

Journal of Hazardous Materials B127 (2005) 120-128

www.elsevier.com/locate/jhazmat

Journal of Hazardous Materials

Investigations of nickel(II) removal from aqueous solutions using tea factory waste

Emine Malkoc*, Yasar Nuhoglu

Department of Environmental Engineering, Ataturk University, 25240 Erzurum, Turkey

Received 23 February 2005; received in revised form 21 June 2005; accepted 26 June 2005 Available online 24 August 2005

Abstract

This paper presents the data for the effect of adsorbent dose, initial metal concentration, solution pH, agitating rate and temperature on the adsorption of nickel(II) on waste tea. Batch adsorption studies have been carried out. The equilibrium nature of nickel(II) adsorption at different temperature (25–60 °C) has been described by the Freundlich and Langmuir isotherm. The adsorption capacity (Q_0) calculated from Langmuir isotherm was 15.26 mg Ni(II) g⁻¹ at initial pH of 4.0 at 25 °C. The results of the thermodynamic investigations indicate that the adsorption reactions are spontaneous ($\Delta G^{\circ} < 0$), slightly endothermic ($\Delta H^{\circ} > 0$) and irreversible ($\Delta S^{\circ} > 0$). © 2005 Elsevier B.V. All rights reserved.

Keywords: Nickel; Waste tea; Thermodynamic; Isotherm

1. Introduction

Heavy metal pollution is an environmental problem of worldwide 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(II) ion is one such heavy metal frequently encountered in raw wastewater streams from industries, such as non-ferrous metal, mineral processing, electroplating [2–4], porcelain enameling, copper sulfate manufacture [2], battery and accumulator manufacturing [5]. The maximum permissible concentration of nickel in effluents in the U.S. for plants discharging 38,000 L or more per calendar day of electroplating process wastewater the following limitations shall apply: maximum for any 1 day is 4.1 mg L^{-1} and average of daily values for four consecutive monitoring days shall not exceed 2.6 mg L^{-1} [6]. In drinking water, nickel may cause health problems if found in amounts greater than the health standard set (MCLG: 0.1 mg L^{-1}) by

the United States Environmental Protection Agency (EPA). The MCLG for nickel has been set at 0.1 parts per million (ppm) because EPA believes this level of protection would not cause any of the potential health problems [7].

Higher concentrations of nickel cause cancer of lungs, nose and bone. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and jewellery. Acute poisoning of Ni(II) causes headache, dizziness, nausea and vomiting, chest pain, tightness of the chest, dry cough and shortness of breath, rapid respiration, cyanosis and extreme weakness [8].

A number of methods are available for the removal of metal ions from aqueous solutions. These are ion exchange [9], solvent extraction [10], reverse osmosis, electrodialysis [3], precipitation [11], flocculation [12], sorption [13], activated carbon adsorption and membrane separation processes [14]. However, these techniques have certain disadvantages, such as high capital and operational costs or the treatment and disposal of the residual metal sludge. Since the cost of these processes are rather expensive, the use of agricultural residues or industrial by-product having biological activities have been received with considerable attention [3]. In recent years, a number of adsorptive material, such as moss peat

^{*} Corresponding author. Tel.: +90 442 2314602; fax: +90 442 2360957. *E-mail address:* emalkoc@atauni.edu.tr (E. Malkoc).

 $^{0304\}text{-}3894/\$$ – see front matter 0 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2005.06.030

[15], coconut husk, a sugar industry waste [9], chitin [16], sawdust [17], green algae [18,19], fly ash [20], bone char [21], lignite [22] were used in heavy metal removal from wastewaters.

Tea plants (*Camellia sinensis* of the family Theaceae) are commonly grown in the Eastern Black Sea region of Turkey. High quality tea is harvested the three top leaves of the shoot on tea plant in the teagarden. While tea producer cut the top tea leaves with special tea shears, some overgrown woody shoots, which may include six-seven top leaves, mixed in the tea harvest. During the tea production procedure, this woody overgrown shoots were not treated by tea factory and formed into tea factory waste. There is much tea factory in the Eastern Black Sea region and its produce about 30,000 tonnes of tea factory wastes. Tea factory wastes are not used any purpose and its deposits in depository area or occasionally discharge in small bay in the Black Sea [23]. The objective of this study was to investigate the possibility of using tea production waste as an adsorbent material in nickel adsorption.

