

Sequestration of nickel from aqueous solution onto activated carbon prepared from *Parthenium hysterophorus* L.

Hem Lata^a, V.K. Garg^b, R.K. Gupta^{a,*}

^a Department of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar 125001, Haryana, India

^b Department of Environmental Science and Engineering, Guru Jambheshwar University of Science and Technology, Hisar 125001, Haryana, India

Received 28 October 2007; received in revised form 7 January 2008; accepted 7 January 2008

Available online 12 January 2008

Abstract

In the present study, nickel removal efficiency of sulphuric acid-treated *Parthenium* carbon (SWC) from simulated wastewater has been investigated. Batch mode adsorption experiments have been conducted by varying pH, nickel concentration, adsorbent dose and contact time. Ni(II) removal was pH-dependent and found to be maximum at pH 5.0. The maximum removal of Ni(II) was achieved within 4 h after the start of every experiment. The equilibrium adsorption data were fitted to Freundlich and Langmuir adsorption isotherm models to evaluate the model parameters. Both models represented the experimental data satisfactorily. The monolayer adsorption capacities of SWC as obtained from Langmuir isotherm was found to be 17.24 mg/g. The Lagergren first-order model was less applicable than pseudo-second-order reaction model. The adsorbent was also characterized including infrared spectroscopy and scanning electron microscopy. The FT-IR study indicated the presence of O–H, C–H, C=O and C–O groups in the adsorbent.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Ni(II); *Parthenium* weed; Adsorption; SEM; FT-IR

1. Introduction

Heavy metal pollution is an environmental problem of global concern. The heavy metals such as lead, copper, cadmium, zinc and nickel are among the most common pollutants found in industrial effluents. Even at low concentrations, these metals can be toxic to organisms, including humans [1]. Nickel is a toxic heavy metal that is widely used in silver refineries, electroplating, zinc base casting and storage battery industries. It has also been reported in the groundwater near landfills, where discarded batteries were also found in the municipal solid waste [2]. In India, the acceptable limit of nickel in drinking water is 0.01 mg/l and for discharge of industrial wastewater is 2.0 mg/l [3]. At higher concentrations, Ni(II) causes cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of

exposure to Ni, such as coins and costume jewellery. Ni carbonyl [Ni (CO)₄] has been estimated as lethal in humans at atmospheric exposures of 30 ppm for 30 min. Nickel poisoning causes headache, dizziness, nausea, vomiting, tightness of the chest, dry cough, shortness of breath, rapid respiration, cyanosis and extreme weakness [3].

Several methods are available for the removal of metal ions from water and wastewater. These include ion exchange, solvent extraction, reverse osmosis, electrodialysis, precipitation, flocculation, sorption, activated carbon adsorption and membrane separation processes [1]. However these techniques have certain disadvantages, including higher operational cost, residual metal sludge disposable, etc. Due to prohibitive cost of these processes, the use of agricultural residues or industrial by-product having biological activities have been received with considerable attention [2]. In recent years, a number of adsorptive material, such as moss peat [4], melon seed husk [5], tea factory waste [6], sheep manure waste [7], bagasse and fly ash [8], waste apricot [9], activated carbon [10], *Parthenium hysterophorus* [11–13] etc., have been tested to remove heavy metals from wastewater.

* Corresponding author. Tel.: +91 1662 263152; fax: +91 1662 276240.

E-mail addresses: vinodkgarg@yahoo.com (V.K. Garg), rkgtic@yahoo.com (R.K. Gupta).

Parthenium (*P. hysterophorus* L.) also known as white top or carrot weed, an annual herbaceous weed—a native of north-east Mexico, has now widely spread in India, China, Australia, Pacific Islands, etc. Parthenium plant contains Parthenon, hymenin and ambrosin etc., which may induce allergic dermatitis. It causes several health problems in human beings and animals, e.g. allergy, dermatitis, eczema, black spots, blisters around eyes, burning, rings and blisters over skin, asthma, hay fever, etc. The biomass of this plant is not put to any use and disposed along the roadsides, agricultural fields and railway tracks after uprooting. The biomass of this plant is available whole year at zero prices. The objective of this work was to study the adsorption capacity of Parthenium plant for the removal of nickel from aqueous solution by varying parameters such as agitation time, Ni(II) concentration, adsorbent dose and pH.

