

Removal of Ni(II) ions from aqueous solutions using waste of tea factory: Adsorption on a fixed-bed column

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Abstract

The removal efficiency of waste tea from nickel containing aqueous solutions was investigated. All experiments were conducted fixed-bed columns. Experiments were carried out as a function of liquid flow rate (5–20 mL/min), initial Ni(II) concentration (50–200 mg/L), bed height (10–30 cm), pH of feed solution (2.0–5.0) and particle size (0.15–0.25 to 1.0–3.0 mm) of adsorbent. The total adsorbed quantities, equilibrium uptakes and total removal percents of Ni(II) related to the effluent volumes were determined by evaluating the breakthrough curves obtained at different flow rates, different inlet Ni(II) concentrations, different pH value, different bed height and different particle size for waste tea. The longest breakthrough time and maximum of Ni(II) adsorption is obtained at pH 4.0. Decrease in the particle size from 1.0–3.0 to 0.15–0.25 mm resulted in significant increase in the treated volume, breakthrough time and bed capacity. The results show that the column performed well at lowest flow rate. Also, column bed capacity and exhaustion time increased with increasing bed height. When the initial Ni(II) concentration is increased from 50 to 200 mg/L, the corresponding adsorption bed capacity appears to increase from 7.31 to 11.17 mg/g. The bed depth service time (BDST) model and the Thomas model were used to analyze the experimental data and the model parameters were evaluated. Good agreement of the experimental breakthrough curves with the model predictions was observed.

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1. Introduction

The discharge of metal ions in industrial effluents is of great concern because their presence and accumulation have a toxic or carcinogenic effect on living species [1]. Heavy metals are toxic to aquatic organisms even at very low concentration. Industrial wastewater containing nickel(II) is common because nickel(II) is used in a large number of industries, such as electroplating, batteries manufacturing, mine, metal finishing and forging and so on. The nickel(II) concentration in wastewater from mine drainage, tableware plating, metal finishing and forging was up to 130 mg/L [2]. The maximum permissible concentration of nickel in effluents in the US 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 and average of daily values for 4 consecutive monitoring days shall not exceed 2.6 mg/L [3]. In drinking water, nickel may cause health problems if found in amounts greater than the health standard set (MCLG: 0.1 mg/L) 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 [4].

Conventional methods for the removal of heavy metals from wastewaters, however, are often cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range of 1–100 mg/L. Some of these methods, furthermore, generate toxic sludge, the disposal of which is an additional burden on the techno-economic feasibility of treatment procedures. These constraints have caused the search for alternative technologies for metal sequestering to cost-effective environmentally acceptable levels. The ability of biological materials to adsorb metal ions has received considerable attention for the development of an efficient, clean and cheap technology for

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wastewater treatment at metal concentrations as low as 1 mg/L [5]. In fact, wastewater treatment using activated carbon is one of the most important uses of activated carbon. The use of activated carbon as an adsorbent for industrial wastewater treatment is capital-intensive and has several other problems, such as: (1) regeneration of activated carbon, (2) intra-particle resistance in adsorption processes in practice, and (3) high cost of manufacture [6].

Most previous research using biosorbents for metal ions is based on batch kinetic and batch equilibrium studies. However, in the practical operation of full-scale biosorption processes, continuous-flow fixed-bed columns are often preferred. In such systems, the concentration profiles in the liquid and adsorbent phases vary in both space and time. As a result, design and optimization of fixed-bed columns are difficult to carry out a priori without a quantitative approach. From the perspective of process modeling, the dynamic behavior of a fixed-bed column is described in terms of breakthrough curve [7].

Tea plants (*Camellia sinensis* (L.) Kuntze) are commonly grown in the Eastern Black Sea region of Turkey. Dried and cured leaves widely used for a beverage, which has a stimulant effect due to caffeine. High quality tea is harvested the three top leaves of the shoot on tea plant in the teagarden. Tea, considered astringent, stimulant, and acts as a nerve or nerve sedative, frequently relieving headaches. It may also cause unpleasant nerve and digestive disturbances. While tea producer cut the top tea leaves with special tea shears, some overgrown woody shoots, which may include six to 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 [8].

Tea factory waste has been used as adsorbent for copper(II) and cadmium(II) by Çay et al. [9], and it has been newly used for the removal of Ni(II) ions in batch studies by Malkoc and Nuhoglu [10]. Their experimental results show it may be used effectively in removal of copper(II), cadmium(II) and nickel ions from aqueous solutions. The removal of Ni(II) has been studied using seaweeds [11], crab shell [12], dried aerobic activated sludge [13], loofa sponge-immobilized biomass of *Chlorella sorokiniana* [14], activated carbon prepared from almond husk [15], spent animal bones [16].

