

## Equilibrium and kinetic studies on Ni(II) removal from aqueous solution by *Citrus Limettioides* peel and its carbon adsorbent

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Activated carbon has been prepared from *Citrus limettioides* peel (CLPC); a novel waste material by chemical modification with sulphuric acid followed by bicarbonate treatment applied for the adsorption of Ni(II) from aqueous solutions. Batch experiments have been carried out to study the effect of various parameters such as contact time, pH and adsorbent dosage on various Ni(II) concentrations along with, raw *Citrus limettioides* peel (CLP). The optimum pH required for the maximum adsorption of Ni(II) is found to be 4.0-9.0 and 5.0-8.0 for CLPC and CLP, respectively. The optimum contact time is found to be 4 hr in all cases of carbon and raw peel. The presence of hydroxyl and carboxylic acid groups are confirmed by FT-IR spectra. Equilibrium data agreed well with Langmuir model. Based on Langmuir isotherm the adsorption capacity is found to be 38.46 mg g<sup>-1</sup> for CLPC and 25.64 mg g<sup>-1</sup> for CLP at 300K. The kinetic data follow pseudo-second order model with film diffusion process. Similar studies have also been carried out using commercial available activated carbon (CAC) for evaluation purposes. The adsorption capacity of CAC is found to be 11.36 mg g<sup>-1</sup>. Hence the adsorption capacity (Q<sub>o</sub>) of CLPC and CLP is found to be 3.4 and 2.3 times greater than that of CAC. These adsorbents are also tested for the removal of Ni(II) from electroplating wastewater and found to remove 85% and 99% for CLP and CLPC respectively whereas the CAC show 75% removal only with an initial concentration of 220 mg/100 mL. The overall results indicate that carbon derived from *Citrus limettioides* peel (CLPC) could effectively be used to remove 99% of Ni(II) from water and wastewater.

**Keywords:** *Citrus limettioides* peel, Nickel (II) adsorption, Isotherms, Kinetics.

Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders<sup>1</sup>. Nickel (II) ion is one such heavy metal frequently encountered in raw wastewater streams from industries, such as non-ferrous metal, mineral processing, electroplating units, battery, paint formulation, porcelain enamelling, ceramic, accumulator and stainless steel manufacturing plants<sup>2-4</sup>. The tolerance limit of nickel in drinking water is 0.01 mg L<sup>-1</sup>. Higher concentration of nickel causes cancer of lungs, nose and bones. Acute Ni(II) poisoning causes dizziness, headache, nausea and vomiting, chest pain, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness<sup>5</sup>.

Many methods have been developed to remove heavy metals from wastewater, namely adsorption, chemical precipitation<sup>6</sup>, ion exchange<sup>7</sup>, coagulation and flocculation<sup>8</sup>, electrochemical reduction<sup>9</sup>, membrane filtration<sup>10</sup> and reverse osmosis. Among these methods, the adsorption is one of the easiest,

safest and less cost effective methods because it is widely used in effluent treatment process. Activated carbon is considered to be universal adsorbent because of its inherent physical properties such as large surface area, porous structure, high adsorption capacity and large reactive surface<sup>11</sup>. It has the unique property of removing both organic and inorganic materials. Activated carbon derived from a variety of waste materials such as almond husk<sup>12</sup>, peanut shells<sup>13</sup>, maize cob<sup>14</sup>, guava seed<sup>15</sup>, tamarind nut<sup>16</sup>, apricot stone<sup>17</sup>, Olivestone<sup>18</sup>, cotton seed<sup>19</sup>, and coconut oil cake residue<sup>20</sup>, alumina-coated carbon nanotubes<sup>21</sup>, CNT/ magnesium oxide<sup>22</sup>, carbon nanotubes/ iron oxide<sup>23</sup>, bottom ash and de-oiled soya<sup>24-29</sup>, blast furnace dust, sludge and slag<sup>30</sup> have been applied to remove heavy metals and dyes from water and wastewater.

*Citrus Limettioides* fruit is one of the hybrid varieties in Tamil Nadu and commonly consumed in rural areas. The fruits belong to *Rataceae* family and are highly nutritious. Extracted acid from this fruits

are used as flavouring and preservative in food and beverages, especially soft drinks and the peel is disposed off as waste material.

Studies reported here deals with activated carbon prepared from peel and evaluated with commercial granular activated carbon (CAC) for the removal of Ni(II) from aqueous solution and plating industry wastewater. Effects of parameters such as contact time, pH and adsorbent dosage on the Ni(II) adsorption were investigated along with adsorption isotherms and kinetic studies.