2. Experimental procedure

2.1. Material development

2.1.1. Preparation of sulphuric acid-treated Parthenium carbon (SWC)

Fully grown plants of Parthenium (stem, branches and leaves) were collected from the uncultivated fields of Guru Jambheshwar University of Science and Technology, Hisar (India), cut in to small pieces of 2–3 cm and dried in sunlight. The dried biomass was used for carbon preparation by mixing with concentrated sulphuric acid (Parthenium:acid, 1:1.5 w/v ratio) and keeping it at 120 °C for 24 h. This carbonized material was washed with distilled water several times to remove the free acid and soaked in 1% sodium bicarbonate solution overnight to remove any residual acid. This material was then again washed with distilled water and dried at 105 °C in a hot air oven for 24 h. It was ground and sieved in the size range of 0.3–1.0 mm. The various physico-chemical characteristics of SWC were: particle size = 0.3–1.0 mm; bulk density = 0.57 g ml⁻¹; pH 7.2; moisture content (%) = 0.15; water solubility (%) = 2.86; acid solubility (%) = 4.0. The material was placed in airtight plastic containers for further use.

2.2. Preparation of Ni(II) containing simulated wastewater

A stock solution of 1000 mg/l of Ni(II) was prepared by dissolving 4.4790 g of nickel sulphate [NiSO₄·6H₂O] in double distilled water, acidified with nitric acid to prevent hydrolysis formation. The stock solution was further diluted with distilled water to obtain the required standard solutions.

2.3. Batch adsorption studies

Batch mode experiments were conducted at 23 ± 2 °C temperature by shaking 0.2 g of adsorbent with 100 ml of simulated wastewater of desired concentration in 250 ml glass stoppered conical flasks. The flasks were agitated on a rotary shaker at 180 rpm for 6 h to ensure equilibrium. The adsorbent from the mixture was separated by centrifugation at pre-determined time intervals. Then residual nickel concentration in the supernatant

Table 1
Some fundamental FT-IR frequencies of studied adsorbent (native and after use)

Adsorbent	Band position (cm ⁻¹)			
	O–H	C–H	C=O	C–O
SWC native	3385.9	2923.1	1708.5	1037.4
SWC–Ni loaded	3376.8	2923.8	1703.4	1035.3

was estimated spectrophotometrically using dimethyl glyoxime method [14]. All the experiments were carried out at pH 5.0 (except when the pH effect was studied). The effect of solution pH on metal uptake was investigated under similar experimental conditions between pH 2.0 and 9.0. pH of the solution was adjusted with dilute NaOH and HCl solution. Adsorbent dose was varied from 0.2 g to 1.0 g/100 ml of simulated wastewater. Contact time was also varied from 60–360 min. Adsorption isotherm studies were carried out by using 10–50 mg/l Ni(II), pH 5.0 and 0.2 g adsorbent/100 ml. The percent removal of Ni(II) was calculated from the difference between the concentration of Ni(II) before and after adsorption. All the experiments were conducted in duplicate and mean values were used in the analysis of data.

2.4. Fourier transform infrared analysis (FT-IR)

Infrared spectra of the adsorbents were obtained using a Fourier transform infrared spectrometer (FT-IR, PE-RXI). For the FT-IR study, finely ground biomass was encapsulated with KBr in the ratio of 1:20 in order to prepare the translucent sample disks.

2.5. Scanning electron microscopy (SEM)

After the metal–carbon contact experiments, the samples were characterized by SEM. The samples mounted directly onto metal studs were analyzed in a LEO-435 VP microscope to obtain information regarding the surface morphology.

3. Results and discussion

3.1. FT-IR spectral analysis

The FT-IR spectra of Parthenium weed carbon (SWC) in the range of 500–4000 cm⁻¹ were recorded to obtain information regarding vibrational frequency changes in the functional groups present in the adsorbent using (Perkin Elmer, PE-RXI) (Table 1). The FT-IR spectra of native and nickel(II) loaded (SWC) are presented in (Fig. 1a and b). The FT-IR spectroscopic analysis of SWC indicated broad band at 3385.9, 2923.1, 1708.5, 1614.7 and 1037.4 cm⁻¹ when compared with that of nickel(II) loaded SWC which showed the same absorption at 3376.8, 2923.8, 1703.4, 1617.3 and 1035.3 cm⁻¹. These groups are of the bonded hydroxyl group (–OH), stretching vibration of the C–H group, C=O stretching due to carboxyl group and strong C–O band due to –OCH₃ groups. The difference between peaks in the FT-IR spectra of native and nickel(II) loaded SWC