Tea factory waste as an adsorbent for Ni(II) is an economical material, which has been used fixed bed for the removal of Ni(II) from aqueous solutions. The objectives of the present study is to adsorb Ni(II) from aqueous solution by waste tea using fixed-bed column. The important design parameters such as column bed height, flow rate of fluid, pH of solution, initial concentration of metal solution and particle size of waste tea have been investigated. The breakthrough curves for the adsorption of metals were analyzed using bed depth service time (BDST) and Thomas model.

Table 1

Physical and chemical properties of waste tea used in the experiments

Chemical characteristics [9]	
Moisture (%)	11.01
Water soluble components (%)	6.04
Insoluble components (%)	80.24
Ash (%)	2.97
Total loss of ignition (%)	94.06
Physical characteristics	
Bulk density (g/cm ³)	0.112
Particle size (mm)	1.00–3.00
BET surface area (m ² /g)	0.39

2. Material and methods

2.1. Adsorbent

The tea factory 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 waste tea 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.

Scanning electron microscopy (SEM) of material used waste of tea factory was carried out in a JEOL JSM T-330 unit. In order to see the surfaces of particles after and before adsorption, SEM images were obtained for the raw and treated adsorbents (Figs. 1 and 2).

2.2. Adsorbate

A stock solution of Ni(II) (1000 mg/L) was prepared in distilled water with NiCl₂·6H₂O. All working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. The amount of Ni(II) in filtrate was analyzed by standard complexometric method [17].

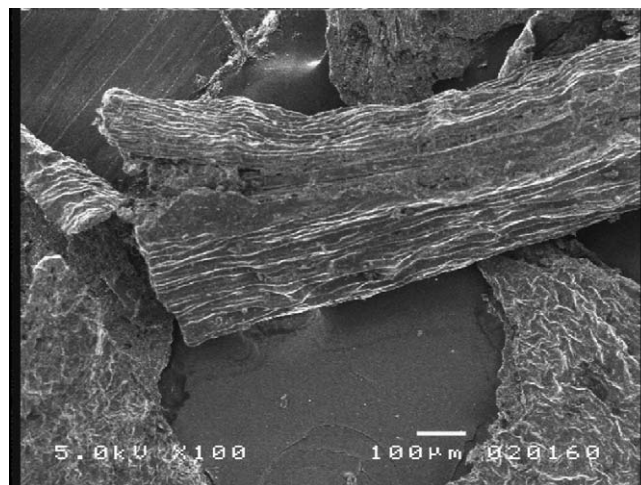


Fig. 1. SEM micrograph of the particles of waste tea before Ni(II) adsorption.

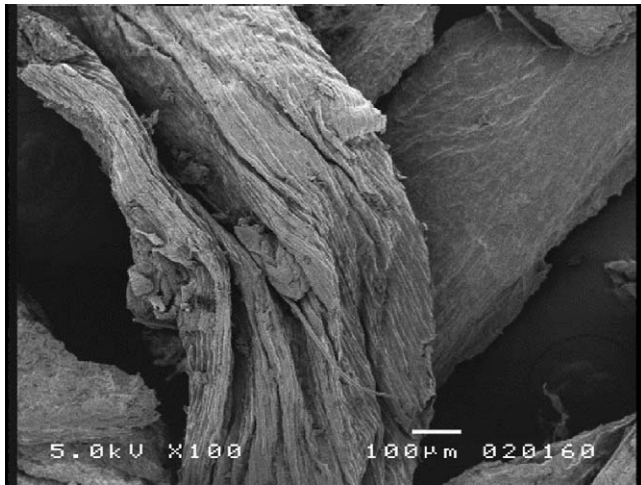


Fig. 2. SEM micrograph of the particles of waste tea after Ni(II) adsorption.

2.3. Fourier transform infrared spectroscopy

The infrared spectra were obtained (and transferred to Microsoft Excel) using Perkin-Elmer Spectrum One FTIR spectrometer. The FTIR spectra before and after adsorption of tea factory waste are shown in Fig. 3a and b.