## Experimental Section

### Preparation of carbon adsorbent

The *Citrus limettioides* peel, was collected from local juice manufacturing unit in Rasipuram and sun dried. Then the material was washed with boiled, deionised water five to six times for removing water soluble, extractable organics and acids. The washed material was dried in sun light for 2 days and cut into small pieces using a cutter machine and sieved to 20-50 ASTM mesh size (average 0.575 mm diameter) (CLP). The dried raw material was then treated with concentrated sulphuric acid in 1:2 weight ratios and kept in an air-oven at  $160 \pm 5^\circ\text{C}$  for 24 h. The carbonized material was then washed with distilled water and soaked in 1% sodium bicarbonate for 24 h to remove free acid. The material was washed with distilled water again, dried at  $110 \pm 5^\circ\text{C}$ , sieved to 20-50 ASTM mesh size and used for experiments (CLPC). The commercially available activated carbon (CAC) (SD fine chemicals) was procured from the market and sieved to 20-50 ASTM mesh size. The characteristics of both carbons were tested as per ISI-877<sup>31</sup> and given in Table 1. The raw peel under the same particle size was also evaluated along with carbon.

### Preparation of Ni(II) solutions

Stock solution of Ni(II)  $100 \text{ mg L}^{-1}$  was prepared by dissolving 0.4479 g of AR  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  in 1000 mL of distilled water. Nickel(II) solutions of desired concentrations were prepared by dilution of the stock solution. The pH of the solution was adjusted to the required value by using 0.1 M HCl or 0.1 M NaOH solutions.

### Batch adsorption experiments

Adsorption experiments were conducted in plastic bottles of 300 mL capacity on a temperature controlled shaker. 100 mg of adsorbents were added

Table 1 — Characteristics of the carbon

Parameter	CLPC	CAC
Bulk density ( $\text{g mL}^{-1}$ )	0.51	0.62
Moisture (%)	15.70	5.85
Ash (%)	7.70	1.00
Solubility in water (%)	1.74	0.44
Solubility in 0.25 M HCl (%)	14.90	2.24
pH	5.50	9.00
Decolorizing power ( $\text{mg g}^{-1}$ )	2.70	1.50
Phenol number	69.00	50.00
Ion exchange capacity (m equiv $\text{g}^{-1}$ )	0.47	NIL
Surface area ( $\text{m}^2 \text{g}^{-1}$ )	123	230
Iron (%)	0.01	0.01
Silica (%)	NIL	0.57
Potassium (%)	0.08	0.80
Sodium (%)	1.18	5.83

to 100 mL of Ni(II) solutions of  $10 \text{ mg L}^{-1}$  concentration at a predetermined pH at 300 K and agitated for a definite period of time. For optimization, contact time was varied between 0.5 to 7 h, adsorbent dosage between 50 to 700 mg for  $10\text{-}50 \text{ mg L}^{-1}$  Ni(II) concentrations and pH between 2 to 12. Adsorption isotherms were conducted with  $10\text{-}60 \text{ mg L}^{-1}$  of Ni(II) solutions by adding 100mg/100mL of adsorbent and equilibrated for 24 h at different temperatures (300-320 K). In kinetic studies, contact time was varied from 0.5 to 8 h by adding 100mg of adsorbent, for various Ni(II) concentrations over the range  $3\text{-}10 \text{ mg L}^{-1}$  at optimum pH and at 300K. The batch experiments were repeated for three times and the average results are presented in this work.

At the end of agitation, the solutions were centrifuged and the concentrations of Ni(II) ions were determined by an atomic absorption spectrophotometer (Elico Model-SL 163). Nickel(II) removal (%) was calculated using the following equation:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad \dots(1)$$

The adsorption capacity of Ni(II) ions adsorbed per gram of adsorbent ( $\text{mg g}^{-1}$ ) was calculated by:

$$q_e = \frac{C_0 - C_e}{M} \times V \quad \dots(2)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium Ni(II) concentrations ( $\text{mg L}^{-1}$ );  $V$  is the volume of the Ni(II) solution (L);  $M$  is the mass of the adsorbent used (g) respectively.

#### FT-IR study

Fourier transform infrared spectroscopy (FTIR) studies were carried out to identify the functional groups on the surface of the adsorbents over the range  $400\text{--}4000\text{ cm}^{-1}$  using KBr as background.

### Results and Discussion

Carbon characteristics (Table 1) show that CLPC has considerable bulk density and moderate ion exchange capacity. The moisture content of CLPC is higher than that of CAC, which suggests that the acid treatment has made the CLPC more porous in nature. CLPC has higher ash content than CAC which indicates less carbon content. CAC also shows lower value for decolourizing power and phenol number which implies that it is more suitable for organic adsorption.

#### FT-IR analysis

The FT-IR spectral data of CLP, CLPC and CAC before and after Ni(II) adsorption are given in Table 2. It could be seen from spectra for CLP and CLPC that the broad and intense peak at  $3422$  and  $3444\text{ cm}^{-1}$  corresponds to the OH stretching. The peak at  $1741$  and  $1706.06\text{ cm}^{-1}$  shows C=O stretching vibration of the carboxyl group. The peak at  $1377\text{ cm}^{-1}$  in CLPC due to S=O asymmetric stretching of sulphonic acid group. The presences of hydroxyl and

carboxyl groups are thus confirmed for CLP and CLPC by FT-IR spectra. It is obvious from Table 2 that after Ni(II) sorption, some of the peaks such as  $-\text{OH}$ ,  $-\text{C}=\text{O}$  in carboxyl group,  $-\text{S}=\text{O}$  in sulphonic acid group,  $-\text{C}=\text{C}-$ , are shifted indicating the participation of these functional groups in metal binding process.