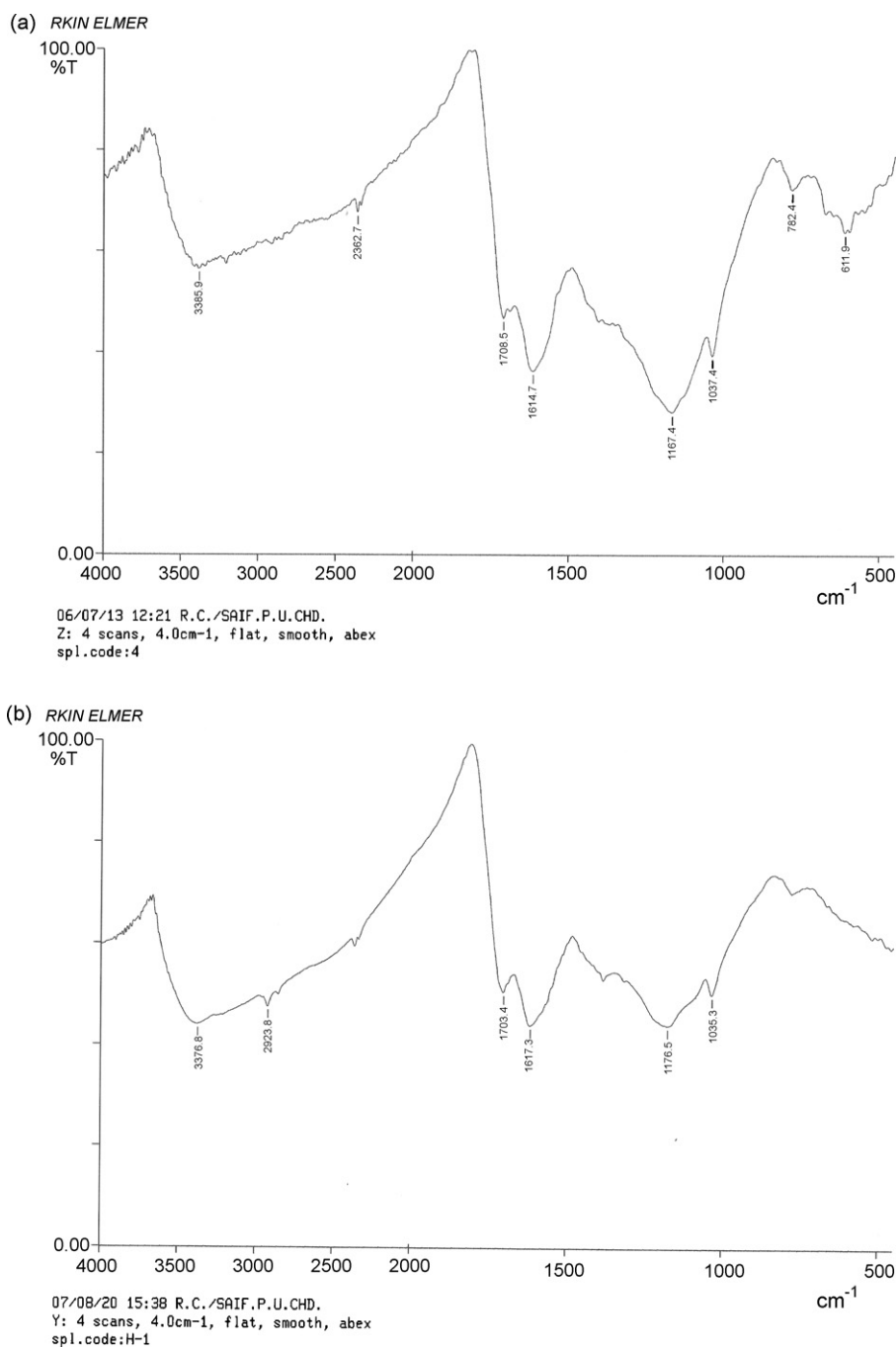


Fig. 1. (a) FT-IR spectra of sulphuric acid-treated carbon (SWC) before use and (b) FT-IR spectra of Ni(II) loaded sulphuric acid-treated carbon (SWC).

ranged from 9.1, 0.7, 5.1 and 2.1 cm^{-1} . These results indicated the involvement of some of functional groups in metal binding. Malkoc and Nuhoglu; Garg et al. [6,15] have also reported that there is a small difference in the absorption peaks of spectra before and after metal adsorption.

