Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.888678

54 (2015) 1629–1641
May

Equilibrium and kinetic studies on the adsorption of Ni(II) ion from an aqueous solution using activated carbon prepared from *Theobroma cacao* (cocoa) shell

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Received 2 August 2013; Accepted 23 January 2014

ABSTRACT

The adsorption of Ni(II) ion from an aqueous solution was successfully carried out using activated carbon prepared from *Theobroma cacao* (cocoa) shell, an agricultural solid waste biomass. The activated carbon prepared at ambient temperature (TCAC1) and the one prepared at 350 ℃ (TCAC2) were characterised by the FT-IR, BET, SEM, EDAX and Particle size analysis methods. The effects of the pH, dosage, initial metal ion concentration and agitation time were studied. The maximum adsorption was observed at pH 6 and the adsorption equilibrium was attained within 60 min. Adsorption isotherm data have been analysed, and the data fitted well in the order Langmuir > Redlich–Peterson > Temkin > Freundlich isotherm models. The maximum adsorption capacities of TCAC1 and TCAC2 for Ni(II) ions were calculated from the Langmuir isotherm as 97.59 and 158.8 mg/g, respectively. The kinetics of Ni(II) ion adsorption has been described, using five kinetic models viz, the pseudo-first order, pseudo-second order, Elovich, Intra-particle diffusion and Boyd kinetic models. The pseudo-second order kinetic model fits well with good correlation values. Thermodynamic parameters such as gibbs free energy (ΔG°), the enthalpy (ΔH°) and the entropy change of adsorption (ΔS°) have been calculated and it has been suggested that the adsorption process was feasible, spontaneous and exothermic in nature. The results obtained indicate that the activated cocoa shell prepared at 350 ℃, has higher adsorption capacity when compared to the one prepared at room temperature. High surface area and low particle size are the prime factors for the increased efficiency.

Keywords: Adsorption; Cocoa shell; Nickel (II) ion; Isotherm; Kinetics

1. Introduction

Heavy metal ion contamination in water is one of the most important environmental problems and this environmental issue is threatening the health and well-being of people. This heavy metal ion pollution has increased drastically due to upsurging industrialisation. Heavy metal ions are non-biodegradable and accumulate in living tissues, causing many harmful effects. Some heavy metal ions like Ni(II), Pb(II),

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Cu(II), Cr(VI), Zn(II), Co(II), Hg(II) cause various types of diseases in human beings and hence, their removal from the environment is necessary.

Nickel is one of the most toxic heavy metals and also the most widespread heavy metal contaminant in the environment. Nickel is mainly discharged from electroplating, smelting, stabilizer and alloy manufacturing industries. Water consumption is less in electroplating industries, when compared to other industries, but the effluent is more toxic than other waste waters [1–5]. Heavy metal containing waste water flows directly into fertile lands, thereby reducing their productivity. The presence of Ni(II) in drinking water above the permissible limit (3 mg/L) may cause headache, dizziness, nausea and vomiting, chest pain, rapid respiration, cyanosis and extreme weakness [6].

Several conventional methods are available for the removal of heavy metal ions from aqueous media. These methods include precipitation, ion-exchange, membrane filtration, electro coagulation, electro dialysis, reverse osmosis, adsorption etc. [7–11]. However, the selection of a suitable treatment method is based on the concentration of metal ions in waste water, and the cost of the treatment. Of late, the adsorption technique has evolved as an economically feasible method for the removal of heavy metal pollutants. Low cost adsorbents are generally preferred in adsorption techniques, especially low-cost activated carbon prepared from naturally obtained bio waste, such as pomegranate peel [12], rice husk [13], coir pith [14], corn cob [15], cashew nut shell [16], coconut shell [17], pistachio nut shell [18], *Guazuma ulmifolia* seeds [19], palm shell [20], etc.

The objective of the present research work is to develop a surface modified, less expensive, effective adsorbent, from low-cost natural waste such as *Theobroma cacao* (cocoa shell), which is available in large quantities in the southern parts of India. 18 N sulphuric acid was utilized for the surface modification of *T. cacao* (cocoa shell), and this modified adsorbent was taken for the adsorption studies of Ni(II) ions. The influence of various parameters such as the pH, adsorbent dosage, contact time and initial Ni(II) ion concentration on adsorption has been investigated. Equilibrium modelling was carried out using different isotherms, namely, Langmuir, Freundlich, Temkin and Redlich–Peterson. The adsorption mechanism has been investigated through various adsorption kinetic models, such as the pseudo-first order, pseudo-second order, Elovich, intra-particle diffusion and Boyd. In addition, thermodynamic studies also were carried out.

2. Materials and methods

2.1. Preparation of the adsorbent

The raw *T. cacao* (cocoa shell) was collected from the agricultural fields of Semmedu village, Coimbatore District, Tamilnadu, India. The shells were repeatedly washed with double-distilled water to remove unwanted dusts and other impurities. Then they were allowed to dry under sunlight for 48 h and treated with 18 N sulphuric acid. Cocoa shells were soaked in 18 N sulphuric acid for 4 h at room temperature (30℃). One half of the acid soaked cocoa shells (18 N sulphuric acid) were kept in a muffle furnace at 350 ℃ for 4 h. Both the samples were allowed to attain room temperature and washed with double distilled water, and soaked in 10% sodium-bi-carbonate solution and allowed to stand overnight, to remove the residual acid from the pores of the carbon. The obtained samples were again washed with double distilled water until the pH of the filtrate reached neutral. The resultant activated carbon was dried in a hot air oven at 105 ℃ for 6 h. The activated carbon powder obtained by just soaking the cocoa shell in acid is identified as TCAC1. The activated carbon powder obtained after heating the acid soaked shell in a muffle furnace is identified as TCAC2. These two, TCAC1 and TCAC2, were used as adsorbents for the uptake of Ni(II) ions from an aqueous solution.

2.2. Preparation of adsorbate

$NiSO_4 \cdot H_2O$ (AR grade) (qualigens chemicals) was used for preparing 500 mg/L of stock solution using double distilled water. Appropriate test solutions were prepared by subsequent dilutions of the stock solution. The concentration of the heavy metal ion solution varies from 25 to 200 mg/L for experimental studies. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value, by adding either 0.1 N NaOH or 0.1 N HCl.

2.3. Analysis

The concentration of Ni(II) ions in the solution before and after adsorption was determined by the AA6300 atomic absorption spectrometer (Shimadzu, Japan). The pH of the solution was measured with a Hanna pH meter using a combined glass electrode. The fourier transform infra red spectrometer (FT-IR) analysis was used to identify the different functional groups present in the adsorbent, and also to identify the functional group responsible for binding with the metal ions in the aqueous solution. The EDAX analysis was employed to confirm the adsorption of the Ni(II) ions onto the adsorbent, and the surface morphology of the adsorbent was studied, using the Leo Gemini 1530 scanning electron microscope (SEM), at an accelerating voltage of 10 kV and at a working distance of 20 μm. The surface area of the activated carbon sample was measured by nitrogen adsorption at 77 K, with an ASAP-2010 Porosimeter (Micromeritics Corporation, Norcross, GA). Particle size analysis was carried out to measure the particle size of the activated carbon sample by using Malvern Zetasizer ver. 6.20 particle size analyser.