2. Materials and methods

2.1. Adsorbent

The tea waste was obtained from tea plants located in black sea region in Giresun-Eynesil, Turkey. The chemical and physical characteristic of the tea waste is presented in Table 1. Prior to the experiments, and other soluble dirtiness and colored components were removed from the tea wastes by washing with distilled water for much times until a colorless solution of tea waste was spectrometrically observed at room temperature. Decolorized and cleaned tea waste was dried at room temperature for a few days.

2.2. Batch adsorption studies

Experiments were conducted in 250 mL Erlenmeyer flasks containing known nickel(II) synthetic solutions. Flasks were agitated on a shaker at 360 rpm constant shaking rate for 120 min to ensure equilibrium was reached and filtered through (Schleicher&Schüll589). Samples (5 mL) were taken

Table 1

Physical and chemica	l properties of waste	e tea used in the experiments
----------------------	-----------------------	-------------------------------

5 1 1	1
Chemical characteristic [24]	Percent
Moisture	11.01
Water soluble components	6.04
Insoluble components	80.24
Ash	2.97
Total loss of ignition	94.06
Physical characteristic	Units
Surface area $(m^2 g^{-1})$	0.39
Bulk density $(g \text{ cm}^{-3})$	0.112
Particle size (mm)	0.15-0.25

before mixing the biosorbent solution and nickel(II) ion bearing solution and at pre-determined time intervals (1, 3, 5, 7, 10, 20, 30, 60, 120 min) for the residual metal ion concentration in the solution. Uptake values were determined as the difference between the initial nickel(II) concentration and the one in the supernatant. The initial pH adjustments were carried out either by sulfuric acid and sodium hydroxide. Adsorption experiments were carried out 0.15–0.25 mm at adsorbent particle size.

NiCl₂·6H₂O was an analytical grade chemical and was prepared in deionized water. The amount of nickel in filtrate was analyzed by standard complexometric methods [25].

2.3. Column experiments

The fixed-bed columns were made of Perspex tubes 2.0 cm internal diameter and 30 cm in height. The bed length used in the experiments was 30 cm. In a typical experiment the metal of a known concentration was pumped at a fixed flow rate to the filled with known bed height of adsorbent. The particle size of adsorbent used in the experiment was 1.0-3.0 mm. The pH of the solutions was maintained constant at 4.0. The temperature of stream feeding solution and of the column was controlled at 25 °C through a thermostatic bath.

2.4. Fourier transform infrared spectroscopy

The FTIR spectra of the waste tea are shown in Fig. 1. As shown in the figure, the spectra display a number of absorption peaks, indicating the complex nature of the material examined. The FTIR spectroscopic analysis indicated broad bands at 3412 cm^{-1} , representing bonded –OH groups. The bands observed at about $2921-2851 \text{ cm}^{-1}$ could be assigned to the C–H stretch. The peaks around 1733 cm^{-1} correspond to the C=H group and at $1652-1512 \text{ cm}^{-1} \text{ C=O}$ stretch. This C–O band absorption peak is observed to shift to 1035 cm^{-1} . Thus, it seems that this type of functional group is likely to participate in metal binding.



Fig. 1. FTIR spectra of waste tea.



Fig. 2. The uptake and residual amount of Ni(II) by waste tea as a function of initial metal concentration.(adsorbent dose = 10 g L^{-1} , agitating rate = 360 rpm, pH 4.0).

3. Results and discussion

3.1. Effect of initial Ni(II) concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of nickel(II) between the aqueous and solid phases [5]. Nickel(II) adsorption capacities of waste tea were presented as a contact time in Fig. 2.