#### Effect of contact time

From Fig. 1(a), it could be seen that the removal of Ni(II) ions increased rapidly with time and attains equilibrium in 4 h in the case of CLPC, CLP and CAC. The uptake of Ni(II) ion was found to be 97, 85 and 28% by CLPC, CLP and CAC respectively. Hence the optimum equilibrium was taken as 4 h for subsequent experiments. It could be seen further that CLPC is more efficient to an extent of 1.2 times than CLP and 3.5 times than CAC.

#### Effect of pH

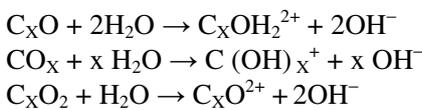
From Fig. 1(b), it could be observed that the adsorption increases with increase in pH and attains maximum removal of 97% over the pH range at 4.0-9.0 for CLPC, 85% at pH of 5.0-8.0 for CLP and 40% at pH 8.0 for CAC. It could be noticed that CLPC and CLP are two times more effective in the removal of Ni(II) ions when compared with CAC under optimum pH conditions. Moreover CLPC and CLP have a wide range of pH when compared with CAC which is a favourable aspect for batch treatment processes. The fact that at low pH values, the proton to Ni(II) ratio is large thereby Ni(II) sorption decreases. When pH is increased the ratio of proton to Ni(II) ion decreases, and Ni(II) ions gets precipitated

Table 2 — Shift in major functional groups of CLP, CLPC and CAC before and after adsorption of Ni(II). Unit  $\text{cm}^{-1}$ .

CLP		CLPC		CAC		Functional groups
Before adsorption	After adsorption	Before adsorption	After adsorption	Before adsorption	After adsorption	
3421.69	3430.93	3444.43	3425.25	3421.69	3433.26	Bonded $-\text{OH}$ groups
2926.33	2922.78	2914.96	2920.65	2929.89	2920.65	Aliphatic C-H groups (C-H stretching of $\text{CH}_3$ , $\text{CH}_2$ and $\text{OCH}_3$ groups)
1740.88	1743	1706.06	1706	-	-	C=O stretching (carboxyl group)
1625.75	1628.59	1625.75	1620.06	1590.92	1566.05	C=C stretching (aromatic)
1435.28	1445	-	-	-	-	C-H groups in the plane deformation ( $\text{CH}_3$ , $\text{CH}_2$ and $\text{OCH}_3$ groups)
-	-	1377	1372.03	-	-	S=O asymmetric stretching
1314.46	1320	1170.90	disappear	-	-	C-O stretching of carboxylic acids
1256.89	1237	1030.18	1020.94	-	-	S=O symmetric stretching
1015.25	1015.25	-	-	1009.57	Disappear	C-O stretching (alcohol)
790.67	790	-	-	-	-	C-H bending (aromatic)

in the form of nickel hydroxide, and hence adsorption decreases.

The mechanism of Ni(II) removal by CLPC may also be explained based on ion exchange model. A pure carbon surface is considered to be non-polar, but in actual practice some carbon-oxygen complexes (C<sub>X</sub>O, CO<sub>X</sub> and C<sub>X</sub>O<sub>2</sub>) are usually present, which render the surface slightly polar<sup>32</sup>. The surface oxygen complexes hydrolyse water molecules as shown below.



Since the CLPC is prepared upon treatment with H<sub>2</sub>SO<sub>4</sub> followed by treatment with NaHCO<sub>3</sub>, groups such as C<sub>X</sub>O Na<sup>+</sup>, C<sub>X</sub>O Na<sub>2</sub><sup>2+</sup>, C<sub>X</sub>SO<sub>3</sub>H and C<sub>X</sub>SO<sub>3</sub>Na are also expected to be present. Hence it is expected that Na<sup>+</sup> may be exchanged with Ni(II) and soluble complexes of Ni(II) as follows:

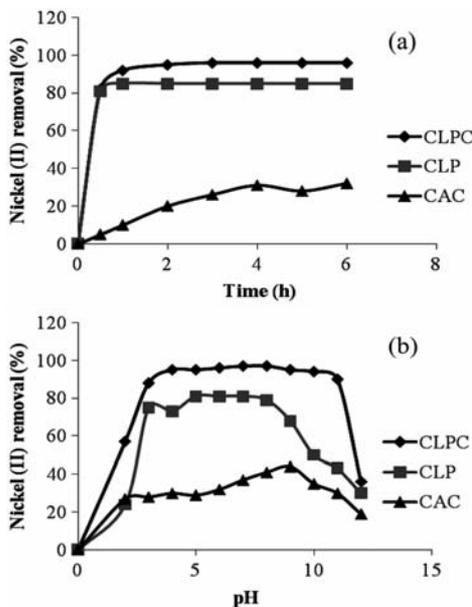
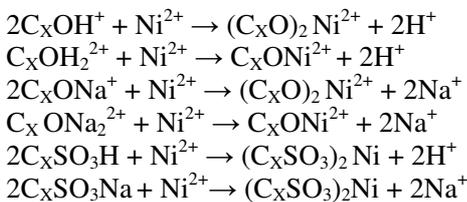