3. Results and discussion

3.1. Characterization of the adsorbent

3.1.1. Fourier transform infrared (FT-IR) spectral analysis of the adsorbent

The FT-IR spectra of TCAC1, TCAC2 and Ni(II)-TCAC2 are shown in Fig. 1. The broad peak around 3,395–3,422 cm^{-1} is due to the –OH stretching vibration. A strong band at 2,343 cm^{-1} is assigned to the C=O stretching frequency of the carbonyl group on the adsorbent. The band in the region 1,582–1,623 cm^{-1} suggests the presence of C=C in the adsorbent. C–OH and C–O–C stretching frequencies are observed at 1,152 and 1,235 cm^{-1}, respectively. The disappearance of the C=O stretching frequency (2,343 cm^{-1}) in FT-IR spectrum of the Ni(II) ion loaded activated carbon and C–OH, C–O–C stretching frequencies (1,152 and 1,235 cm^{-1}) of the activated carbon had undergone major changes. This indicates that the structural functional groups (C–OH, C–O–C and C=O) of TCAC2 involved in the complex formation with Ni(II) ion due to vander Waals force to form strongly bounded Ni(II)-TCAC2 complex in the aqueous solution. Since the activated adsorbent is of cellulosic origin, the FT-IR spectra result shows the presence of hydroxyl and ether active functional groups, which might help the adsorption process.

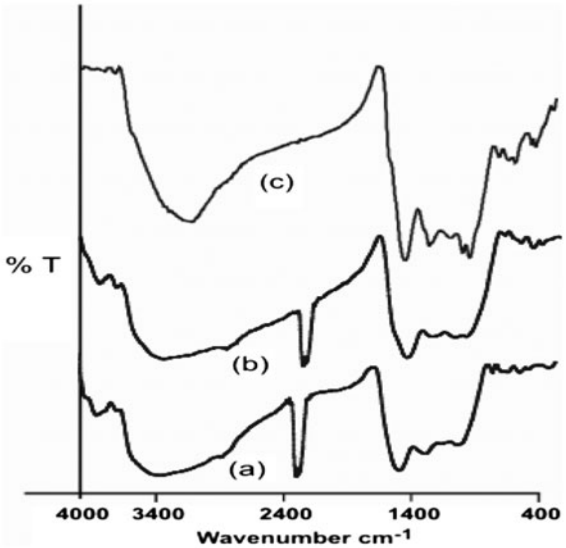

Fig. 1. IR spectra of TCAC1 (a), TCAC2 (b) and Ni(II)-TCAC2 (c) respectively.

3.1.2. Brunauer–Emmett–Teller (BET) analysis

The surface area of the activated carbon (TCAC1) and (TCAC2) were found to be 392.18 and 480.23 m^2/g, respectively. The higher surface area is a key factor in the enhancement of the adsorption capacity towards Ni(II) ion removal from the aqueous solution.

3.1.3. Scanning electron microscopy (SEM)

The SEM technique was used to observe the surface morphology of the prepared activated carbon, before and after adsorption of the metal ions. The SEM images of TCAC1 and TCAC2 and Ni(II) ion loaded TCAC2 are shown in Fig. 2(a)–(c), respectively. It can be seen from the images, that the external surface of the chemically activated carbon contains a large number of cavities. The TCAC2 surface is more porous when compared to that of the TCAC1. The SEM image of Ni(II)-TCAC2 shows that the porous surface gets filled with the metal ions. Hence, there is a change in the Ni(II)-TCAC2, to a smooth surface, due to the adsorption of the Ni(II) ions on the adsorbent.

3.1.4. Energy dispersive X-ray (EDAX) spectroscopy

The EDAX analysis was employed to prove the adsorption of Ni(II) ion onto the activated carbon (TCAC2). The EDAX Spectra of TCAC2 before and after the adsorption of Ni(II) ions are shown in the Fig. 3(a) and 3(b), respectively. Before the adsorption of the metal ions, only the peaks of C, O and S elements are present in the EDAX analysis of the TCAC2. After adsorption, three strong peaks for Ni(II) ion are present in the EDAX spectra of Ni(II)-TCAC2. This confirms that the Ni(II) ions have been successfully loaded on to the surface of the TCAC2. Moreover, the increase in the peak for S and O suggests the possibilities of involvement of SO_4 ions forming a chemical bond with the active sites.

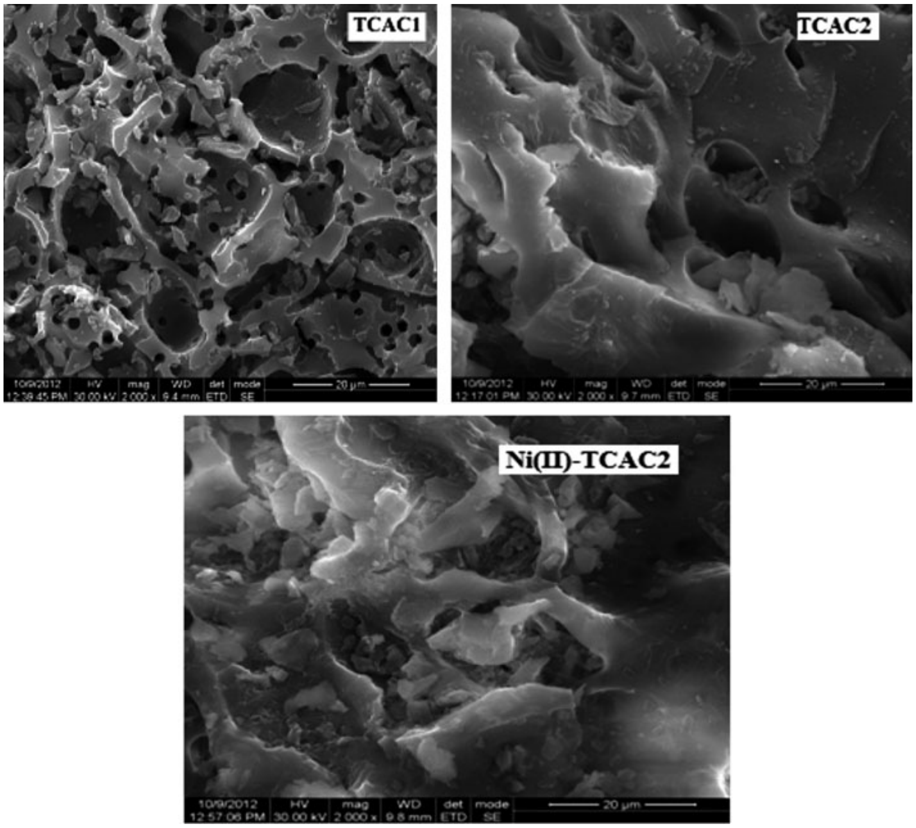

Fig. 2. SEM images for TCAC1, TCAC2 and Ni(II)-TCAC2 respectively.