The initial concentration $(C_0, \text{mg L}^{-1})$ was changed in the range 50–300 mg L⁻¹. When the initial nickel(II) ion concentration increased from 50 to 300 mg L⁻¹, the residual Ni(II) concentration $(C_{\text{res}}, \text{mg L}^{-1})$ of solution increased from 5.8 to 159 mg L⁻¹. The removal of Ni(II) ions increased rapidly with time up to 20 min and thereafter increased slowly. While initial metal concentration was 100 mg L^{-1} , the uptake of Ni(II) ions was 8.12 mg g^{-1} at 30 min and 8.24 mg g^{-1} at 120 min. According to results, the adsorption equilibrium reached at 120 min. The amount of nickel(II) ions adsorbed per unit mass of the biosorbent increased with the initial concentration increased from 50 to 300 mg L⁻¹, the initial adsorption capacity of waste tea increased from 4.413 to 14.04 mg g⁻¹.

3.2. Effect of adsorbent dosage

Fig. 3 shows that adsorption capacity of nickel(II) as function of waste tea concentration. The effect of waste tea on the sorption kinetics of nickel(II) ion was studied at pH of 4.0 and 200 mg L⁻¹ initial nickel(II) ion concentration. The sorbent dose was varied between 5.0 and 15 g L⁻¹. The increase in adsorbent dosage from 5.0 to 15 g L⁻¹ resulted in an increase from 49.5 to 79.5% in adsorption of nickel(II) ions. This is



Fig. 3. The uptake and residual Ni(II) concentration by waste tea as an adsorbent dosage (agitating rate = 360 rpm, pH 4.0, $C_0 = 200 \text{ mg L}^{-1}$).

because of the availability of more and more binding sites for complexation of nickel(II) ions [26]. However, nickel uptakes showed a reverse trend to the percentage adsorptions. With increasing adsorbent dosage from 5.0 to 15 g L⁻¹, the adsorption of nickel(II) ion per unit weight of adsorbent decreased from 19.8 to 10.6 mg g⁻¹.

3.3. Effect of solution pH

Metal biosorption is critically linked with pH. In order to establish the effect of pH on the biosorption of nickel(II) ions onto waste tea, the batch adsorption studies at different pH values were carried out in the range of 2.0–5.0. As seen in Fig. 4, the maximum adsorption of nickel(II) ions were



Fig. 4. Effect of pH on Ni(II) uptake and residual concentration by waste tea (adsorbent dosage = 10 g L⁻¹, agitating rate = 360 rpm, $C_0 = 100$ mg L⁻¹).

observed at pH 4.0 and significantly decreased by reducing the pH values to 2.0. At lower pH value, the H⁺ ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter, which compete with the M^{2+} ions for the adsorption sites of waste tea.

Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes. The heavy metal cations are completely released under circumstances of extreme acidic conditions [27]. Untreated biomass generally contains light metal ions, such as K^+ , Na^+ , Ca^{2+} and Mg^{2+} . Treated biomass generally implies one of two chemical alterations. The first is protonation of the biomass with a strong acid, such as HCl whereby the proton displaces the light metal ions from the binding sites. In the second, the biomass is reacted with an aqueous solution of a given ion at high concentration so that the majority of sites are occupied by, for example, calcium or potassium [28]:

 $Ca^{2+} + light metal ions : biomas \leftrightarrow Ca :$

biomas + light metal ions

In order to assure the optimal performance of the biomass, ionic form should be used for removing heavy metals and what chemicals should be selected for desorbing the metals [28].

The removal of Ni(II) increased rapidly at pH 4.0–5.0 and reached upto 82.4% at pH 4.0. As seen in Fig. 4, while the residual concentration of Ni(II) ions was 17.6 mg L⁻¹ at pH 4.0, this value was 20 mg L⁻¹ at pH 5.0. At pH < 3.0, H⁺ ions compete with Ni(II) ions for the surface of the adsorbent which would hinder Ni(II) ions from reaching the binding sites of the sorbent caused by the repulsive forces. At pH > 5.0, the Ni(II) ions get precipitated due to hydroxide anions forming a nickel hydroxide precipitate [3]. For this reason, the maximum pH value was selected to be 5.0.

The electrical potential at the surface of a particle is zetapotential. It can be determined by the measurement of the velocity of particles in the electric field. At 3.0, 4.0, 5.0, 6.0 and 7.0 the zeta potentials of waste tea were -14.5, -23.8, -22.5, -21.5 and -19.5 mV, respectively. The zeta potential values could not be measured due to the high ionic strength at pH 2.0. All samples indicated negative charge values that should be favorable to the attraction between active sites and positive charges of metal ions, resulting in electrostatic interaction. The waste tea at pH 4.0 gave the greatest zeta-potential value (Fig. 5).

