|----------------|------------------------|--------------------------|----------------|
|                                    | $Q_{\max}$ (mg g <sup>-1</sup> ) | B (L mg <sup>-1</sup> ) | R <sup>2</sup> | $K_f$ (mg g <sup>-1</sup> ) | n (L mg <sup>-1</sup> ) | R <sup>2</sup> | A (L g <sup>-1</sup> ) | B (J mol <sup>-1</sup> ) | R <sup>2</sup> |
| Concentration                      | 237.78                           | 1.71447                 | 0.9319         | 129.8307                    | 0.32558                 | 0.9310         | 35.627                 | 41.9232                  | 0.90542        |
| pH                                 | 86.988                           | 7.59726                 | 0.9968         | 98.83871                    | 0.03                    | 0.7743         | 24.634                 | -0.0055                  | 0.75540        |
| Dosage                             | 87.700                           | 3.84258                 | 0.9983         | 96.59201                    | 0.007                   | 0.6221         | 14.082                 | 0.06058                  | 0.66364        |

Table 3. Biosorption kinetics of Ni (II) on *Citrus limetta* peel biochar.

| Conc. (mg L <sup>-1</sup> ) | Q <sub>e</sub> (Expt.) mg g <sup>-1</sup> | Pseudo first-order           |                                  |                | Pseudo second-order          |  |                |
|-----------------------------|---|------------------------------|----------------------------------|----------------|------------------------------|--|----------------|
|                             |   | q (Calc.) mg g <sup>-1</sup> | K <sub>1</sub> min <sup>-1</sup> | R <sup>2</sup> | q (Calc.) mg g <sup>-1</sup> | K <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> ) | R <sup>2</sup> |
| 50                          | 49.935                                    | 63.60231                     | -0.03568                         | 0.980008       | 71.7751                      | 0.0002874  | 0.7877         |
| 100                         | 99.806                                    | 145.031                      | -0.03844                         | 0.923076       | 171.064                      | 0.0000753  | 0.4536         |
| 150                         | 147.42                                    | 231.5246                     | -0.04213                         | 0.968226       | 187.158                      | 0.0001638  | 0.9239         |
| 200                         | 195.48                                    | 310.7597                     | -0.03989                         | 0.954364       | 224.504                      | 0.0001114  | 0.8730         |
| 250                         | 244.19                                    | 418.7852                     | -0.04456                         | 0.974525       | 377.026                      | 0.0000461  | 0.6877         |

Note: Conc.-Concentration, Expt.-Experimental, Calc.-Calculated; triplicate experiments were carried out and mean values were reported.

isotherm plot for the Ni(II) ions is presented in Table 2. It was observed that the Temkin adsorption isotherm also fits the adsorption data with the sorption of Ni(II) from aqueous solution using *Citrus limetta* peel biochar and has correlation coefficient (R<sup>2</sup>) of 0.9054. Comparative R<sup>2</sup> values (correlation coefficients) of the Langmuir, Freundlich, and Temkin isotherm models are furnished in Table 3. However, the Langmuir model is the perfect fit in this study as reported earlier for the removal of Ni(II) and other heavy metals [9, 35-36].

### Kinetic Model

The kinetics of divalent nickel ion adsorption on to the *Citrus limetta* peel biochar were determined by pseudo first-order and pseudo second-order equations using data obtained from optimized conditions. In the case of the pseudo first-order model, the correlation coefficient (R<sup>2</sup>) was found to be 0.98, indicating that the model perfectly fits the kinetic data for the adsorption system in the present study (Fig. 7). But for the pseudo second-order (R<sup>2</sup> = 0.787), kinetic data was incapable of explaining the sorption kinetics suitably. In addition, from Table 3 it can be concluded that the adsorption of Ni(II) on the surface of *Citrus limetta* peel biochar effectively followed the pseudo first-order kinetics as demonstrated earlier with Cr(VI) on to *Citrus limetta* peel biochar [9] and Ni(II) on to *Thespesia populnea* bark [37]. The adsorption reaction proceeds through the following three steps: (1) transmitting adsorbate from bulk solution to adsorbent surface, (2) moving the adsorbate into pores, and (3) the interaction of adsorbate with accessible sites on the inner surface of pores [38].

### Conclusion

The present study evaluates the use of *Citrus limetta* peel biochar for the removal of Ni(II) ions from aqueous solution. The removal of Ni(II) ions was found to be reliant on different parameters such as adsorbent dose, contact time, pH, and initial concentration. The study validates that the removal was more than 99.8% of

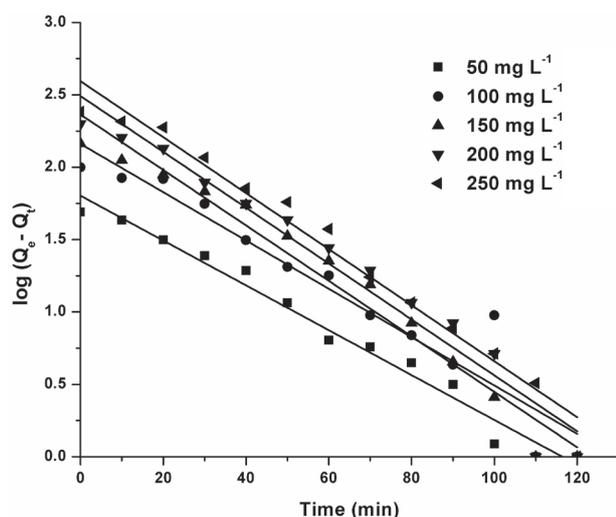


Fig. 7. Lagergren's pseudo first order kinetic plots for biosorption of Ni (II) by *Citrus limetta* peel biochar.

Ni(II) when the concentration was 100 ppm at pH 7 over 120 min. The Ni(II) adsorption on *Citrus limetta* peel biochar followed the first-order kinetics. The adsorption data befittingly match the Langmuir isotherm. Furthermore, this was sufficiently proved from morphological structure analyses like SEM and FT-IR, which showed that the surface of the biochar had a higher number of pores or sites available for adsorption. The Ni(II) ions were bound to the active sites of the biosorbent, *Citrus limetta* peel biochar, through either electrostatic attraction or a complex forming mechanism. Higher adsorption capacity indicates that *Citrus limetta* peel biochar can be used efficiently to remove Ni (II) ions from industrial effluents by using the cost-effective adsorption technique.

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