3.1.5. Particle size analysis

The particle size of TCAC1 and TCAC2 was found to be 682.7 and 93.26 nm, respectively. This suggests that the heat treatment of the cocoa shell at 350 ℃ has significantly decreased the particle size, and hence there is an increase in the surface area.

3.2. Batch adsorption experiment

Batch adsorption experiments were carried out by agitating the Ni(II) ion solution and the adsorbent in a 250 mL conical flask in a horizontal bench shaker (Orbiteck) at a constant speed of 180 rpm. The removal of the Ni(II) ions from the aqueous solution by the adsorbent in a batch system was studied. The data obtained from the batch studies were used to calculate the metal adsorptive capacity of the adsorbent, by using the following mass balance relationship:

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

The metal ion removal percentage can be calculated as follows:

$$\%\,\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L) of Ni(II) ions respectively, V is the volume of the Ni(II) ion solution (mL), and m is the mass of adsorbent (g).

3.2.1. Effect of the solution pH on nickel (II) ion adsorption

The solution pH is an important controlling factor that affects the surface charge of the adsorbent as well as the presence of free heavy metals. The effect of the solution pH on the adsorption of Ni(II) ion was investigated using 20 ml of 50 mg/L metal ion solution, in the pH range of 2–10. The percentage removal of Ni(II) ion increases as the pH of the solution increases and reaches a maximum value at pH 6. With further increase in the pH value, the percentage removal gradually decreases. At a very low pH, the adsorption of Ni(II) ion is very low, due to the greater H^+ (protons) ion density on the surface of the adsorbent,

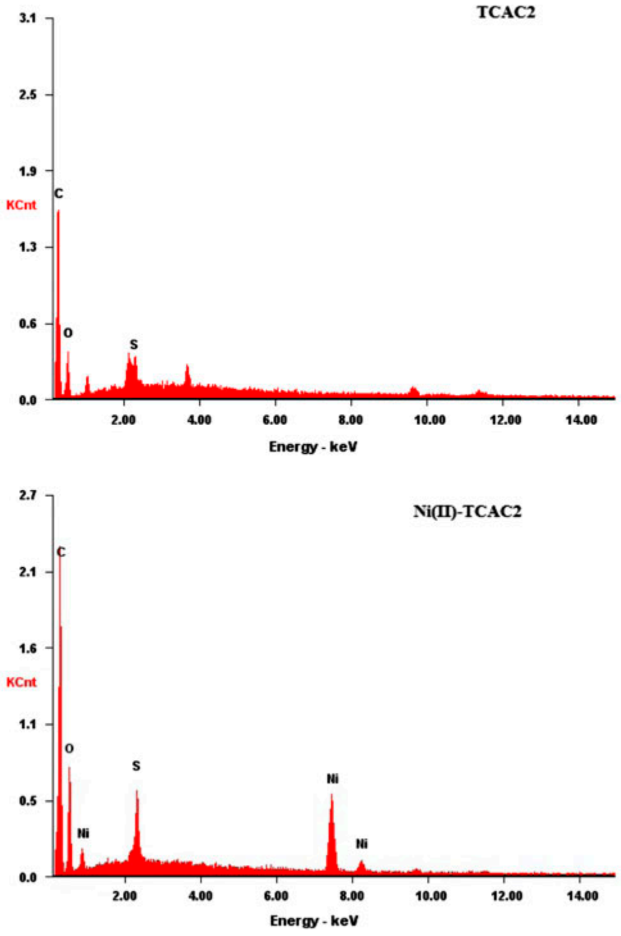

Fig. 3. EDAX images of TCAC2 and Ni(II)-TCAC2 (Ni adsorbed activated carbon).

resulting in electrostatic repulsion between the metal ions and the adsorbents. As the pH value increases, the adsorbent surface is negatively charged, because of the lowering of the H^+ ion density on the adsorbent surface. This results in an increase in the Ni(II) ion adsorption on the adsorbent surface. The maximum removal efficiencies of TCAC1 and TCAC2 were found to be 74.56 and 98.28%, respectively, at pH 6 (Fig. 4) and the zero point charge (pH_{zpc}) was found to be 4.8 and 4.3 for TCAC1 and TCAC2, respectively. At $pH < pH_{zpc}$, the adsorption of anion is favoured, because of positively charged surface of the adsorbent. When $pH > pH_{zpc}$ indicates that the adsorbent is negatively charged, so the adsorption of cation is much favoured. This indicates the electrostatic attraction between adsorbent and Ni(II) ion increases. In present work reveals the adsorption of Ni(II) ion increases in the solution pH above pH_{zpc}. But the pH values higher than 6, the Ni(II) ion adsorption decreases as the existence of free Ni(II) ions is less probable in the basic medium due to the formation of nickel hydroxide. Hence, an optimum pH value of 6 was fixed for further studies.

3.2.2. *Effect of the adsorbent dose on nickel(II) ion adsorption*

Adsorbent dosage is one of the important factors which determine the adsorption capacity of the adsorbent for a given initial Ni(II) ion concentration. The percentage removal of Ni(II) ion increases as the adsorbent dosage increased from 10 to 50 mg (Fig. 5). The percentage removal gradually increases with the adsorbent dosage and shows a sharp increase with 30 mg of the adsorbent. The maximum percentage removal at 30 mg dosage of TCAC1 and TCAC2 were found to be 80.42% and 96.98%, respectively. There was no significant increase in the percentage removal beyond 30 mg, and this is due to the fact that the maximum adsorption had already been completed at the adsorbent dose of 30 mg. Hence, the optimum dosage of 30 mg was fixed for further studies.