Fig. 1 — Effect of agitation (a) time and (b) pH on Ni(II) adsorption: Ni(II) conc. – 10 mg L<sup>-1</sup>; adsorbent dosage –100 mg/100 mL and temp - 300 K

**Effect of adsorbent dosage**

The effect of adsorbent dose for Ni(II) removal on these adsorbents has been shown in Figs. 2(a-c). It could be seen from the figure that initially the percentage removal increases very sharply with the increase in adsorbent dose but tends to remain constant at higher doses of adsorbents (300mg/100mL for CLPC and 500 mg/100 mL for CLP, CAC) under optimum pH conditions. CLPC and CLP showed Ni(II) removal to an extent of 99% and 85% respectively. For CAC, the maximum removal was found to be 48% only. The data clearly indicate that CLPC is nearly 1.7 times more effective than CLP and CAC with respect to adsorbent dosage. This is may be due to the moderate ion-exchange capacity exhibited by CLPC as compared to CLP and CAC. From Fig. 2(a), it could be seen that for various concentrations of Ni(II) removal, the optimum dosage remaining constant for CLPC. From Fig 2(b) CLP

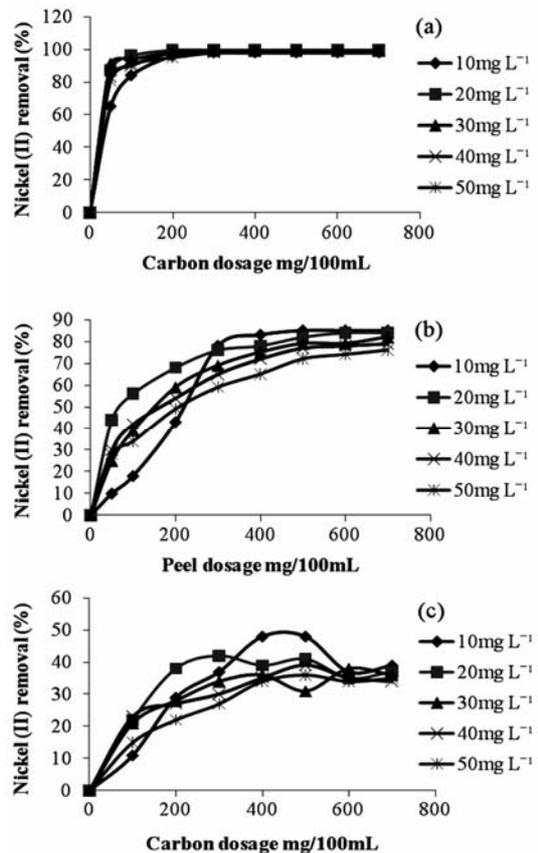


Fig. 2 — (a) (b) & (c) Effect of adsorbent dosage on the CLPC, CLP and CAC for the adsorption of Ni(II) concentration range from 10-50 mg L<sup>-1</sup>; adsorbent dosage - 50-700 mg, pH - 5.5 for CLPC, CLP and 8.0 for CAC; agitation time – 4 h and temp - 300 K

indicated a variation in optimum dosages as the Ni(II) concentration increases. Similar trend is also observed with respect to CAC from Fig 2(c). These observations indicated that highly non uniform distribution of adsorption sites are available in CLP and CAC.

#### Adsorption Isotherms

Adsorption isotherm is important to describe how solutes interact with adsorbent. Two isotherm models, Freundlich and Langmuir, were used to describe the equilibrium sorption isotherms at different temperatures (300-320 K).

The Freundlich<sup>33</sup> isotherm is derived by assuming a heterogeneous surface with a non uniform distribution of the heat of sorption over the surface. It can linearly be expressed as follows:

$$\log q_e = \log K_F + (1/n) \log C_e \quad \dots(3)$$

where  $K_F$  ( $\text{mg g}^{-1}$ ) and  $1/n$  are the Freundlich constants related to sorption capacity and intensity, respectively. The values of  $1/n$  less than 1 represent a favourable adsorption<sup>34</sup>. The Freundlich constants can be obtained from the plot of  $\log q_e$  versus  $\log C_e$ .

The Langmuir<sup>35</sup> isotherm assumes that adsorption occurs at specific homogenous sites within the adsorbent. The equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad \dots(4)$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of the adsorbate;  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of adsorbate per unit mass of adsorbent;  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir adsorption constant; and  $Q_0$  ( $\text{mg g}^{-1}$ ) is the amount of maximum adsorption. To determine whether the adsorption is favourable, a dimensionless constant separation factor or equilibrium parameter  $R_L$  is defined based on the following equation<sup>36</sup>:

$$R_L = \frac{1}{1 + bC_0} \quad \dots(5)$$

where  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir isotherm constant,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial Ni(II) concentration. The  $R_L$  values indicate whether the type of the isotherm is favourable ( $0 < R_L < 1$ ), unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), or irreversible ( $R_L = 0$ )<sup>37</sup>. The Langmuir constants can be obtained from the plot of  $C_e/q_e$  versus  $C_e$ .