3.2. Effect of solution pH

One of the most important process parameters in adsorption is pH of the medium. In order to study the effect of pH on Ni(II)

adsorption onto SWC, pH of solution was varied from 2.0 to 9.0. From Fig. 2, it is observed that the adsorption of nickel varies with pH and is highly pH-dependent. Adsorption is high at pH 5.0 and decreases as the pH increases or decreases. At low pH values, concentrations of H^+ ions far exceeds that of the metal ions and hence H^+ ions compete with Ni(II) ions for the surface of the adsorbent which would hinder the Ni(II) ions from reaching the binding sites of the adsorbent caused by repulsive forces. However, the metal removal is minimum presumably due to enhanced competition of proton with nickel ions for the binding sites and complex formation. When pH is increased, the

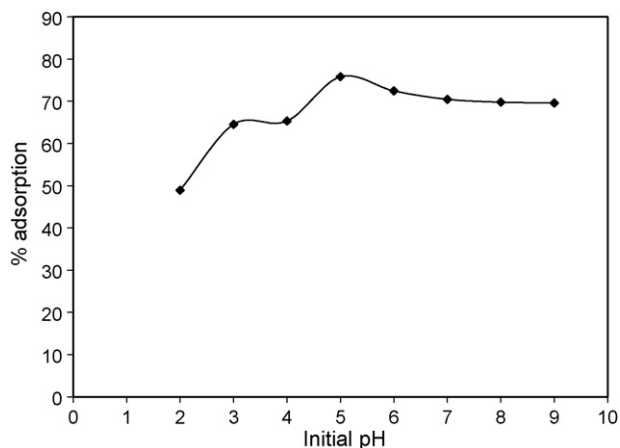


Fig. 2. Effect of pH on the adsorption of Ni(II) on SWC (initial concentration = 20 mg/l, adsorbent dose = 0.2 g/100 ml, contact time = 5 h).

Ni(II) ions get precipitated due to hydroxide anion forming a nickel hydroxide precipitates. For this reasons, the optimal pH was selected to be 5.0 for the further experiments.

3.3. Effect of agitation time and initial concentration

Effect of agitation time and initial concentration on removal of Ni(II) by SWC at $23 \pm 2^\circ\text{C}$ and pH 5.0 was studied. The results so obtained are given in Fig. 3. It is evident from the results that percent adsorption of metal ion increases rapidly with time and attains equilibrium at about 4 h for all the concentrations studied (10–25 mg/l). The percent adsorption of metal ion is inversely related to the initial metal ion concentrations. Percentage of Ni(II) removal was decreased as its concentration was increased at fixed adsorbent dose. But the amount of Ni(II) ions adsorbed per unit mass of adsorbent increased with the increase of the initial ion concentrations. When the Ni(II) ion concentration was increased from 10 to 25 mg/l, the adsorption capacity of SWC increased from 4.51 to 9.47 mg/g at equilibrium.

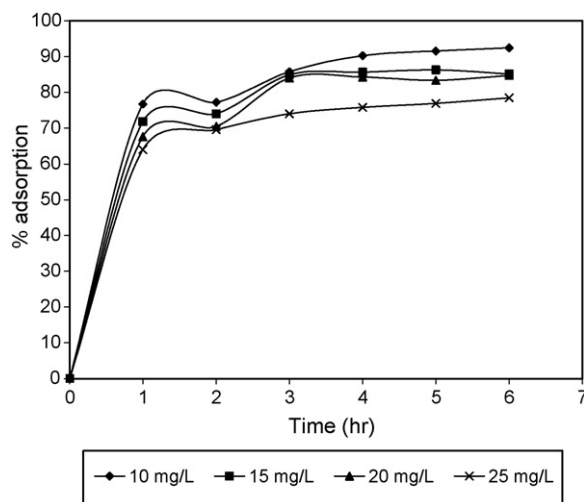


Fig. 3. Effect of initial concentration on adsorption of Ni(II) on SWC (adsorbent dose = 0.2 g/100 ml, pH 5.0).

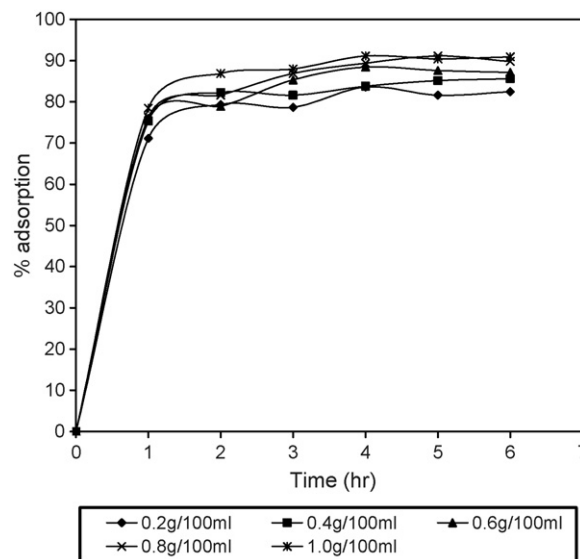


Fig. 4. Effect of adsorbent dose on the adsorption of Ni(II) on SWC (initial concentration = 20 mg/l, pH 5.0).