3.2.3. *Effect of contact time on nickel(II) ion adsorption*

Contact time is an important factor for determining the kinetics of adsorption. The data obtained from the adsorption of Ni(II) ions onto the adsorbents with respect to different contact times are shown in the Fig. 6. The percentage removal of Ni(II) ions is higher during the initial stages, which may be due to the large surface area available. The maximum uptakes at 60 min for adsorption of Ni(II) ions onto TCAC1 and TCAC2 were found to be 80.34% and 98.66%

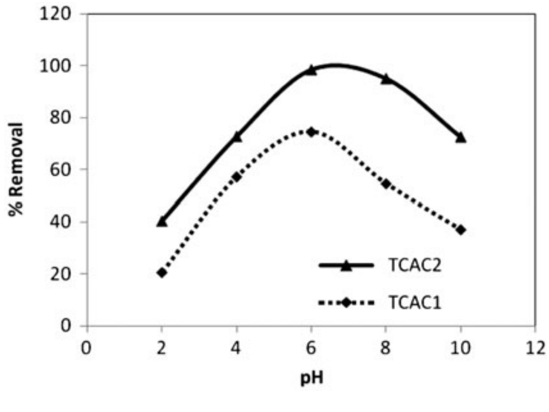

Fig. 4. Effect of pH for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

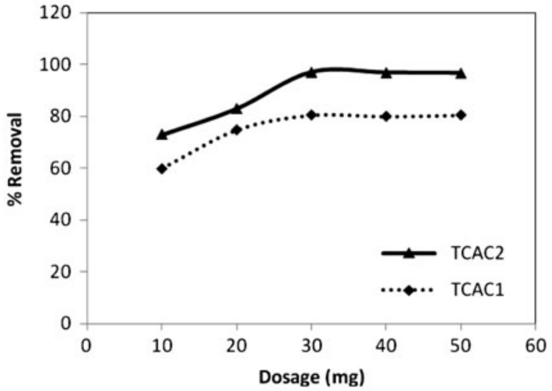

Fig. 5. Effect of adsorbent dosage for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

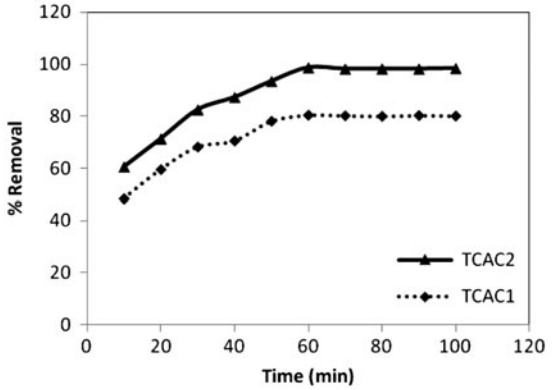

Fig. 6. Effect of contact time for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

respectively. Beyond 60 min, there is no profound increase in the percentage removal. Hence, 60 min can be fixed as the equilibrium time.

3.2.4. Effect of initial ion concentration on nickel(II) ion adsorption

Adsorption experiments were carried out with Ni(II) metal ion initial concentrations in the range of 25–200 mg/L, and the results are shown in Fig. 7. The percentage removal was the maximum at 25 mg/L because of less Ni(II) ion concentration. As the initial metal ion concentration increases beyond 25 mg/L, the percentage removal gradually decreases. After a particular concentration of 150 mg/L, there is a sharp decrease in the percentage removal. This is because of the saturation of the adsorbent sites with Ni(II) ions. This data had been utilized to study the equilibrium isotherm.

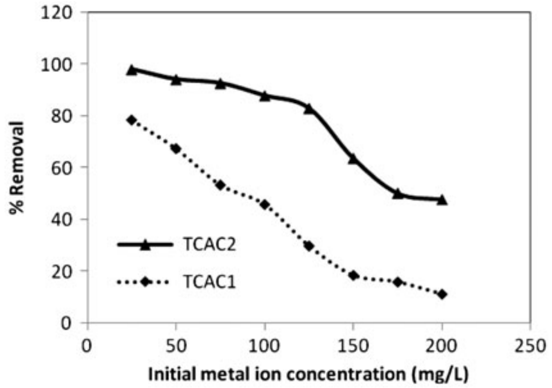

Fig. 7. Effect of initial metal ion concentration for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

3.2.5. Effect of temperature on nickel(II) ion adsorption

The adsorption of Ni(II) ion onto TCAC1 and TCAC2 was carried out at five different temperatures 303, 313, 323, 333 and 343 K at 50 mg/L, adsorbent dose of 30 mg and an optimum pH of 6.0. Fig. 8 shows that the percentage removal of the Ni(II) ion onto activated carbons decreased with increase in temperature. The adsorption of Ni(II) ion onto TCAC1 and TCAC2 is exothermic in nature.

3.3. Adsorption isotherms

An adsorption isotherm explains mainly the distribution of the solute between the adsorbent and the solvent at equilibrium. Isotherms provide information on the efficiency of the adsorbent or the amount of adsorbent required for metal ion removal. The effect of the initial metal ion concentration shows that the removal efficiency was high with lower metal ion concentration (25 mg/L). The higher removal efficiency shows that the Ni(II) ions easily occupy the available sites. The non-linear forms of the Langmuir [21], Freundlich [22], Temkin [23] and Redlich–Peterson [24] isotherm models were tested with the adsorption obtained in this present study using MATLAB R2009b.

3.3.1. Langmuir isotherm model

The Langmuir isotherm model explains the monolayer adsorption on a surface containing more number of adsorption sites. The maximum adsorption depends on the saturation level of the monolayer. This shows that there is no interaction between the molecules adsorbed on neighbouring sites. The non-linear equation of the Langmuir isotherm model is expressed as follows:

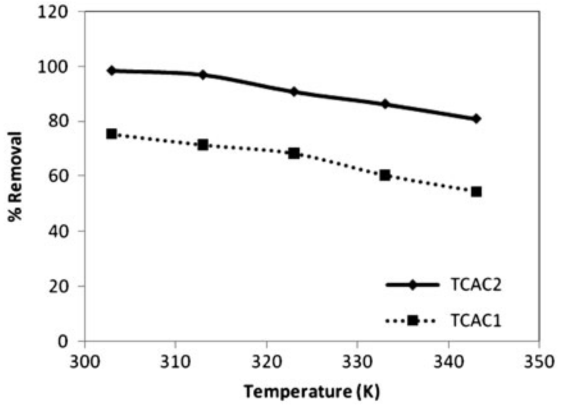

Fig. 8. Effect temperature for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where C_e (mg/L) is the equilibrium concentration of the metal ion in the solution, q_m (mg/L) and K_L (L/mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading, and the energy constant related to the heat of adsorption, respectively.

The Langmuir isotherm model can be explained in terms of the dimensionless constant "R_L" expressed in the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

where K_L is the Langmuir constant and C_0 is the initial Ni(II) metal ion concentration. The separation factor "R_L" provides information about the nature of adsorption. The "R_L" value indicates Langmuir isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). In the present study the "R_L" values were found to be in the range of 0.7930–0.1039 and 0.7564–0.0144 for Ni(II) ions onto TCAC1 and TCAC2, respectively. This suggests that the Langmuir isotherm is favourable. All the parameters are listed in Table 1.

3.3.2. Freundlich isotherm

The Freundlich adsorption model is based purely on adsorption over a heterogeneous surface and is related to multilayer adsorption. The non-linear equation for the Freundlich isotherm model is given by the following equation:

$$q_e = K_f C_e^{1/n} \tag{5}$$

where K_f is the Freundlich constant ((mg/g) (L/mg)$^{1/n}$) related to the bonding energy. $1/n$ is the heterogeneity factor and n is the value of deviation from the linearity of adsorption. The value of n between 1 and 10 indicates favourable adsorption. In the present study, the value of n is greater than 1, which shows that the adsorption of Ni(II) onto adsorbents (TCAC1 and TCAC2) is favourable. All other constants and parameters of the Freundlich isotherm model are listed in Table 1.