The linear plots of Langmuir equation representing Ni(II) adsorption by the CLPC, CLP and CAC are illustrated in Figs 3(a-c). The adsorption constants of Freundlich and Langmuir equation and their correlation coefficients ( $R^2$ ) are calculated and represented in Table 3. The correlation coefficients show that the adsorption process is better defined by Langmuir than by the Freundlich equation. Furthermore, the values of  $R_L$  are in between 0.009-0.51 indicating a favourable adsorption process. Lower  $R_L$  values at higher initial Ni(II) concentrations and lower temperature showed that adsorption is more favourable at higher concentration and at lower temperature. These results indicate that the homogeneous distribution of active sites on the adsorbent surface. According to Langmuir isotherm, the monolayer saturation capacity ( $Q_0$ ) of Ni(II) on CLPC and CLP was found to be  $38.46 \text{ mg g}^{-1}$  and  $25.64 \text{ mg g}^{-1}$  at 300 K and significantly higher than CAC ( $Q_0 = 11.36 \text{ mg g}^{-1}$ ). The ratio of  $Q_0$  values of

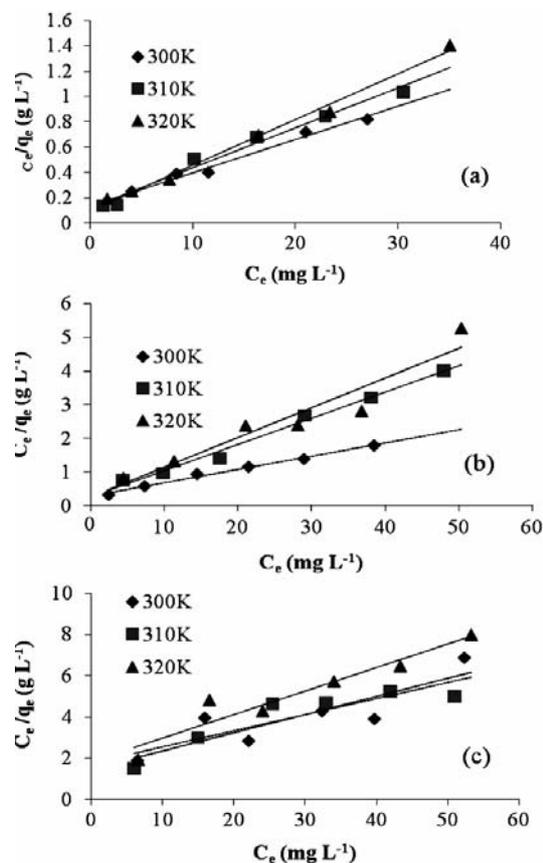


Fig. 3 — (a) (b) & (c). Langmuir isotherm for Ni(II) adsorption on CLPC, CLP and CAC at different temperature: ( $C_0 = 10\text{-}60 \text{ mg L}^{-1}$ ; contact time - 24 h; adsorbent dosage -  $100\text{mg}/100\text{mL}$ ; pH - 5.5 for CLPC, CLP and 8.0 for CAC)

Table 3 — Isotherm parameters for Ni(II) adsorption onto CLPC, CLP and CAC at different temperatures

Adsorbent	Temp K	Freundlich Isotherm			Langmuir Isotherm		
		$K_F$ mg g <sup>-1</sup>	1/n	R <sup>2</sup>	$Q_0$ mg g <sup>-1</sup>	b L mg <sup>-1</sup>	R <sup>2</sup>
CLPC	300	9.89	0.44	0.964	38.46	0.135	0.986
	310	8.79	0.32	0.893	32.26	0.120	0.981
	320	8.34	0.35	0.842	27.78	0.097	0.992
	300	5.43	0.39	0.988	25.64	0.292	0.991
CLP	310	4.61	0.27	0.709	12.99	0.265	0.988
	320	3.88	0.29	0.728	11.36	0.255	0.914
	300	1.94	0.49	0.756	11.36	1.450	0.765
CAC	310	1.47	0.36	0.899	10.99	1.523	0.907
	320	1.35	0.39	0.821	8.70	1.756	0.905

CLPC and CAC, CLP and CAC works out to be 3.39 and 2.26. The maximum adsorption capacity ( $Q_0$ ) decreases with the increasing temperature, indicating an exothermic process.

**Adsorption kinetics**

In order to investigate the mechanism of Ni(II) sorption, characteristic constants of sorption were determined using a pseudo-first order, pseudo-second order, elovich model and an intra-particle diffusion model.

The pseudo-first order reaction equation of Lagergren<sup>38</sup> was widely used for the adsorption of liquid/solid system on the basis of solid capacity. Its linear form is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2} \cdot 303t \quad \dots(6)$$

where  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) are the adsorption amount at equilibrium and at time  $t$  (min), respectively.  $k_1$  (min<sup>-1</sup>) is the rate constant of the pseudo-first order adsorption process. The constants were determined experimentally by plotting of  $\log(q_e - q_t)$  versus  $t$  and given in Table 4. The correlation coefficient ( $R^2$ ) values are found to be lower than that of pseudo-second order kinetics and the theoretical values ( $q_{e, cal}$ ) are far lower than those experimental data,  $q_{e, exp}$  (Table 4a), implying that the adsorption process does not follow fully the pseudo-first order adsorption rate expression.