3.4. Effect of agitation rate

Adsorption studies were carried out with a magnetic shaker at pH 4.0 and initial nickel(II) concentration was 100 mg L^{-1} . The agitation speed varied from 3.0 to 8.0 rps (180, 360, 480 rpm). According to in Fig. 6, as agitating rate on adsorption increased from 3.0 to 8.0 rps, adsorption capacity of waste tea increased from 7.89 to 8.59 mg g⁻¹. The adsorption removal efficiency increased weakly with



Fig. 5. Zeta-potential of waste tea in different solution pH (1 g L^{-1} adsorbent dosage, room temperature, 6 rps, time = 60 min.).

increasing agitation rate because an agitation rate of 150 rpm was enough to remove fluoride as seen in Fig. 6. When the agitation speed was increased from 180 to 480 rpm, the removal of nickel(II) ion increased from 78.9% to 85.9%.

3.5. Effect of temperature

The effect of temperature on the adsorption of Ni(II) ions is presented in Fig. 7. The results revealed that the sorption capacity for initial metal concentration 300 mg L^{-1} increased from 14.04 to 17.1 mg g⁻¹ with the temperatures increasing from 25 to 60 °C. The effect of temperature is fairly common and increasing the mobility of the metal cation. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the waste tea enabling metal cation to penetrate further [5].

As seen from Fig. 7, at 25 °C for a nickel concentration of 50 mg L^{-1} after a 60 min of sorption time, while nickel concentration was measured as 5.87 mg L^{-1} , for 60 °C no nickel was remained. The equilibrium uptake and adsorption yield of nickel(II) onto waste of tea factory was also affected



Fig. 6. Effect of agitation speed on Ni(II) uptake and residual concentration by waste tea (adsorbent dosage = 10 g L^{-1} , pH 4.0, $C_0 = 100 \text{ mg L}^{-1}$).



Fig. 7. The uptake and residual concentration of Ni(II) ions at different temperature (pH 4.0, adsorbent dosage = 10 g L^{-1} , 360 rpm agitating rate, $C_0 = 50 \text{ mg L}^{-1}$).

by temperatures. The effect of temperature on the equilibrium sorption capacity and adsorption yield of waste tea is also presented in Table 2. As seen in Table 2, the maximum adsorption yields were determined as 88.30, 95.30 and 100% at 50 mg L⁻¹ initial nickel(II) concentration for 25, 45 and $60 \,^{\circ}$ C, respectively. It was indicated that nickel(II) adsorption capacity increased with increasing temperature from 25 to $60 \,^{\circ}$ C. Similar results were observed for nickel(II) adsorption yields of waste tea and the adsorption yields increased with increasing temperature. The increase of the adsorption yield and adsorption capacity at increased temperature indicated that the adsorption of nickel(II) ions by waste tea may involve not only physical but also chemical sorption. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture [5].

3.6. Adsorption isotherms

The purpose of the adsorption isotherms is to relate the adsorbate concentration in the bulk and the adsorbed amount at the interface [29]. The simplest adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is

Table 2 The equilibrium uptake capacities and adsorption yields obtained at different initial concentrations and temperatures

		· · · · · ·				
$\frac{C_0}{(\operatorname{mg} \mathrm{L}^{-1})}$	25 °C		45 °C		60 °C	
	$q (mg g^{-1})$	% Ads	$q (mg g^{-1})$	% Ads	$q (mg g^{-1})$	% Ads
50	4.41	88.30	4.77	95.30	5.00	100.0
100	8.24	82.40	8.83	88.30	9.06	90.60
200	14.72	73.60	14.95	74.75	15.07	75.35
300	14.04	46.80	16.38	54.60	17.1	57.00

independent of whether or not adjacent sites are occupied [30]. Langmuir and Freundlich isotherm are commonly used in batch adsorption studies. Biosorption of metal ions usually can be classified as two types: the Freundlich model, in which the amount of metal uptake by the biomass increases with time, and the Langmuir model, in which the amount of metal uptake by the biomass reaches equilibrium. The Freundlich expression is an empirical equation based on sorption on a heterogeneous surface. The Langmuir isotherm assumes that a monomolecular layer is formed when biosorption takes place and that there is no interaction between molecules (i.e., metals) adsorbed on adjacent binding sites [31]. The results obtained of nickel(II) were analyzed by the well-known models given by Langmuir and Freundlich.