Table 2

Isotherm constants of Langmuir and Freundlich models for Ni(II) adsorption by SWC

Adsorbent	Langmuir constants			Freundlich constants		
	Q_0 (mg/g)	b (l/mg)	R^2	K_f (mg/g)	n	R^2
SWC	17.24	0.27	0.9978	4.99	2.58	0.986

3.4. Effect of adsorbent dose and contact time

Nickel removal at different adsorbent doses was studied at $23 \pm 2^\circ\text{C}$ temperature and 5.0 pH by varying the adsorbent dose from 2.0 to 10.0 g/l while keeping the volume and concentration of the metal solution constant. The results have been presented in Fig. 4. It is evident from Fig. 4 that percent adsorption of Ni(II) ion was increased with time as well as adsorbent dose. This is because of the availability of more and more adsorption sites for complexation of nickel(II) ions [16]. Time required for the equilibrium attainment was 4 h. However, the unit adsorption capacity showed a reverse trend to the percent adsorptions.

Table 3

Comparison of adsorption capacity of Ni(II) onto various adsorbents

Adsorbent	Adsorption capacity (mg/g)	References
Tea factory waste	15.26	Malkoc [1]
Sphagnum moss peat	9.18	Ho [4]
Melon seed husk	5.9	Okieman [5]
Sheep manure waste	7.20	Abu Al-Rub [7]
Fly ash	0.03	Rao [8]
Bagasse	0.001	Rao [8]
<i>Aspergillus niger</i>	5.0	Huseyin [19]
Red mud	15.0	Zouboulis [20]
<i>Rhizopus nigricans</i>	1.0	Kapoor [21]
Granular activated carbon	1.49	Periasamy [22]
Natural clay	12.5	Hawash [23]
<i>Parthenium hysterophorus</i>	17.2	This work

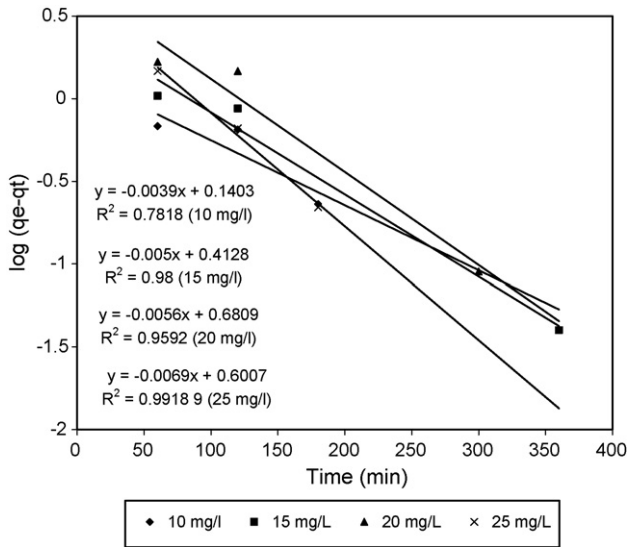


Fig. 5. Pseudo-first-order kinetic plot for adsorption of Ni(II) on SWC.

With increasing adsorbent dose from 2.0 g to 10.0 g/l, the adsorption of Ni(II) ion per unit mass of adsorbent decreased from 8.4 to 1.82 mg/g. This is due to overlapping and aggregation of adsorption sites when dose increased from 2.0 to 10.0 g/l.

3.5. Adsorption isotherms

Among various models employed for analyzing the nature of adsorbate–adsorbent interaction, adsorption isotherms are the most significant. Removal of nickel at different concentrations (10–50 mg/l) on a fixed amount of adsorbent has been expressed by two different models viz., Freundlich and Langmuir isotherms. The Freundlich isotherm is represented by the following equations [17]:

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

$$\log q_e = \log(K_f) + \left(\frac{1}{n}\right) \log(C_e) \tag{2}$$

where C_e is the equilibrium concentration (mg/l); q_e is the amount adsorbed per specified amount of adsorbent (mg/g) at equilibrium, K_f and n are constants which are adsorption capacity (mg/g) and intensity of adsorption, respectively. Linear plots of $\log q_e$ versus $\log C_e$ (figure not given) shows that the adsorption followed Freundlich model well. K_f and n were calculated from the intercept and slope of the plots. The values of constants are given in Table 2.