The pseudo-second order model proposed by Ho and McKay<sup>39</sup> is based on the assumption that the adsorption follows second-order rate equations. The linear form can be written as follows:

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots(7)$$

where  $k_2$  (g mg<sup>-1</sup>min<sup>-1</sup>) is the rate constant of adsorption. By plotting a curve of  $t/q_t$  against  $t$ ,  $q_e$  and

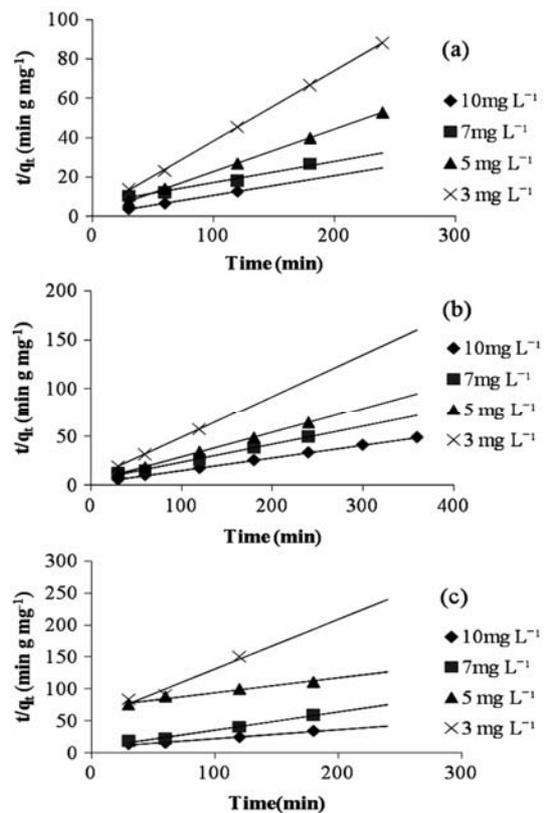


Fig. 4 — (a) (b) & (c). Pseudo second order kinetics for the adsorption of Ni(II) on CLPC, CLP and CAC: (pH - 5.5 for CLPC, CLP and 8.0 for CAC; adsorbent dosage - 100 mg/100 mL; temp - 300 K)

$k_2$  can be evaluated. The initial adsorption rate,  $h_0$  (mg g<sup>-1</sup> min<sup>-1</sup>) is defined as<sup>40</sup>:

$$h_0 = k_2 q_e^2 \quad \dots(8)$$

The values of  $q_e$ ,  $k_2$ ,  $h_0$  and  $R^2$  are listed in Table 4a. The dependence of  $t/q_t$  versus  $t$  gives an excellent straight line relation for all the experimental concentrations Figs 4(a-c).  $R^2$  values are also closer to

unity (Table 4a), confirming the applicability of the pseudo-second order equation. In addition, difference between the  $q_{e,exp}$  and  $q_{e,cal}$  is very little (Table 4a), reinforcing the applicability of this model. This suggests that the rate-limiting step of this sorption system may be controlled by chemical sorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate. Therefore the pseudo-second order constant  $k_2$  is applied to calculate the film and pore diffusion coefficients.

The Elovich kinetic model can be expressed as follows<sup>41</sup>:

$$qt = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t \quad \dots(9)$$

where  $\alpha$  is the initial adsorption rate ( $\text{mg g}^{-1}\text{min}^{-1}$ ) and  $\beta$  ( $\text{g mg}^{-1}$ ) is related to the extent of surface

coverage and activation energy for chemisorptions. Both kinetic constants ( $\alpha$ ,  $\beta$ ) will be estimated from the slope and intercept from the plot of  $q_t$  versus  $\ln(t)$ . Table 4b shows that the correlation coefficient ( $R^2$ ) value is much lower than unity indicating that Elovich model cannot be applied.

The kinetic data was analyzed by an intra-particle diffusion model to elucidate the diffusion mechanism<sup>42</sup> based on Weber model.

$$q_t = k_d t^{1/2} \quad \dots (10)$$

where  $q_t$  is the amount of sorbate on the surface of the sorbent at time  $t$  ( $\text{mg g}^{-1}$ ),  $k_d$  ( $\text{mg g}^{-1}\text{min}^{-1/2}$ ) is the intra-particle diffusion rate constant and  $t$  is the time (min). According to this model, the plot of ( $q_t$ ), versus the square root of time ( $t^{1/2}$ ) should be linear if intraparticle diffusion is involved in the overall

Table 4a — Pseudo-first order and Pseudo second order constants for Ni(II) adsorption onto CLPC, CLP and CAC at different initial concentrations