Langmuir isotherm model:

$$\frac{C_{\rm e}}{q_{\rm e}} = \frac{1}{Q_0 K} + \frac{C_{\rm e}}{Q_0} \tag{1}$$

where C_e is the equilibrium concentration (mg L^{-1}) , q_e the amount absorbed at equilibrium (mg g^{-1}) , Q_0 and K is the Langmuir constants related to adsorption capacity and energy of adsorption. The linear plot of C_e/q_e versus C_e shows that the adsorption obeys the Langmuir model. Q_0 versus K were determined from the slope and intercept of the plot and are presented in Table 1.

Freundlich isotherm model:

$$q_{\rm e} = K_{\rm f} C_{\rm e}^n \tag{2}$$

where q_e is the amount of metal ion sorbed at equilibrium per gram of adsorbent (mg g⁻¹), C_e the equilibrium concentration of metal ion in the solution (mg L⁻¹), K_f , *n* the Freundlich model constants. Freundlich parameters K_f and *n*, by plotting ln q_e versus ln C_e .

The linearized Langmuir and Freundlich adsorption isotherms of nickel(II) ions obtained at the temperatures of 25, 45 and 60 $^{\circ}$ C are given in Figs. 8 and 9.

As can be observed in Table 3, experimental data were better fitted to the Langmuir equation than to the Freundlich equation in different temperature. However, the Freundlich model also seemed to agree well with the experimental data



Fig. 8. Langmuir isotherm for the adsorption of nickel(II) on waste tea at different temperature.



Fig. 9. Freundlich isotherm for the adsorption of nickel(II) on waste tea at different temperatures.

of the nickel(II) considering that obtained linear regression coefficients are greater than 0.92. From Table 3, the magnitude of K_f showed a high nickel(II) adsorptive capacity of waste tea from aqueous solution at 45 and 60 °C temperatures studied and increased with the rise in temperature. The highest K_f value was found as 5.31 at 60 °C. Table 3 also indicated that n is greater than 1.0, indicating that nickel(II) is favorably adsorbed by waste of tea factory at 45 and 60 °C. At 25 °C, when the Freundlich constant n is lower than 1, then the nickel(II) uptake on waste of tea plant is not favored.

From Langmuir isotherm constants, the monolayer saturation capacities, Q^0 , increased from 15.26 to 18.42 mg g⁻¹ as the temperature of solution increased ranging from 25 to 60 °C. Thus, the equilibrium adsorption capacity of waste tea was found to be 18.42 mg g⁻¹ of waste tea under optimized conditions. A higher value of K implies a shift of the adsorption equilibrium to the right at 60 °C. Increase of *K* with temperature shows that there is a chemical interaction between adsorbent and nickel(II).

To confirm the favorability of the adsorption process the separation factor (r) was calculated by the following equation [32]:

$$r = \frac{1}{1 + KC_0} \tag{3}$$

where *r* is a dimensionless separation factor, indicating the shape of the isotherm. The isotherm is unfavorable when r > 1,

Table 3 The comparison of the Freundlich and Langmuir adsorption constants obtained from the Freundlich and Langmuir adsorption isotherms of nickel(II) ions at different temperatures

Temperature (°C)	Langmuir constants			Freundlich constants		
	$\overline{Q^0 (\mathrm{mg}\ \mathrm{g}^{-1})}$	<i>K</i> (L mg ⁻¹)	<i>R</i> ²	<i>K</i> _f	п	<i>R</i> ²
25	15.26	0.088	0.9921	0.258	0.934	0.9228
45	17.73	0.093	0.9996	3.858	3.16	0.9681
60	18.42	0.098	0.9999	5.31	4.0	0.9673

Table 4

r values at different temperatures relating to the initial Ni(II) ion concentrations

$C_0 ({ m mg}{ m L}^{-1})$	25 °C	45 °C	60 ° C
50	0.185	0.177	0.169
100	0.102	0.097	0.093
200	0.054	0.051	0.049
300	0.036	0.035	0.033

the isotherm is linear when r=1, the isotherm is favorable when 0 < r < 1 and the isotherm is irreversible when r=0. As seen in Table 4, the values of r for adsorption of nickel on waste tea at studied different concentrations and temperatures were between 0 and 1, which indicates favorable adsorption of nickel on waste of tea plant.