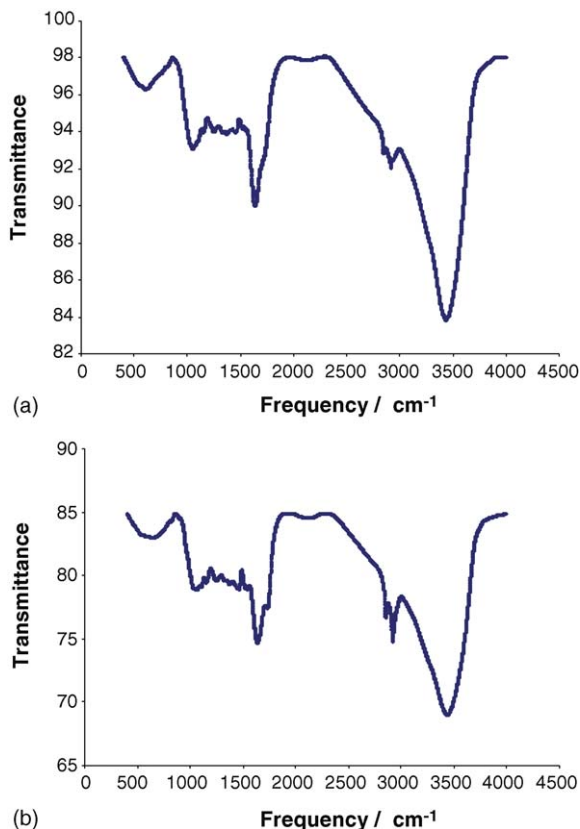
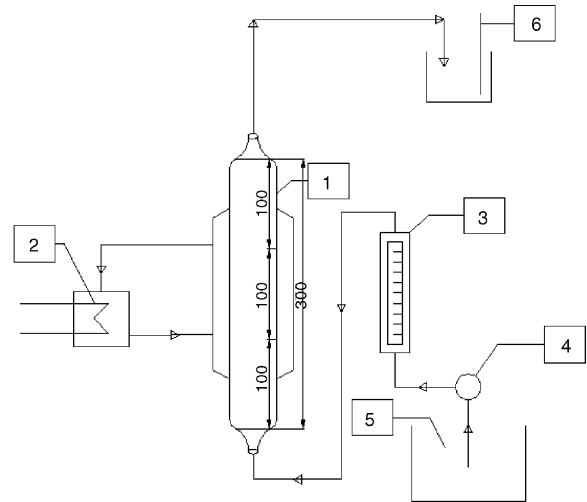


Fig. 3. (a) FTIR spectra of waste tea before adsorption and (b) FTIR spectra of waste tea after adsorption.



1. Column 3. Rotameter 5. Feed storage
2. Thermostat 4. Pump 6. Sample collection

Fig. 4. Experimental system for fixed bed operation: (1) column, (2) thermostat, (3) rotameter, (4) pump, (5) feed storage and (6) sample collection.

2.4. Experimental set-up

A schematic diagram for the pilot plant fixed-bed column systems is shown in Fig. 4. 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 except particle size. 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. The bed porosity was 0.42.

2.5. Analysis of column data

The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The breakthrough curves show the loading behavior of metal to be removed from solution in a fixed bed and is usually expressed in terms of adsorbed metal concentration (C_{ad} = inlet metal concentration (C_0) – outlet metal concentration (C_t)) or normalized concentration defined as the ratio of effluent metal concentration to inlet metal concentration (C_t/C_0) as a function of time or volume of effluent for a given bed height [18]. Effluent volume (V_{eff}) can be calculated from Eq. (1):

$$V_{eff} = Qt_{total} \quad (1)$$

where t_{total} and Q are the total flow time (min) and volumetric flow rate (mL/min). The area under the breakthrough curve (A) obtained by integrating the adsorbed concentration (C_{ad} ; mg/L) versus t (min) plot can be used to find the total adsorbed metal quantity (maximum column capacity). Total adsorbed metal quantity (q_{total} ; mg) in the column for a given feed concentration

and flow rate (Q) is calculated from Eq. (2):

$$q_{\text{total}} = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t=t_{\text{total}}} C_{\text{ad}} dt \quad (2)$$

Total amount of metal ion sent to column (m_{total}) is calculated from Eq. (3):

$$m_{\text{total}} = \frac{C_0 Q t_{\text{total}}}{1000} \quad (3)$$

Total removal is calculated from Eq. (4):

$$\text{Total removal (\%)} = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100 \quad (4)$$

Equilibrium metal uptake (q_{eq}) (or maximum capacity of the column) in the column is defined by Eq. (5) as the total amount of metal sorbed (q_{total}) per g of sorbent (X) at the end of total flow time [17]:

$$q_{\text{eq}} = \frac{q_{\text{total}}}{X} \quad (5)$$

2.6. Mathematical model

Successful design of a column sorption process required prediction of the concentration–time profile or breakthrough curve for the effluent [19]. Various mathematical models can be used to describe fixed-bed adsorption. Among these, the Thomas model (1948) model is simple to use in the design of a fixed-bed adsorption column and the Thomas solution is one of the most general and widely used methods in column performance theory. Therefore, the breakthrough data obtained from the column studies was examined using the kinetic model developed by Thomas model (1948). Successful design of a column adsorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. The Thomas or reaction model, which assumes Langmuir kinetics of adsorption–desorption and no axial dispersion is derived with the adsorption that the rate driving force obeys second-order reversible reaction kinetics [20,21].