Adsorbent	$C_0$ $\text{mg L}^{-1}$	$q_e$ (exp) $\text{mg g}^{-1}$	Pseudo-first order			Pseudo-second order			
			$k_1$ $\text{min}^{-1}$	$q_e$ (cal) $\text{mg g}^{-1}$	$R^2$	$k_2$ $\text{g mg}^{-1}\text{min}^{-1}$	$q_e$ (cal) $\text{mg g}^{-1}$	$h_0$ $\text{mg g}^{-1}\text{min}^{-1}$	$R^2$
CLPC	10	9.60	0.028	2.80	0.974	0.015	9.90	1.470	0.999
	7	6.90	0.023	2.98	0.957	0.029	7.00	1.421	0.990
	5	4.70	0.007	0.74	0.868	0.041	4.65	0.887	1.000
	3	2.80	0.007	0.49	0.829	0.054	2.80	0.423	0.999
CLP	10	7.40	0.012	2.96	0.983	0.009	7.69	0.532	0.999
	7	4.90	0.012	1.43	0.981	0.008	5.10	0.208	0.993
	5	3.80	0.012	1.26	0.962	0.020	3.94	0.310	0.999
	3	2.20	0.018	1.00	0.985	0.031	2.30	0.164	0.999
CAC	10	5.40	0.021	6.21	0.900	0.003	5.63	0.095	0.999
	7	3.20	0.014	1.65	0.881	0.010	3.08	0.094	0.988
	5	1.70	0.018	2.75	0.924	0.016	1.66	0.044	0.989
	3	1.00	0.012	0.79	0.873	0.031	1.00	0.031	0.952

Table 4b — Elovich, Intra-particle diffusion constants and Diffusion coefficients for Ni(II) adsorption onto CLPC, CLP and CAC at different initial concentrations

Adsorbent	$C_0$ $\text{mg L}^{-1}$	Elovich model			Intra-particle diffusion model		Diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )	
		$\alpha$ $\text{mg g}^{-1}\text{min}^{-1}$	B $\text{g mg}^{-1}$	$R^2$	$k_{id}$ $\text{mg g min}^{1/2}$	$R^2$	Pore diffusion	Film diffusion
CLPC	10	229.37	1.071	0.909	0.083	0.640	$3.818 \times 10^{-6}$	$9.775 \times 10^{-7}$
	7	0.305	0.450	0.954	0.252	0.700	$5.030 \times 10^{-6}$	$1.301 \times 10^{-6}$
	5	6980.39	3.390	0.941	0.040	0.737	$5.083 \times 10^{-6}$	$1.274 \times 10^{-6}$
	3	188.54	4.410	0.813	0.030	0.646	$4.017 \times 10^{-6}$	$9.962 \times 10^{-7}$
CLP	10	6.799	1.140	0.962	0.144	0.878	$2.256 \times 10^{-6}$	$4.452 \times 10^{-7}$
	7	0.589	0.961	0.835	0.136	0.640	$1.388 \times 10^{-6}$	$2.592 \times 10^{-7}$
	5	5.627	2.088	0.919	0.067	0.760	$2.480 \times 10^{-6}$	$5.023 \times 10^{-7}$
	3	0.976	2.732	0.970	0.031	0.639	$2.307 \times 10^{-6}$	$4.490 \times 10^{-7}$
CAC	10	0.239	0.587	0.974	0.241	0.799	$7.440 \times 10^{-7}$	$1.071 \times 10^{-7}$
	7	0.288	1.309	0.853	0.099	0.649	$1.735 \times 10^{-6}$	$2.129 \times 10^{-7}$
	5	0.037	1.374	0.959	0.113	0.917	$7.440 \times 10^{-7}$	$6.745 \times 10^{-8}$
	3	0.037	3.165	0.907	0.030	0.618	$2.307 \times 10^{-6}$	$2.030 \times 10^{-7}$

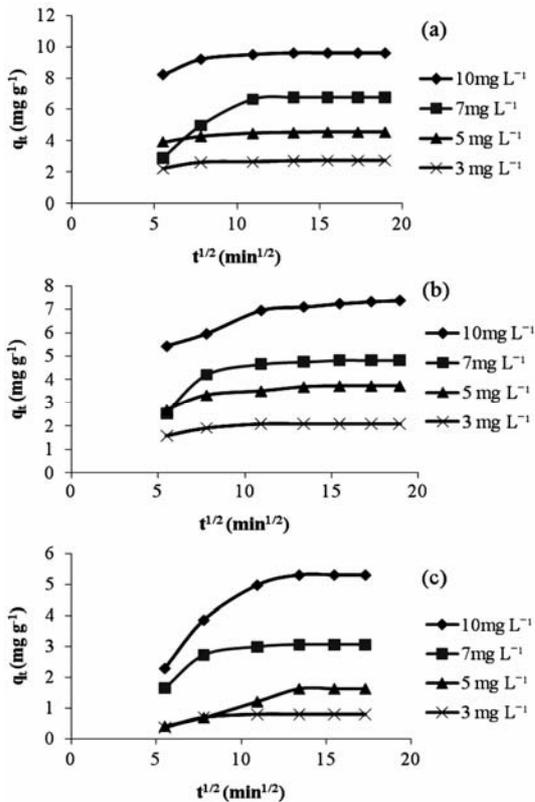


Fig. 5 — (a) (b) & (c). Plots for intra-particle diffusion for the adsorption of Ni(II) on CLPC, CLP and CAC: (pH - 5.5 for CLPC, CLP and 8.0 for CAC; adsorbent dosage - 100mg/100 mL; temp - 300 K)

adsorption mechanism. Furthermore, if this line passes through the origin then the intra-particle diffusion is the rate-controlling step of the process<sup>43</sup>.