Table 5 shows a comparison between the results of this work and others found in the literature. The values of nickel(II) specific uptake found in this work were higher, with two exception [33,34], than reported elsewhere. The comparison of sorption capacities of waste tea used in this study with those obtained in the literature shows that the waste tea is the effective fort he removal of nickel(II) from aqueous solution.

3.7. Thermodynamic parameters

Based on fundamental thermodynamics concept, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously [29].

The apparent equilibrium constant (K_C) of the biosorption is defined as:

$$K_{\rm C} = \frac{C_{\rm ad,eq}}{C_{\rm eq}} \tag{4}$$

where $C_{ad,eq}$ and C_{eq} are the concentration of nickel(II) on the adsorbent and residual nickel(II) concentration at equilibrium, respectively. In this case the activity should be used instead of concentration in order to obtain the standard thermodynamic equilibrium constant (K_C) of the adsorption system [37].

Table 5

Comparison between the nickel(II) removal by waste tea and other found in the literature

Adsorbent	Adsorbent capacity (mg g^{-1})	References
Sphagnum moss peat	9.18	[15]
Baker's yeast	11.40	[2]
C. sorokiniana (FBCS)	48.08	[33]
Sheep manure waste	7.20	[34]
PAC	31.08	[35]
Fly ash	0.03	[35]
Bagasse	0.001	[35]
Carbon aerogel	12.875	[8]
Turkish fly ash	1.160	[36]
Waste tea	18.42	This study



Fig. 10. Plot of ΔG° against T for nickel(II) on waste tea.

The free energy change of the sorption reaction is given by the following equation [22,26,38]:

$$\Delta G^{\circ} = -RT \ln K_{\rm C} \tag{5}$$

where *R* is the gas constant $(8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1})$ and *T* is the temperature (K).

The Gibbs free energy change, ΔG° , can be represented as follows:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{6}$$

As seen in Fig. 10, a plot of ΔG° versus *T* was linear. Enthalpy change, ΔH° and entropy change, ΔS° , were determined from the slope and intercept of the plots (Eq. (6)). The free energy of the process at all temperatures was negative and changed with the rise in temperature. The negative values of ΔG° at all temperatures studied are due to the fact that adsorption process is spontaneous. The positive value of ΔS° suggests increased randomness at the solid/solution interface during the adsorption of metal ions onto adsorbent [5]. Positive values of ΔH° indicate the endothermic nature of the adsorption process. Table 6 summarizes the values of these thermodynamic properties. The change of the standard free energy decreases with increasing temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures.

3.8. Column studies

Breakthrough curve between concentration ratio (C/C_0) and eluted volume (V_{eff}) was plotted and used for the calculation of column capacity at its complete exhaustion (Fig. 11). From the graph, it can be seen that the column achieved breakthrough $(C/C_0 = 0.05)$ almost immediately (50 mL; 0.53

Table 6 Thermodynamic parameters for the adsorption of nickel(II) on waste tea

2	1	1 (,
Temperature (°C)	ΔG° (kJ mol ⁻¹)	ΔH° (J mol ⁻¹)	$T\Delta S^{\circ}$ (K J mol ⁻¹)
25	-3.82		20.92
45	-5.34	17.07	22.32
60	-6.27		23.38



Fig. 11. Breakthrough curves for Ni(II).

bed volumes) and took approximately 2700 mL (28.66 bed volumes) to exhaust. The value of q is a measure of the adsorptive capacity of the waste tea for nickel. In the present case, $q = 10.35 \text{ mg g}^{-1}$; this means that every gram of waste tea could sorb 10.35 mg of nickel under the present column experimental conditions. Based on batch studies, a value of 15.26 mg g^{-1} was obtained as the adsorption capacity of waste tea for nickel(II).