The expression of the Thomas model for an adsorption column is as follows [20,21]:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{k_{\text{TH}}}{Q}(q_{\text{eq}}X - C_0 V_{\text{eff}})\right)}$$

where k_{TH} is the Thomas rate constant (mL/min mg), q_{eq} the maximum solid-phase concentration of the solute (mg/g), V_{eff} the effluent volume (mL), X the mass of adsorbent (g), and Q is the flow rate (mL/min).

The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{k_{\text{TH}} q_{\text{eq}} X}{Q} - \frac{k C_0 V_{\text{eff}}}{Q}$$

The kinetic coefficient k_{TH} and the adsorption capacity of the bed q_{eq} can be determined from a plot of $\ln[(C_0/C_t) - 1]$ against t at a given condition.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy (FTIR) analysis

The FTIR spectra before and after adsorption of tea factory waste are shown in Fig. 3a and b, and the FTIR spectroscopic characteristics are shown in Table 2.

As shown in Fig. 3a and b, the spectra display a number of absorption peaks, indicating the complex nature of the material examined. The FTIR spectroscopic analysis indicated broad bands at 3420 cm^{-1} , representing bonded –OH groups. The bands observed at about $2915\text{--}2848 \text{ cm}^{-1}$ could be assigned to the aliphatic C–H group. The peak around 1631 cm^{-1} correspond to the C=O stretch. The peaks observed at 1546 and 1511 cm^{-1} correspond to the secondary amine group. Symmetric bending of CH_3 is observed to shift to 1448 , 1435 and 1345 cm^{-1} . Thus, it seems that this type of functional group is likely to participate in metal binding [10,22,23]. The peaks observed at 1232 , 1141 and 634 cm^{-1} could be assigned to – SO_3 stretching, C–O stretching of ether groups and –CN stretching, respectively. As seen in Table 2, the spectral analysis before and after metal adsorption indicated that especially the bonded –OH

Table 2
The FTIR spectral characteristics of tea factory waste before and after adsorption

IR peak	Frequency (cm^{-1})			Assignment
	Before adsorption	After adsorption	Differences	
1	3420	3415	–5	Bonded –OH groups
2	2915	2917	+2	Aliphatic C–H group
3	2848	2849	+1	Aliphatic C–H group
4	1631	1627	–4	C=O stretching
5	1546	1525	–21	Secondary amine group
6	1511	1510	–1	Secondary amine group
7	1448	1442	–6	Symmetric bending of CH_3
8	1435	1436	+1	Symmetric bending of CH_3
9	1345	1363	+18	Symmetric bending of CH_3
10	1232	1230	–2	– SO_3 stretching
11	1141	1141	0	C–O stretching of ether groups
12	634	634	0	–CN stretching

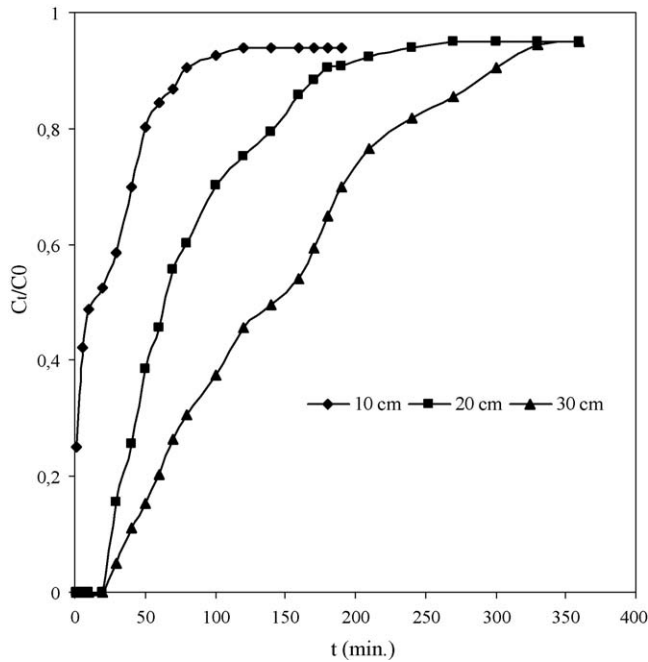


Fig. 5. Breakthrough curves for Ni(II) biosorption onto waste tea biomass at different bed heights (flow rate = 10 mL/min, initial nickel concentration = 100 mg/L, pH 4.0).

groups, C=O stretching, secondary amine group and symmetric bending of CH₃ were especially involved in nickel biosorption [22–24]. There were clear band shifts and intensity decrease of the band at 3420, 1631, 1546 and 1448 cm⁻¹.