Table 4
Adsorption kinetic constants for Ni(II) adsorption by SWC

Initial concentration (mg/l)	First-order kinetic model				Second-order kinetic model		
	q_e , exp (mg/g)	k_{ad} (1/min)	q_e , cal (mg/g)	R^2	k' (g/mg/min)	q_e , cal (mg/g)	R^2
10	4.51	8.98×10^{-3}	1.38	0.7818	0.017	4.72	0.9956
15	6.42	0.012	2.59	0.98	0.017	6.56	0.997
20	8.42	0.013	4.79	0.9592	9.37×10^{-3}	8.67	0.9945
25	9.47	0.016	3.99	0.9918	0.010	9.94	0.998

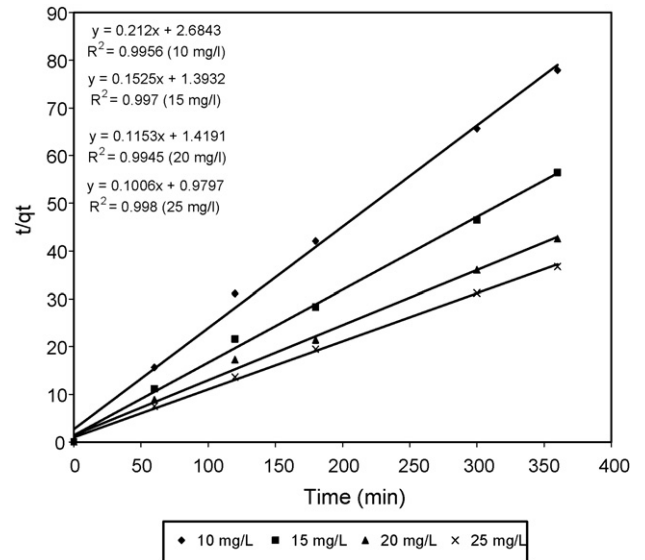


Fig. 6. Pseudo-second-order plot for the adsorption of Ni(II) on SWC (volume of sample = 100 ml, pH 5.0).

Value of ‘ n ’ between 1 and 10 represents beneficial adsorption.

Langmuir model is commonly used for liquid phase adsorption. Langmuir model assumes that the uptake of metal ions occur on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.

The Langmuir isotherm is expressed as [18]:

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0 b}\right) + \left(\frac{C_e}{Q_0}\right) \tag{3}$$

where, q_e is the amount of Ni(II) adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/l), Q_0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. The linear plot of C_e/q_e versus C_e (figure not given) shows that the nickel removal by SWC obeys the Langmuir model too. Q_0 and b were calculated from the slope and intercept of the plot and are presented in Table 2. On the basis of correlation coefficients, it can be observed in Table 2, experimental data were better fitted to the Langmuir equation than that of the Freundlich equation.