Comparing capacities for batch and column studies, consistently more metal is sorbed in the batch system. The reason for the lower adsorption capacity of waste tea in column experiments than in batch experiments may be due to a high flow rate (10 mL min^{-1}) employed in the column studies, which could nickel to short circuiting and flow through preferred path in the column which may avoid contact with some waste tea particles.

4. Conclusion

The use of waste tea for the adsorption of nickel(II) from aqueous solutions has been examined. The following results were obtained:

- The capacity of adsorption of nickel(II) increased with increasing temperatures and pH. The maximum adsorption capacity was obtained at pH 4.0.
- Increase in the mass of the adsorbent leads to increase in nickel(II) adsorption owing to corresponding increase in the number of adsorption sites.

- The Langmuir and Freundlich adsorption models were used to represent the experimental data fitted very well to the Langmuir isotherm model. The monolayer adsorption capacity (Q^0) was obtained 18.42 mg g⁻¹ at optimum pH (4.0) and temperature (60 °C).
- Zeta potential measurement indicated that negatively charge presented in waste tea resulting in the electrostatic interaction between active sites and metal ions.
- From FTIR study, –OH, C–H, C=H and C–O groups were the main functional groups of waste tea participate in metal binding.
- Thermodynamic calculations showed that the nickel sorption process by waste tea has endothermic and spontaneous nature.
- Waste tea which is a factory waste could be used to as a potential adsorbent fort he removal of nickel(II) ions from aqueous solution and is inexpensive material for treating the industrial wastewater.
- The lower adsorption capacity of waste tea for nickel(II) was obtained in column experiments.

References

- P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Colloid Interface Sci. 275 (2004) 131–141.
- [2] V. Patmavathy, P. Vasudevan, S.C. Dhingra, Biosorption of nickel(II) ions on Baker's yeast, Process Biochem. 38 (10) (2003) 1389– 1395.
- [3] H. Hasar, Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, J. Hazard. Mater. B97 (2003) 49–57.
- [4] I. Villaescusa, N. Fiol, M. Martinez, N. Miralles, J. Poch, J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalks wastes, Water Res. 38 (4) (2004) 992–1002.
- [5] Z. Aksu, Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel(II) ions onto chlorella vulgaris, Process Biochem. 38 (2002) 89– 99.
- [6] US EPA, Guidance Manual for Electroplating and Metal Finishing Pretreatment Standards, 1984, Available: http://yosemite.epa.gov/ water/owrccatalog.nsf/0/b972a030fef65a5f85256b0600723b4e?Open Document.
- [7] US EPA, National Primary Drinking Water Regulations, Ground Water & Drinking Water > Consumer Factsheet on: NICKEL, 1995, Available: www.epa.gov/ogwdw/dwh/t-ioc/nickel.html.
- [8] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, J. Hazard. Mater. 122 (2005) 161–170.
- [9] M. Rio, A.V. Parwate, A.G. Bhole, Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash, Waste Manage. 22 (2002) 821–830.
- [10] V.K. Gupta, C.K. Jain, I. Ali, M. Sharma, V.K. Saini, Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste, J. Colloid Interface Sci. 271 (2) (2003) 321– 328.
- [11] E. Remoudaki, A. Hatzikioseyian, K. Tsezos, M. Tsezos, The mechanism of metals precipitation by biologically generated alkalinity in biofilm reactors, Water Res. 37 (6) (2003) 3843– 3854.