3.2. Effect of bed height

Accumulation of metals in the fixed-bed column is largely dependent on the quantity of sorbent inside the column. In order to yield different bed heights, 3.5, 7.0 and 10.5 g of waste tea were added to produce 10, 20 and 30 cm, respectively. The sorption breakthrough curves obtained by varying the bed heights from 10 to 30 cm at 10 mL/min flow rate and 100 mg/L initial nickel concentration for waste tea biomass are given in Fig. 5. Both bed capacity and exhaustion time increased with increasing bed height, as more binding sites available for sorption, also resulted in a broadened mass transfer zone. The increase in adsorption with that in bed depth was due to the increase in adsorbent doses in larger beds which provide greater service area (or adsorption sites). The maximum bed capacities for different bed depth 10, 20 and 30 cm were 10.57, 11.67 and 13.6 mg/g, respectively. In addition, the Ni(II) uptake capacity of waste tea increased with the increase in bed height due to availability of more binding sites for sorption [21]. The Ni(II) removal percentage was significantly affected by bed height, as 30.8 increased to 39.7% when the bed height increased from 10 to 30 cm.

BDST is a simple model, which states that bed height (Z) and service time (t) of a column bears a linear relationship. The equation can be expressed as [1] follows:

$$t = \frac{N_0 Z}{C_0 Q} - \frac{1}{K_a C_0} \ln \left(\frac{C_0}{C_t} - 1 \right)$$

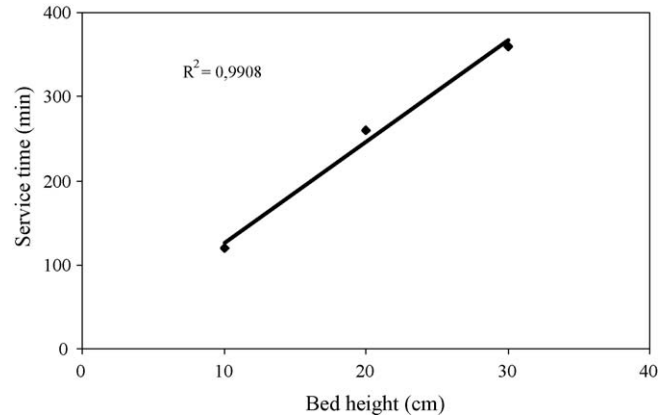


Fig. 6. BDST model plot for nickel biosorption by waste tea (flow rate = 10 mL/min, initial nickel concentration = 100 mg/L, pH 4.0).

where C_t is the breakthrough metal ion concentration (mg/L), N_0 the sorption capacity of bed (mg/L), Q the linear velocity (mL/min), and K_a is the rate constant (L/mg min). The column service time was selected as time when the effluent nickel concentration reached 100 mg/L. The plot of service time against bed height at a flow rate of 10 mL/min (Fig. 6) was linear ($R^2 = 0.9908$) indicating the validity of BDST model for the present system.

The slope of the BDST plot is equal to $N_0/C_0 Q$. The initial concentration C_0 and flow velocity Q may be assumed to be reasonably constant during the column operation. The process parameter that is most likely to change with time is the bed capacity N_0 . This is used to predict the performance of the bed, if there is a change in the initial solute concentration, C_0 to a new value of solute concentration. As the bed depth increases, the residence time of the fluid inside the column increases, allowing the adsorbate molecules to diffuse deeper inside the adsorbent. Thus, the bed capacity will change with the service time [1].

The rate constant, K_a , calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase [21]. The computed N_0 and K_a were 12000 mg/L and 0.089 L/mg min, respectively. If K_a is large, even a short bed will avoid breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough [21]. The BDST model parameters can be helpful to scale up the process for other flow rates without further experimental run.

3.3. Effect of flow rate

The influence of flow rate on the biosorption of Ni(II) by waste tea was investigated by keeping initial nickel(II) concentration (100 mg/L) and bed height (30 cm) constant and varying the flow rate from 5 to 20 mL/min. In contrast to bed height results, the column performed well at lowest flow rate.

Initially the adsorption was very rapid at lower flow rate probably associated with the availability of reaction sites able to capture metal ions around or inside the cells. In the next stage of the process due to the gradual occupancy of these sites, the uptake becomes less effective. The breakthrough curve becomes steeper when the flow rate is increased with which the break