Figure 5(a-c) show a plot of the Weber and Morris intra-particle diffusion model for the sorption of Ni(II) onto CLPC, CLP and CAC. As shown in Fig 5(a-c) the plot of uptake ( $q_t$ ), versus the square root of time ( $t^{1/2}$ ) was not linear, and this indicated that the intra-particle diffusion was not the rate-controlling step in these adsorption systems. The low correlation coefficient values obtained for the intra-particle diffusion model also indicate that adsorption is not occurring in the pores of sorbent in accordance with surface adsorption. Moreover, distinct ionic species might be present simultaneously in the solution and hence, each of them being adsorbed at variable rates as a function of their affinity to the individual functional groups and depends on the binding mechanism.

In order to further assess the nature of the diffusion process responsible for the adsorption of Ni(II) on CLPC, CLP and CAC, attempts were made to

Table 5 — Characteristics of nickel plating industry wastewater

Parameter	Wastewater concentration mg L <sup>-1</sup>	Diluted wastewater mg L <sup>-1</sup>	After treatment with		
			CLP	CLPC	CAC
Nickel	2200	220.00	29.41	3.61	51.88
Chlorides	789	78.90	69.05	50.20	70.26
Sodium	4113	411.30	380.07	300.27	400.20
Calcium	203	20.30	15.80	12.80	18.30
Magnesium	168	16.80	13.40	9.70	13.27
pH	3.0-4.0	5.0	7.0	7.80	8.50
Nickel removal			86%	98.36%	76%

calculate the pore and film diffusion coefficients for various concentrations of Ni(II) using the following the equation<sup>44</sup>:

$$D_p = 0.03 r_o^2 / t_{1/2} \quad \dots(11)$$

where  $D_p$  is the pore diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $r$  is the radius of the sorbent (cm), and  $t_{1/2}$  is the half-life period (sec).

$$D_f = 0.23 r_o d C^* / C t_{1/2} \quad \dots(12)$$

where  $D_f$  is the film diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $d$  is the film thickness (cm), and  $C^*/C$  is equilibrium loading of the sorbent. According to Michelsen *et al.*<sup>32</sup>, if film diffusion is to be the rate determining process in the adsorption of heavy metals on a sorbent, the values of film diffusion coefficient ( $D_f$ ) should be between 10<sup>-6</sup> and 10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup>. If pore diffusion  $D_p$  were to be rate determining process, its value should be in the range of 10<sup>-11</sup> to 10<sup>-13</sup> cm<sup>2</sup> s<sup>-1</sup>. It is evident from the Table 4b that the removal of Ni(II) follows film diffusion process, since the coefficients values are closer to the range of 10<sup>-6</sup> to 10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup>.

**Experiments with nickel plating wastewater**

Batch experiments with Nickel electro plating wastewater have been carried out to elucidate the applicability of these sorbents under batch mode operations. The characteristic of nickel plating wastewater used for studies are shown in Table 5. As the wastewater has a very high concentration of nickel (2200 mg L<sup>-1</sup>) it was diluted to 10 times to conduct experiments with CLPC, CLP and CAC. 100 mL wastewater containing 220 mg L<sup>-1</sup> Ni(II), required a minimum dosage of 400 mg CLPC to get the maximum removal of 98.36%. However, in the case of CLP and CAC, a maximum removal of 86% and

76% Ni(II) could be achieved with a minimum dosage of 1000 mg. These results clearly indicate that the CLPC is more effective when compared to CLP and CAC in removing Ni(II) from wastewater. This may be due to the moderate ion-exchange capacity of CLPC as compared to CLP and CAC.

### Conclusion

The results indicate that the peel of *Citrus limettioides* and its carbon derivative are able to remove Ni(II) to an extent of 85 to 99% from water whereas CAC is able to remove only 40%. The presence of hydroxyl, carboxylic and sulphonic acid groups in CLPC is confirmed by FT-IR spectroscopy which exhibits ion exchange property to the CLPC. Compared with CAC, the CLPC and CLP have a wider applicable pH range from 4.0-9.0 and 5.0-8.0 respectively. Equilibrium data agrees well with Langmuir isotherm and the adsorption capacity ( $Q_0$ ) of CLPC and CLP is 3.39 and 2.26 times greater than CAC respectively. The adsorption capacity ( $Q_0$ ) decreases with the increasing temperature, indicating an exothermic process. It is followed by pseudo-second order kinetics, which indicates the chemisorptions with film diffusion process being essential rate controlling step. Experiments with Ni(II) electroplating wastewater show that CLPC is more effective than CLP and CAC. Therefore, it can be concluded from the present studies that carbon derived from *Citrus limettioides* peel is a very effective and inexpensive adsorbent for the removal of Ni(II) from aqueous solution and electro plating wastewater.

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