- [12] G. Zhao, M. Li, Z. Hu, H. Hu, Dissociation and removal of complex chromium ions containing in dye wastewaters, Sep. Purif. Technol. 43 (3) (2005) 227–232.
- [13] Y.C. Sharma, G. Prasad, D.C. Rupainwar, Removal of Ni(II) from aqueous solutions by sorption, Int. J. Environ. Studies 37 (1991) 183–191.
- [14] G. Yan, T. Viraraghavan, Heavy metal removal in a biosorption column by immobilized M. Rouxii biomass, Bioresour. Technol. 78 (2001) 243–249.
- [15] 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.
- [16] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.
- [17] F.N. Acar, E. Malkoc, The removal of chromium(VI) from aqueous solutions by *Fagus orientalis* L., Bioresour. Technol. 94 (1) (2004) 13–15.
- [18] Y. Nuhoglu, E. Malkoc, A. Gürses, N. Canpolat, The removal of Cu(II) from aqueous solutions by *Ulothrix zonata*, Bioresour. Technol. 85 (2002) 331–333.
- [19] E. Malkoc, Y. Nuhoglu, The Removal of chromium(VI) from synthetic wastewater by *Ulothrix zonata*, Fresenius Environ. Bull. 12 (4) (2003) 376–381.
- [20] C.-J. Lin, J.-E. Chang, Effect of fly ash characteristics on the removal of Cu(II) from aqueous solution, Chemosphere 44 (2001) 1185–1192.
- [21] C.W. Cheung, J.F. Porter, G. McKay, Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char, Water Res. 35 (3) (2001) 605–612.
- [22] C.A. Eligwe, N.B. Okolue, C.O. Nwambu, C.I.A. Nwoko, Adsorption thermodynamics and kinetics of mercury(II), cadmium(II) and lead(II) on lignite, Chem. Eng. Technol. 22 (1) (1999) 45–49.
- [23] E. Malkoc, Removal of Heavy Metals From Waters By Different Adsorbent Types, Ph.D. Thesis, Graduate School of Natural and Applied Sciences Department of Environmental Engineering, Ataturk University, Turkey, 2005.
- [24] S. Çay, A. Uyanık, A. Özaşık, Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste, Sep. Purif. Technol. 38 (2004) 273–280.
- [25] H. Gülensoy, Kompleksometrenin Esasları ve Kompleksometrik Titrasyonlar, Fatih Yayınevi Matbaası, İstanbul, pp. 76–77, 1984.
- [26] A. Özer, D. Özer, A. Özer, The adsorption of copper(II) ions on to dehydrated wheat bran (DWB): determination of the equilibrium and thermodynamic parameters, Process Biochem. 39 (12) (2004) 2183–2191.
- [27] M. Ajmal, R.A.K. Rao, R. Ahmad, J. Ahmad, Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni(II) from electroplating wastewater, J. Hazard. Mater. B79 (2000) 117–131.
- [28] A.H. Hawari, C.N. Mulliga, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresour. Technol. (2005) in press.
- [29] O. Demirbaş, M. Alkan, M. Doğan, The removal of Victoria Blue from aqueous solution by adsorption on a low-cost material, Adsorption 8 (2002) 341–349.
- [30] S.S. Shukla, L.J. Yu, K.L. Dorris, A. Shukla, Removal of nickel from aqueous solutions by sawdust, J. Hazard. Mater. B121 (2005) 243–246.
- [31] H.-L. Liu, B.-Y. Chen, Y.-W. Lan, Y.-C. Cheng, Biosorption of Zn(II) and Cu(II) by the indigenous *Thiobacillus thiooxidans*, Chem. Eng. J. 97 (2–3) (2004) 195–201.
- [32] V.K. Gupta, A. Mittal, L. Krishnan, V. Gabje, Adsorption kinetics and column operations for the removal and recovery of malachite green from wastewater using bottom ash, Sep. Purif. Technol. 40 (1) (2004) 87–96.

- [33] N. Akhtar, J. Iqbal, M. Iqbal, Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: characterization studies, J. Hazard. Mater. B108 (2004) 85–94.
- [34] F. Abu Al-Rub, M. Kandah, N. Aldabaibeh, Nickel removal from aqueous solutions using sheep manure wastes, Eng. Life Sci. 2 (2002) 111–116.
- [35] M. Rao, A.V. Parwate, A.G. Bhole, Removal of Cr^{6+} and Ni²⁺ from aqueous solution using bagasse and fly ash, Waste Manage. 22 (2002) 821–830.
- [36] B. Bayat, Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel(II), copper(II) and zinc(II), J. Hazard. Mater. B95 (2002) 251–273.
- [37] Z. Aksu, İ.A. İşoğlu, Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp, Process Biochem. 40 (2005) 3031–3044.
- [38] İ. Uzun, F. Güzel, Kinetic and thermodynamics of the adsorption of some dyestuffs and *p*-nitrophenol by chitosan from aqueous solution, J. Colloid Interface Sci. 274 (2004) 398–412.