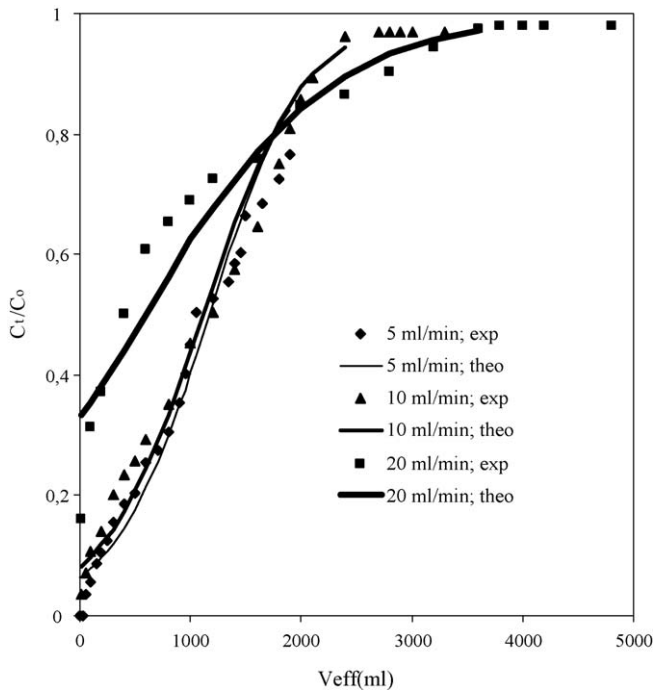


Fig. 7. The measured and modeled breakthrough curves for adsorption of Ni(II) onto waste tea at different flow rates ($C_0 = 100$ mg/L, bed depth = 30 cm, particle size = 1.0–3.0 mm, pH 4.0).

point time and adsorbed ion concentration decreases. The probable reason behind this is that when the residence time of the solute in the column is not long enough for adsorption equilibrium to be reached at that flow rate, the nickel solution leaves the column before equilibrium occurs. Thus, the contact time of nickel ions with activated alumina is very short at higher flow rate, causing a reduction in removal efficiency [25].

An earlier breakthrough and exhaustion time were observed in the profile, when the flow rate was increased to 20 mL/min. The flow rate also strongly influenced the nickel uptake capacity of waste tea as 11.13, 10.57 and 7.48 mg/g, which were recorded at 5, 10 and 20 mL/min, respectively. Breakthrough curves, C_t/C_0 against volume throughput is shown in Fig. 7 for three different flow rates 5, 10 and 20 mL/min.

The sorption data were evaluated and the total sorbed quantities, maximum nickel uptakes and removal percents with respect to flow rate are presented in Table 3. As seen in Table 3, in general the total sorbed nickel quantity, maximum nickel uptake and nickel removal percentage values decreased with increasing flow rate and maximum values of total sorbed nickel quantity,

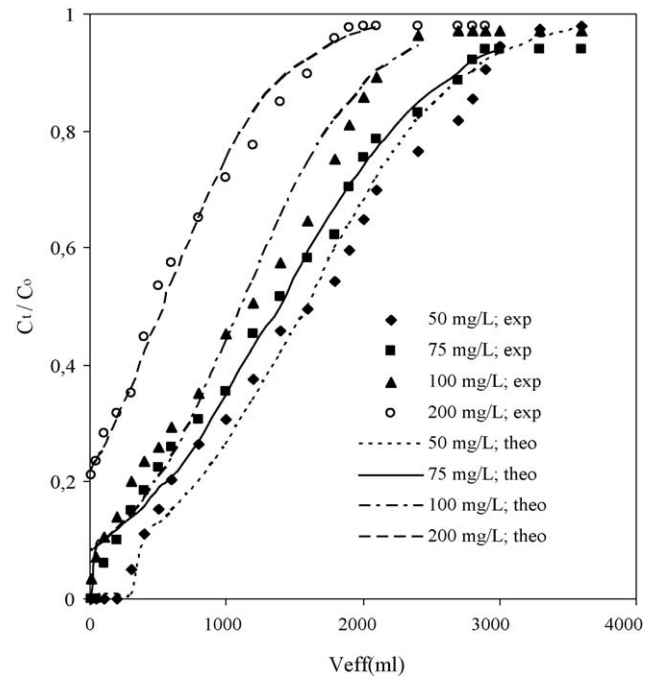


Fig. 8. The measured and modeled breakthrough curves for adsorption of Ni(II) onto waste tea at different initial nickel concentration ($Q = 10$ mL/min, bed depth = 30 cm, particle size = 1.0–3.0 mm, pH 4.0).

maximum nickel uptake and nickel removal percentage were obtained as 116.85 mg, 11.13 mg/g and 44.9%, respectively, at 5 mL/min flow rate.

It is clear from Fig. 7 that the model gave a good fit of the experimental data at all flow rates examined with high correlation coefficients greater than 0.947. The values of k_{TH} obtained from Thomas model were 0.000115, 0.00022 and 0.0024 L/mg h at 5, 10 and 20 mL/min, respectively. The values of q_{eq} obtained from the Thomas model were 11.14, 10.61 and 5.73 mg/g at 5, 10 and 20 mL/min, respectively.

3.4. Effect of initial Ni(II) concentration

An increase of the initial Ni(II) concentration from 50 to 200 mg/L, when other experimental conditions are kept constant, significantly affected the breakthrough curve as illustrated in Fig. 8 and Table 3.