The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is defined by

$$R_L = \frac{1}{(1 + bC_0)} \tag{4}$$

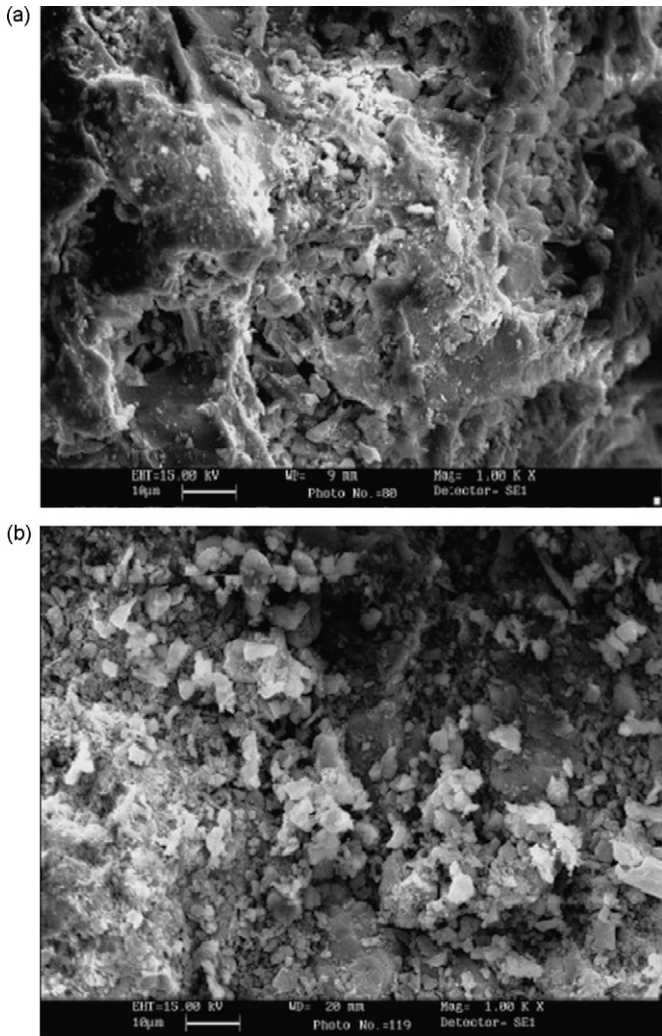


Fig. 7. (a) SEM micrographs of native SWC and (b) SEM micrographs of Ni(II) loaded SWC.

R_L values between 0 and 1 indicate favorable adsorption of Ni(II) onto SWC. The values of Ni(II) uptake by different adsorbent collected from the literature along with the results of this work are given in Table 3 in the form of monolayer adsorption capacity. The value of Ni(II) uptake found in this work is higher than reported elsewhere. The comparison of adsorption capacities of SWC used in this study with those obtained in the literature shows that the SWC is effective for the removal of nickel(II) from aqueous solution.

3.6. Adsorption kinetics

In order to investigate the mechanism of adsorption, kinetics models are used to test experimental data. Pseudo-first-order and pseudo-second-order equations can be used while assuming that the measured concentrations are equal to surface concentrations.

The pseudo-first-order is expressed as [24]:

$$\log(q_e - q_t) = \log q_e - \left[\frac{(k_{ad}t)}{2.303} \right] \quad (5)$$

where q_t and q_e are the amounts of Ni(II) adsorbed (mg/g) at time t (min) and at equilibrium time and k_{ad} is the rate constant of first-order adsorption. Linear plot of $\log(q_e - q_t)$ versus t shows the applicability of the above equation for SWC (Fig. 5). The k_{ad} and q_e values were calculated from slope and intercept of the plot, respectively. The values of these constants for Ni(II) removal by SWC are given in Table 4.

The pseudo-second-order kinetic model is expressed as [25]:

$$\frac{t}{q_t} = \left[\frac{1}{k'q_e^2} \right] + \frac{t}{q_e} \quad (6)$$

where k' (g/mg min^{-1}) is the rate constant of second-order adsorption. The plot of t/q_t versus t should be a straight line if second-order kinetic model is applicable. It was found that although the first-order equation was suitable for some of the data; it was not applicable to all the results. Therefore, no further consideration was given to it. The pseudo-second-order model, however, was applicable to all the data and the results are shown in Fig. 6. The values of k' and correlations coefficients are listed in Table 4.

3.7. Scanning electron microscopy (SEM)

SEM micrographs were obtained before and after Ni(II) adsorption onto SWC are presented in Fig. 7a and b. The scanning electron micrographs clearly reveal the surface texture and porosity of the sample. In Fig. 7a, the surface of the adsorbent is a continuous structure with feature around $10 \mu\text{m}$, while in Fig. 7b, new shiny and bulky particles appear over the surface of Ni(II) loaded SWC.

4. Conclusion

In our laboratory, the work is in progress to look into the possibility of the use of waste biomass for industrial pollution control. In this study removal of Ni(II) on SWC has been investigated. The removal process was affected by process parameters, namely, pH, adsorbent dose, concentration of metal ion and contact time. Maximum removal of nickel on SWC was at pH 5.0. The equilibrium of metal ion removal was attained in 4 h. The data obtained from this study was best described by Langmuir and Freundlich isotherm models. The overall adsorption rate was best described by pseudo-second-order kinetic model. Adsorption of nickel on the surface of SWC was studied by FT-IR and SEM. SEM analysis indicates that nickel adsorption takes place on the surface of SWC. These results demonstrate that SWC could be effective, easily available and low cost adsorbent for the removal of Ni(II) from dilute aqueous solution.

References

- [1] E. Malkoc, Y. Nuhoglu, Investigations of nickel(II) removal from aqueous solutions using tea factory waste, *J. Hazard. Mater.* B127 (2005) 120–128.
- [2] S. Mor, R. Khaiwal, A. de Visscher, R.P. Dahiya, A. Chandra, Municipal solid waste characterization and its assessment for potential methane generation at Gazipur landfill site, Delhi: a case study, *Sci. Total Environ.* 371 (2006) 1–10.