3.3.3. Temkin isotherm model

Temkin isotherm explains the behaviour of adsorption on a heterogeneous surface and predicts the uniform distribution of the binding energies over the population of surface binding adsorption. The distribution of these binding energies depends on the number of functional groups on the adsorbent surface and Ni(II) ion. The non-linear form of the Temkin isotherm model is commonly given by the following equation:

$$q_e = B \ln (A C_e) \tag{6}$$

where $B = RT/b$, b is the Temkin isotherm constant related to heat of adsorption (J/mol), A is the Temkin isotherm constant (L/g), "R" is the universal gas constant (8.314 J/mol/K) and "T" is the absolute temperature (K). The values of all other parameters are represented in Table 1.

Table 1
Isotherm parameters for the adsorption of Ni(II) onto TCAC1 and TCAC2

Isotherm model	Parameters	TCAC1	TCAC2
Langmuir	K	0.0486	0.6553
	q_m	97.59	158.8
	R^2	0.9628	0.9915
Freundlich	K_f	17.93	85.9
	n	3.119	6.816
	R^2	0.8324	0.8827
Temkin	α	0.8636	4.818
	β	7.723	8.72
	R^2	0.9114	0.8762
Redlich–Peterson	α	1.321	4.082
	β	0.7252	0.8319
	K_R	3.08	1.212
	R^2	0.9593	0.928

3.3.4. Redlich–Peterson isotherm model

Redlich–Peterson isotherm model is indicating the both homogeneous and heterogeneous systems of Ni (II) ions onto adsorbents TCAC1 and TCAC2. It is a combination of Langmuir and Freundlich model. The non-linear equation of Redlich–Peterson isotherm model expressed as follows:

$$q_e = \frac{K_R C_e}{1 + \alpha_R C_e^{\beta}} \tag{7}$$

where K_R (L/g) and α_R (L/mg) are the Redlich–Peterson constants and β is the Redlich–Peterson isotherm exponent which lies between 0 and 1. If $\beta = 1$, the Langmuir will be the preferable isotherm; and if $\beta = 0$, the Freundlich isotherm will be the preferable isotherm. In our present work, the adsorption of Ni(II) ions onto the adsorbent, the value of β is near to 1, so Redlich–Peterson isotherm model follows the Langmuir isotherm. In addition, the constants K_R and α_R are greater than 1 and the values indicate that Redlich–Peterson isotherm model follows the Freundlich isotherm. All other parameters were listed in Table 1.

The experimental data were better explained by the Freundlich, Langmuir and Temkin based on the correlation coefficient R^2. From the Figs. 9 and 10, the calculated values fit best in the order Langmuir > Redlich–Peterson > Temkin > Freundlich, and Langmuir > Redlich–Peterson > Freundlich > Temkin which suggest that the adsorption process is a homogeneous surface adsorption rather than a multilayer one, which may be due to the homogeneous distribution of the active sites onto the adsorbent. The isotherm studies suggest that the maximum adsorption capacity (q_e) was higher for the Ni(II) ion. The comparison of the adsorption capacity of various adsorbents for the removal of Ni (II) ions is shown in Table 2.

3.4. Adsorption kinetics

The measurement of the rate constants, and determination of the order of the reaction, are important to evaluate the mechanism of adsorption. Various adsorption kinetic models have been used to explain the adsorption of Ni(II) ions. In this work, the Lagergren pseudo-first order [25], Ho's pseudo-second order [26], Elovich [27] Weber and Morris intra-particle diffusion [28] and Boyd [29] kinetic models were tested for Ni(II) ion adsorption on TCAC1 and TCAC2.

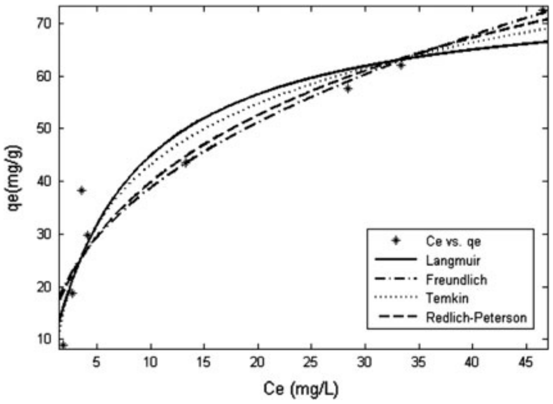

Fig. 9 Non-linear adsorption isotherm for Ni(II) ions with TCAC1.

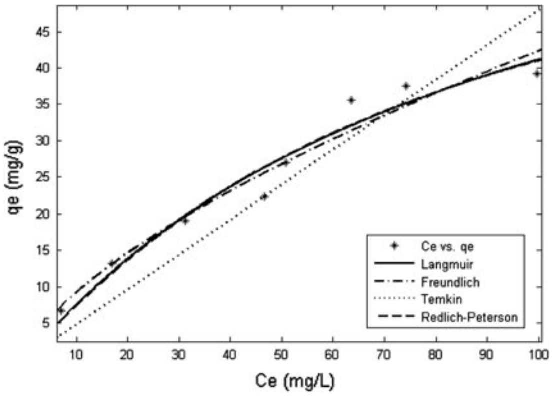

Fig. 10. Non-linear adsorption isotherm for Ni(II) ions with TCAC2.

3.4.1. Lagergren pseudo-first order kinetic model

The rate constant of adsorption was determined by using the following pseudo-first order rate expression obtained from the Lagergren equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{ad}}{2.303}\right) t \tag{8}$$

where q_t is the adsorption capacity at time t (min), and k_{ad} (min^{-1}) is the pseudo-first-order rate constant of adsorption. A straight line was observed for $\log(q_e - q_t)$ vs. t plots for adsorption of Ni(II) ion onto TCAC1 and TCAC2, shown in Fig. 11. The rate constant k_{ad} and q_e values were determined from the slope and intercept of this plot at different contact times. The values of model parameters (k_{ad} and q_e) were obtained from the plot and presented in Table 3.

Table 2
Comparison of adsorption capacity of various adsorbents for Ni(II) ion adsorption

Type of adsorbent	Adsorption capacity (mg/g)	Reference
P-tert[(dimethylamino)methyl]-calix[4]arene	52.80	[31]
Orange peel	158.00	[32]
Red mud	160.00	[33]
HCl-treated clay	80.90	[34]
Modified coir fibers	4.33	[35]
Unmodified coir fibers	2.51	[35]
Cork biomass	44.60	[36]
Dye loaded sawdust	9.87	[37]
Cocoa shell (*T. cacao*) activated carbon	158.8	Present study

3.4.2. Ho's pseudo-second-order kinetic model

A linear form of Ho's pseudo-second-order kinetic model is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{t}{q_e} \tag{9}$$

where k_2 is the equilibrium rate constant of the pseudo-second order adsorption (g/mg/min). A plot was made between t/q_t and t, as shown in Fig. 12. The values of q_e and k_2 were calculated from the slope and intercept of the plots, respectively. Table 3 shows the values of k_2, $q_{\mathrm{e(cal)}}$, $q_{\mathrm{e(exp)}}$ and R^2.