When the initial Ni(II) concentration is increased from 50 to 200 mg/L, the corresponding adsorption bed capacity appears to increase from 7.31 to 11.17 mg/g. Higher initial nickel concen-

Table 3

The effect of flow rate and initial nickel concentration on the total adsorbed quantity of Ni(II) (q_{total}), equilibrium Ni(II) uptake (q_{eq}) and total removal percentage of Ni(II) for nickel adsorption to waste of tea factory

Q (mL/min)	C_0 (mg/L)	q_{total} (mg)	q_{eq} (mg/g)	Total metal removal (%)	Correlation coefficient
5	100	116.85	11.13	44.90	0.965
10	100	108.69	10.57	40.25	0.967
20	100	78.58	7.48	21.82	0.947
10	50	76.74	7.31	46.50	0.969
10	75	98.94	9.42	43.90	0.986
10	200	117.30	11.17	29.32	0.981

trations caused a faster breakthrough as expected. A decreased inlet nickel(II) concentrations gave delayed breakthrough curves and the treated volume was also higher, since the lower concentration gradient caused slower transport due to decreased diffusion coefficient [26]. At the highest Ni(II) concentration (200 mg/L) the waste tea bed saturated quickly leading to earlier breakthrough and exhaustion time.

Table 3 shows that highest uptake and low total Ni(II) removal are obtained at the highest Ni(II) concentration. Also more positive and steep breakthrough curve was obtained for 200 mg/L Ni(II). The driving force for biosorption is the concentration difference between the metal on the waste tea and the metal ion in the solution [18]. Thus the high driving force due to the high Ni(II) concentration resulted in better column performance.

It is clear from Fig. 8 that the model gave a good fit of the experimental data at all flow rates examined with high correlation coefficients greater than 0.967. The values of k_{TH} obtained from Thomas model were 0.00036, 0.00027, 0.00022 and 0.00012 L/mg h at 50, 75, 100 and 200 mg/L, respectively. The values of q_{eq} obtained from the Thomas model were 7.48, 9.81, 10.61 and 10.26 mg/g at 50, 75, 100 and 200 mg/L, respectively.

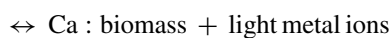
3.5. Effect of initial pH

The pH value of the solution is an important controlling parameter in the adsorption process, and the initial pH value of the solution has more influence than the final pH, which influences both the adsorbent surface metal binding sites and the metal chemistry in water [27]. The pH of feed solution was examined from solutions at different pH, covering a range of 2.0–5.0. In Ni(II) adsorption on waste tea, the highest maximum bed capacity and the longest breakthrough time is obtained at pH 4.0. 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 [15]. For this reason, the maximum pH value was selected to be 5.0.

The hydroxyl groups of waste tea (Fig. 3a and b) are effective binding sites for metal ions, forming stable complexes by coordination. The interaction between the functional groups in waste tea and Ni(II) ions may be responsible for pH increase in the initial stages and as the saturation of the bed proceeds, the pH decreased. A dramatic change in the effluent pH was observed

in this study. For the influent solution with pH 2.0, 3.0, 4.0 and 5.0, the effluent pH was sharply increased to 3.1, 3.8, 4.7 and 5.6, respectively. It was that adsorption of hydrogen ions from the solution and dissolution of some impurities from the adsorbent surface could result in increase in the effluent pH [28]. As continued to flow through the column, the effluent pH dropped to the influent pH value.

Untreated biomass generally contains light metal ions such as K⁺, Na⁺, Ca²⁺, and Mg²⁺. 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 [10,29]:



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 equilibrium nickel(II) uptakes, total sorbed nickel(II) quantities and nickel(II) removal percentages of Ni(II) adsorption onto waste tea related to the solution pH are shown in Table 4. Although the equilibrium nickel(II) uptake and amount of total sorbed nickel(II) increased with increasing pH of inlet solution from 2.0 to 4.0. As seen in Table 4, the removal efficiency was higher at pH 4.0 and for the pH of 2.0, 3.0, 4.0 and 5.0, 17.46, 32.93, 40.25 and 30.68% of total nickel(II) applied to the column was adsorbed by the waste tea beads, respectively.

Predicted and experimental breakthrough curves with respect to solution pH are shown in Fig. 9. As seen in Fig. 9, there is a good agreement between the experimental and predicted values. The lowest and highest correlation coefficient are obtained at pH 2.0 and 4.0 as 0.918 and 0.967, respectively. The values of k_{TH} obtained from Thomas model were 0.00036, 0.00018, 0.00022 and 0.00018 L/mg h at pH 2.0, 3.0, 4.0 and 5.0, respectively. The values of q_{eq} obtained from the Thomas model were 2.01, 6.24, 10.61 and 8.19 mg/g at pH 2.0, 3.0, 4.0 and 5.0, respectively.