- [3] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith, *Sep. Purif. Technol.* 24 (2001) 497–505.
- [4] Y.S. Ho, D.A. John Wase, C.F. Forster, Batch nickel removal from aqueous solution by *Sphagnum* moss peat, *Water Res.* 29 (5) (1995) 1327–1332.
- [5] F.E. Okieman, V.U. Ohyenkpa, Removal of heavy metals ion from aqueous solutions with melon (*Citrullus vulgaris*) seed husk, *Biol. Waste* 29 (1989) 11–16.
- [6] E. Malkoc, Y. Nuhoglu, Removal of Ni(II) ions from aqueous solutions using waste of tea factory: adsorption on a fixed-bed column, *J. Hazard. Mater.* 135 (2006) 328–336.
- [7] F. Abu Al-Rub, M. Kandah, N. Aldabaibeh, Nickel removal from aqueous solutions using sheep manure waste, *Eng. Life. Sci.* 2 (2002) 111–116.
- [8] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr⁶⁺ and Ni²⁺ from aqueous solution using bagasse and fly ash, *Waste Manage.* 22 (2002) 821–830.
- [9] S. Erdogan, Y. Onal, C. Akmil-Basar, S. Bilmez-Erdemoglu, C. Sarici-Ozdemir, G. Icdygu, Optimization of nickel adsorption from aqueous solution by using activated carbon prepared from waste apricot by chemical activation, *Appl. Surf. Sci.* 252 (2005) 1324–1331.
- [10] S. Mor, R. Khaiwal, R.P. Dahiya, A. Chandra, Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site, *Environ. Monit. Assess.* 118 (2006) 435–456.
- [11] H. Lata, V.K. Garg, R.K. Gupta, Removal of a basic dye from aqueous solution by adsorption using *Parthenium hysterophorus*: an agricultural waste, *Dyes Pigment.* 74 (2007) 653–658.
- [12] H. Lata, V.K. Garg, R.K. Gupta, Adsorptive removal of basic dye by chemically activated *Parthenium* biomass: equilibrium and kinetic modeling, *Desalination* 219 (2008) 250–261.
- [13] H. Lata, S. Mor, V.K. Garg, R.K. Gupta, Removal of a dye from simulated wastewater by adsorption using treated *parthenium* biomass, *J. Hazard. Mater.* 153 (2008) 213–220.
- [14] American Public Health Association, Standards Methods for the Examination of Water and Wastewater, APHA, Washington, 1995.
- [15] U.K. Garg, M.P. Kaur, V.K. Garg, D. Sud, Removal of hexavalent chromium from aqueous solution by agricultural waste biomass, *J. Hazard. Mater.* 140 (2007) 60–68.
- [16] A. Ozer, D. Ozer, The adsorption of copper(II) ions onto dehydrated wheat bran (DWB): determination of equilibrium and thermodynamic parameters, *Process Biochem.* 39 (12) (2004) 2183–2191.
- [17] G. Mckay, H.S. Blair, J.R. Garden, Adsorption of dyes on chitin: equilibrium studies, *J. Appl. Polym. Sci.* 27 (1982) 3043–3057.
- [18] I.J. Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, *Am. Chem. Soc.* 40 (1918) 1361–1368.
- [19] B.A.G. Huseyin, A.R. Turker, M. Lale, Determination of trace metals in geological samples by atomic absorption spectrophotometry after pre-concentration by *Aspergillus niger* immobilized on sepiolite, *Anal. Sci.* 15 (1999) 1251–1256.
- [20] A.I. Zouboulis, K.K. Kydros, Use of red mud for toxic metals removal. The case of nickel, *J. Chem. Technol. Biotechnol.* 58 (1993) 95–101.
- [21] A. Kapoor, T. Viraraghavan, Biosorption of heavy metals on *Aspergillus niger*: effect of pretreatment, *Bioresour. Technol.* 63 (1997) 109–113.
- [22] K. Periasamy, C. Namasivayam, Removal of Ni(II) from aqueous solution and nickel plating industry wastewater using an agricultural waste: peanut hull, *Waste Manage.* 15 (1995) 63–68.
- [23] S. Hawash, H. El-Abd, M.S. El-Geundi, M.M. Nassae, J.Y. Farah, Useful equilibrium means of natural clay, *Adv. Sci. Technol.* 9 (1994) 231–243.
- [24] D.B. Singh, D. Prasad, D.C. Rupainwar, V.N. Singh, As(III) removal from aqueous solution by adsorption, *Water, Air Soil Pollut.* 42 (1989) 376–386.
- [25] Y.S. Ho, G. Mckay, Pseudo-second order model for sorption process, *Process Biochem.* 34 (1999) 451–465.