3.4.3. Elovich kinetic model

Ni(II) adsorption kinetics onto various adsorbents (TCAC1 and TCAC2) was also investigated with the Elovich model by plotting $\ln t$ against q_t in Fig. 13.

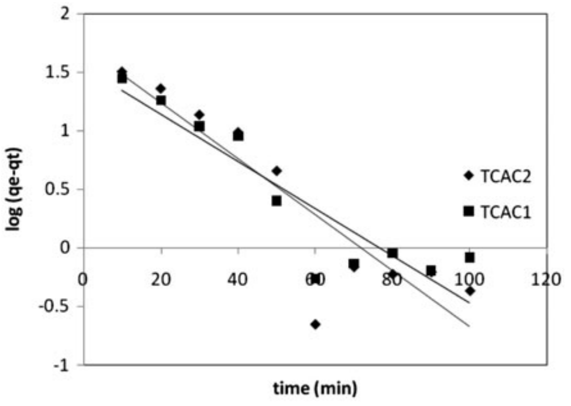

Fig. 11. Pseudo-first-order kinetic for the adsorption of Ni (II) ion onto TCAC1 and TCAC2.

The Elovich model can be expressed as:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{10}$$

where α and β are known as the Elovich co-efficient. α represents the initial adsorption rate in g/mg/min and β relates to the extent of the surface coverage and activation energy for chemisorptions (g/mg) respectively. These α and β values were calculated from the plot of "q_t" against "$\ln t$". The parameter values are listed in Table 3.

3.4.4. Weber and Morris intra- particle diffusion kinetic model

The experimental data were further processed to predict the role of diffusion in the adsorption process by the intra-particle diffusion model. The Intra-particle diffusion model is expressed by the equation given by Weber and Morris:

$$q_e = k_{\mathrm{p}} t^{1/2} + C \tag{11}$$

where t is the time, and k_{p} is the Intra-particle diffusion kinetic rate constant (mg/g/min$^{1/2}$) calculated from the linear plots q_t against $t^{1/2}$ using the experimental data. The intra-particle diffusion straight line does not pass through the origin. The deviation of the straight line from the origin may be because of the difference in the rate of mass transfer between the initial and final stages of adsorption. From the Fig 14, two steps were involved in the adsorption of Ni(II) ions onto the adsorbent process. The first linear portion is due to the film diffusion and the second linear portion is due to the intra-particle diffusion. The deviation of the linear plot deviates from the origin shows that the intra-particle diffusion was not only the rate controlling step but some other steps might have been

Table 3
Kinetic parameters for the adsorption of Ni(II) onto TCAC1 and TCAC2

Kinetic model	Parameters	TCAC1	TCAC2
Pseudo-first order	k_{ad} (min^{-1})	0.0461	0.0529
	$q_{\mathrm{e,cal}}$ (mg/g)	34.834	52.116
	R^2	0.830	0.800
Pseudo-second order	$q_{\mathrm{e,cal}}$ (mg/g)	76.92	90.909
	k (g mg^{-1} min^{-1})	1.509×10^{-3}	1.2604×10^{-3}
	$q_{\mathrm{e,exp}}$ (mg/g)	68.245	82.365
	R^2	0.997	0.997
Elovich equation	α (mg/g min)	38.57	46.13
	β (g/mg)	0.0812	0.0669
	R^2	0.942	0.953
Intra particle diffusion model	k_{p} (mg/g $\mathrm{min}^{1/2}$)	3.852	4.702
	C	33.72	40.37
	R^2	0.859	0.883
Boyd kinetic model	B	0.0460	0.0550
	D_i ($\times 10^{-14}$ m^2/s)	9.044	0.2020
	R^2	0.830	0.800

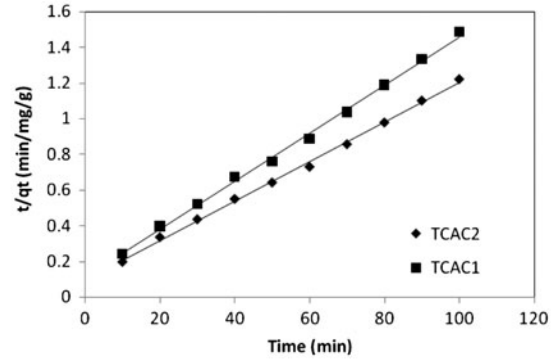

Fig. 12. Pseudo-second-order kinetic for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

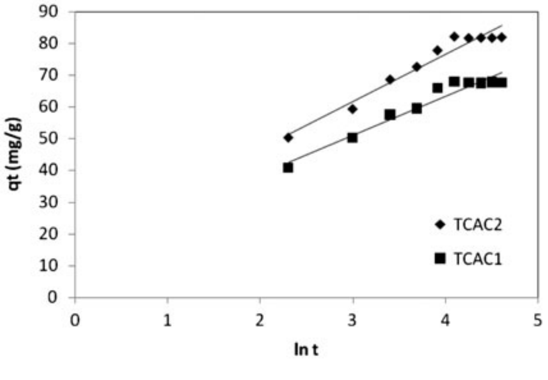

Fig. 13. Elovich kinetic model for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

involved simultaneously. The values of model parameters (k_{p} and C) are given in Table 3.

3.4.5. Boyd kinetic model

Boyd kinetic expression used to predict the actual slow step (rate determining step) involved in the adsorption of Ni(II) ion onto adsorbent. The Boyd kinetic equation is given by the following relationship:

$$F = \frac{q_t}{q_{\mathrm{e}}} = 1 - \frac{6}{\pi^2}\exp(\mathrm{Bt}) \tag{12}$$

The above equation can be modified as following:

$$\mathrm{Bt} = -0.4977 - \ln(1 - F) \tag{13}$$

where q_{e} is the amount of Ni(II) ions adsorbed onto the adsorbent at equilibrium (mg/g), q_t is the amount of Ni(II) ions adsorbed onto the adsorbent at time t, F is the fraction of Ni(II) ions adsorbed at any time t and Bt is a mathematical function of F. The calculated Bt values were plotted against time t (Fig. 15) is found to be linear but did not passes through the origin. This behaviour indicates that the actual slowest step or rate controlling step in the adsorption of Ni(II) ions onto the adsorbent is mainly governed by the adsorption process rather than the intra-particle diffusion. This concluded that the adsorption process is controlled by film diffusion. The value of effective diffusion coefficient, D_i (m^2/s) was calculated by using the following equation:

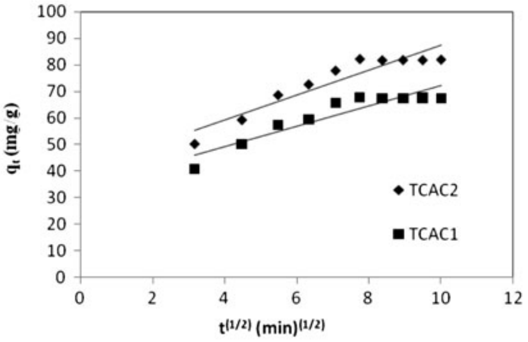

Fig. 14. Intra-particle diffusion model kinetic for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

$$B = \frac{\pi^2 D_i}{r^2} \tag{14}$$

where r is the radius of the adsorbent particle (that is assumed to be spherical) and calculated from particle size analysis and the values are listed in Table 3.

From the R^2 value, it can be explained that the adsorption of metal ions onto TCAC1 and TCAC2 follows the pseudo-second-order model more than that of the Intra-particle diffusion, pseudo-first order, Elovich and Boyd kinetic models.

4. Thermodynamic studies

Adsorption thermodynamics is an essential factor to explain whether the adsorption process is spontaneous or not [30]. Thermodynamic parameters such as free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the following equations:

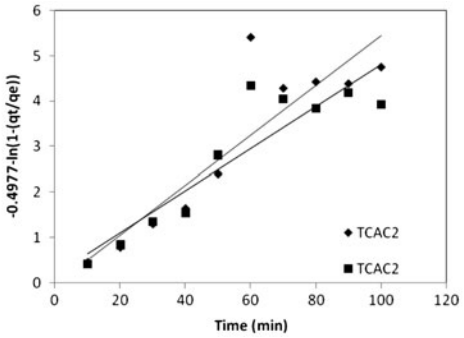

Fig. 15. Boyd kinetic model for the adsorption of Ni(II) ion onto TCAC1 and TCAC2.

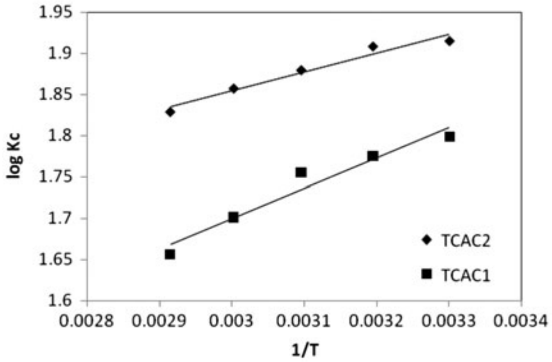

Fig. 16. Plot of $\log K_c$ against $1/T$ for the adsorption of Ni (II) ion onto TCAC1 and TCAC2.

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \tag{15}$$

$$K_c = \frac{C_{Ae}}{C_e} \tag{16}$$

$$\Delta G^\circ = -RT \ln K_c \tag{17}$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the solid-phase concentration at equilibrium (mg/L). ΔG°, ΔH° and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), respectively. R is the universal gas constant (8.314 J/mol/K) and T is the temperature (K). The values of ΔH° and ΔS° are determined from the slope and the intercept of the plots of $\log K_c$ vs. $1/T$ Fig. 16. The negative value of ΔG° shows the adsorption process is spontaneous and feasible in nature, the increase in temperature the ΔG° value decreases indicates that the adsorption process led to decrease in Gibbs energy. The negative value of ΔH° indicates the exothermic nature of adsorption. The positive ΔS° value gives the affinity of the adsorbent for heavy metal ions and the increase of randomness at the solid/liquid interface during the adsorption of Ni(II) ions onto the TCAC1 and TCAC2. The obtained thermodynamic parameters are presented in Table 4.

5. Conclusion

Activated *T. cacao* (cocoa shell) carbon (TCAC1 and TCAC2) prepared at two different temperatures 30 and 350℃ shows considerable potential for the removal of Ni(II) ion from an aqueous solution. The TCAC2 prepared at 350 ℃ shows almost 62% higher efficiency in Ni (II) removal, when compared to

Table 4
Thermodynamic data for adsorption Ni(II) onto TCAC1 and TCAC2

Parameter	Temperature (K)	Adsorbents	
		TCAC1	TCAC2
$-\Delta H^\circ$ (kJ mol^{-1})		7.027	4.394
$-\Delta S^\circ$ (JK^{-1} mol^{-1})		11.45	22.306
$-\Delta G^\circ$ (kJ mol^{-1})	303	10.496	11.150
	313	10.611	11.374
	323	10.725	11.597
	333	10.839	11.819
	343	10.954	12.043

TCAC1. The heat treatment of the adsorbent has resulted in lesser particle size and higher surface area, and hence the increase in the adsorption capacity. The pH value of 6 is found to be more favourable for the adsorption process. Metal ion adsorption increases with an increase in the contact time and equilibrium could be reached within 60 min. The experimental results show that the adsorption data fits well with the Langmuir isotherm and the maximum adsorption capacities of TCAC1 and TCAC2 calculated from the Langmuir isotherm model were found to be 97.59 and 158.8 mg/g, respectively. Kinetic studies show that a better correlation coefficient is obtained with the pseudo-second-order kinetic model, than with the other four kinetic models examined. Thermodynamic parameters such as, ΔG°, ΔH° and ΔS° shows the feasibility, exothermic, and spontaneous nature of adsorption of Ni(II) ion onto TCAC1 and TCAC2 at 303–343 K. This adsorbent is easily available, renewable and inexpensive, and when compared to the other bio adsorbents is highly efficient (Table 4). Therefore, the adsorbent can be an alternative one for the costly adsorbents used for the removal of Ni(II) ions from an aqueous solution.

Acknowledgment

The first author wishes to thank Anna University, Chennai for extending financial support under Anna Centenary Research Fellowship.

References

[1] R. Gowda, A.G Nataraj, and N. Manamohan Rao, Coconut leaves as a low cost adsorbent for the removal of Nickel from electroplating effluents, Int. J. Sci. Eng. Res. 2 (2012) 1–5.

[2] A. Murugesan, T. Vidhyadevi, S.S. Kalaivani, M.P. Premkumar, L. Ravikumar, S. Sivanesan, Kinetic and thermodynamic studies on the removal of Zn^{2+} and Ni^{2+} from their aqueous solution using poly(phenylthiourea)imine, Chem. Eng. J. 197 (2012) 368–378.

[3] M.E. Soltan, M.N. Rashed, G.M. Taha, Heavy metal levels and adsorption capacity of Nile sediments, Int. J. Environ. Anal. Chem. 80 (2001) 167–186.

[4] H.Z. Mousavi, S.R. Seyedi, Nettle ash as a low cost adsorbent for the removal of nickel and cadmium from wastewater, Int. J. Environ. Sci. Tech. 8 (2011) 195–202.

[5] M. Jain, V.K. Grag, K. Kadirvelu, Removal of Ni(II) from aqueous system by chemically modified sunflower biomass, Desal. Water Treat. (2013) 1–15, doi: 10.1080/19443994.2013.811112.

[6] S. Lacour, J.C. Bollinger, B. Serpaud, P. Chantron, R. Arcos, Removal of heavy metals in heavy metals in industrial waste waters by ion-exchanger grafted textiles, Anal. Chim. Acta. 428 (2001) 121–132.

[7] L.P. Singh, J.M. Bhatnagar, S. Tanaka, H. Tsue, M. Mori, Selective anion recognition: charged diaza crown ethers based electrochemical sensors for chromate ions, Anal. Chim. Acta 546 (2005) 199–205.

[8] S. Sthiannopkao, S. Sreesai, Utilization of pulp and paper industrial wastes to remove heavy metals from finishing wastewater, J. Environ. Manage. 90 (2009) 3283–3289.

[9] Y. Zhang, X. Shan, X. Gao, Development of a molecularly imprinted membrane for selective separation of flavonoids, Sep. Purif. Technol. 76 (2011) 337–344.

[10] S. Parama Kalyani, N. Balasubramanian, C. Srinivasakannan, De-colorization and COD reduction of paper industrial effluent using electrocoagulation, Chem. Eng. J. 151 (2009) 97–104.

[11] T. Vidhyadevi, A. Murugesan, S.S. Kalaivani, M.P. Premkumar, V. Vinoth kumar, L. Ravikumar, S. Sivanesan, Evaluation of equilibrium, kinetic, and thermodynamic parameters for adsorption of Cd^{2+} ion and Methyl red dye onto amorphous poly(azomethinethioamide) resin, Desal. Water Treat. (2013) 1–12, doi: 10.1080/19443994.2013.801323.

[12] S.Z. Ashtoukhya, N.K. Amina, O. Abdelwahabb, Removal of lead (II) and copper (II) from aqueous solution using pomegranate peel as a new adsorbent, Desalination 223 (2008) 162–173.

[13] M.F. Taha, C.F. Kiat, M.S. Shaharun, A. Ramli, Removal of Ni(II), Zn(II) and Pb(II) ions from single metal aqueous solution using activated carbon prepared from rice husk, World Acad. Sci. Eng. Technol. 60 (2011) 291–296.

[14] C. Namasivayam, D. Sangeetha, Recycling of agricultural solid waste, coir pith: Removal of anions, heavy metals, organics and dyes from water by adsorption onto $ZnCl_2$ activated coir pith carbon, J. Hazard. Mater. 135 (2006) 449–452.

[15] A. Murugesan, T. Vidhyadevi, S. Dinesh, L. Kirupha, L. Ravikumar, S. Sivanesanan, Removal of chromium (VI) from aqueous solution using chemically modified corncorb-activated carbon: equilibrium and kinetic studies, Environ. Prog. Sust, Energy 32 (2012) 673–680.

[16] P. SenthilKumar, S.R. Ramalingam, V. Abhinaya, K.V. Thiruvengadaravi, P. Baskaralingam, S. Sivanesan, Lead (II) adsorption onto sulphuric acid treated cashew nut shell Sep, Sci. Technol. 46 (2011) 2436–2449.

[17] L. Onyeji, A.A. Aboje, Ring removal of heavy metals from dye effluent using activated carbon produced from coconut shell, Int. J. Eng. Sci. Technol 3 (2011) 8238–8246.

[18] P. Vijayalakshmi, V. Sathya, K.V. Selva Bala, P. Thiruvengadaravi, M. Palanichamy, S. Sivanesan, Removal of acid violet 17 from aqueous solutions by adsorption onto activated carbon prepared from pistachio nut shell, Sep. Sci. Technol. 46 (2011) 155–163.

[19] P. Rajkumar, P. Senthil, S. Kumar, S. Dinesh Kirupha, T. Vidhyadevi, J. Nandagopal, S. Sivanesan, Adsorption of Pb(II) ions onto surface modified guazuma ulmifolia seeds and batch adsorber design environ, Prog. Sust. Energy 32 (2013) 307–316.

[20] Y.B. Onundi, A.A. Mamun, M.F. Al Khatib, Y.M. Ahmed, Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbonInt, J. Environ. Sci. Tech. 7 (2010) 751–758.

[21] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[22] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–470.

[23] M.J. Temkin, V. Pyzhev, Recent modifications to Langmuir isotherms, Acta Physicochim. URSS 12 (1940) 217–225.

[24] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1026.

[25] S. Lagergren, About the theory of so-called adsorption of soluble substances, Kungliga Sven. Vetensk Handl. 24 (1898) 1–39.

[26] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[27] Y.S. Ho, G. McKay, Application of kinetic models to the sorption of copper (II) onto peat, Adsorpt. Sci. Technol. 20 (2002) 797–815.

[28] W.J. Weber, J.C. Morris, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. Am. Soc. Civ. Eng. 89 (1963) 31–60.

[29] G.E. Boyd, A.W. Adamson, L.S. Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics, J. Am. Chem. Soc. 69 (1947) 2836–2848.

[30] V.V. Konovalova, G.M. Dmytrenko, R.R. Nigmatullin, M.T. Bryk, P.I. Gvozdyak, Chromium (VI) reduction in a membrane bioreactor with immobilized pseudomonas cells, Enz. Microb. Technol. 33 (2003) 899–907.

[31] R. Nie, X. Chang, Q. He, Z. Hu, Z. Li, Preparation of p-tert[(dimethylamino)methyl]-calix[4]arene functionalized aminopropolysiloxane resin for selective solid-phase extraction and preconcentration of metal ions, J. Hazard. Mater. 169 (2009) 203–209.

[32] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, Adsorption studies on citrus reticulate (fruit peel of orange) removal and recovery of Ni(II) from electroplating wastewater, J. Hazard. Mater. 69 (1999) 263–268.

[33] A.I. Zouboulis, K.A. Kydros, Use of red mud for toxic metal removal the case of nickel, J. Chem. Technol. Biotechnol. 58 (1993) 95–101.

[34] T. Vengris, R. Binkiene, A. Sveikauskaite, Nickel, copper, and zinc removal from wastewater by a modified clay sorbent, Appl. Clay Sci. 18 (2001) 183–190.

[35] S.R. Shukla, R.S. Pai, A.D. Shendharkar, Adsorption of Ni(II), Zn(II) and Fe(II) on modified coir fibers, Sep. Purif. Technol. 47 (2006) 141–147.

[36] N. Chuber, J.R. Carvalho, M.J.N. Correia, Cork biomass as biosorbent for Cu(II), Zn(II) and Ni(II), Colloids Surf. A: Physicochem. Eng. Aspects 230 (2003) 57–65.

[37] S.R. Shukla, R.S. Pai, Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust. Sep. Purif. Technol. 43 (2005) 1–8.