3.6. Effect of particle size

The experiments were carried out for four different particle (waste tea) sizes: 0.15–0.25, 0.25–0.50, 0.50–1.0 and

Table 4
The effect of solution pH and particle size of adsorbent on the total adsorbed quantity of Ni(II) (q_{total}), equilibrium Ni(II) uptake (q_{eq}) and total removal percentage of Ni(II) for nickel adsorption to waste of tea factory and obtained correlation coefficients by Thomas model

pH	Particle size (mm)	q_{total} (mg)	q_{eq} (mg/g)	Total metal removal (%)	Correlation coefficient, R^2
2.0	1.00–3.00	24.44	2.33	17.46	0.918
3.0	1.00–3.00	69.16	6.59	32.93	0.951
4.0	1.00–3.00	108.69	10.57	40.25	0.967
5.0	1.00–3.00	85.91	8.18	30.68	0.963
4.0	0.15–0.25	216.66	18.05	45.14	0.845
4.0	0.25–0.50	140.64	12.78	42.62	0.866
4.0	0.50–1.00	110.84	11.08	41.05	0.943
4.0	1.00–3.00	37	10.57	30.83	0.929

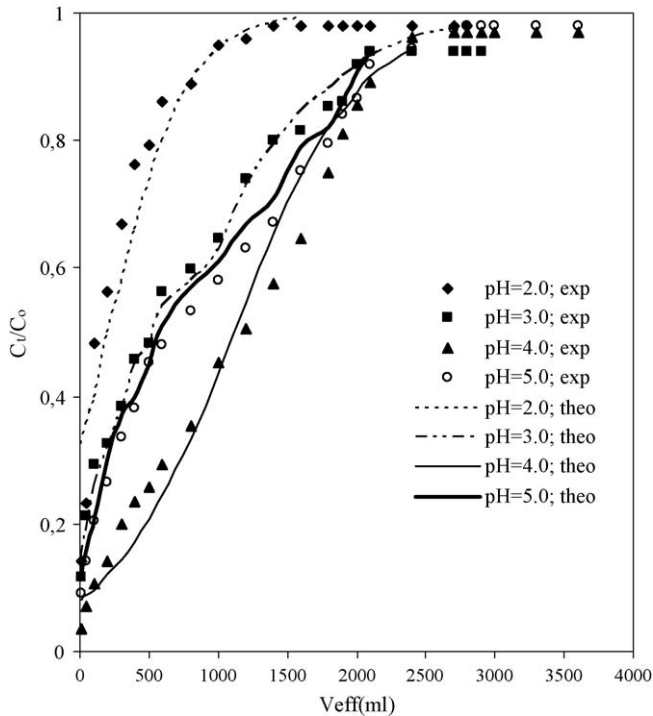


Fig. 9. The measured and modeled breakthrough curves for adsorption of Ni(II) onto waste tea at different pH ($Q=10$ mL/min, bed depth = 30 cm, particle size = 1.0–3.0 mm, $C_0 = 100$ mg/L).

1.0–3.0 mm, under constant flow rates (10 mL/min) and inlet Ni(II) concentrations (100 mg/L). The amount of waste tea adsorbent was taken as 12, 11, 10 and 3.5 g to fill completely beads of 10 cm, 0.15–0.25 mm, 0.25–0.50 mm, 0.50–1.0 mm and 1.0–3.0 mm, respectively.

Fig. 10 and Table 4 show that increasing the size of adsorbent particles reduces the maximum bed capacities and breakthrough time. It is well known that by decreasing the particle size, the performance of adsorption is improved. However, small particle sizes result in high flow resistance of the column and should be avoided [30]. In the finer particle size ranges, adsorption breakthrough curves followed a much more efficient profile than larger particle size ranges, in that the breakthrough time increased and the curves tended towards the classic “S” shape profile [31].

For tested different particle size, maximum bed capacities and breakthrough time at 0.15–0.25, 0.25–0.50, 0.50–1.0 and 1.0–3.0 mm particle size were 18.05, 12.78, 11.08, 10.57 mg/g and 480, 330, 270, 160 min, respectively. Smaller particles will have a shorter diffusion path, thus allowing the adsorbate to penetrate deeper into the adsorbent particle more quickly, resulting in a higher rate of adsorption. In addition, the total external surface area per unit volume for all smaller particle inside the column will be larger [1].

The sorption data were evaluated for nickel adsorption onto waste tea total sorbed quantities of nickel(II) (q_{total}), equilibrium nickel(II) uptakes (q_{eq}) and total removal percentages of nickel(II) with respect to different particle sizes are presented in Table 4. As seen in Table 4, q_{total} , q_{eq} and total nickel(II)

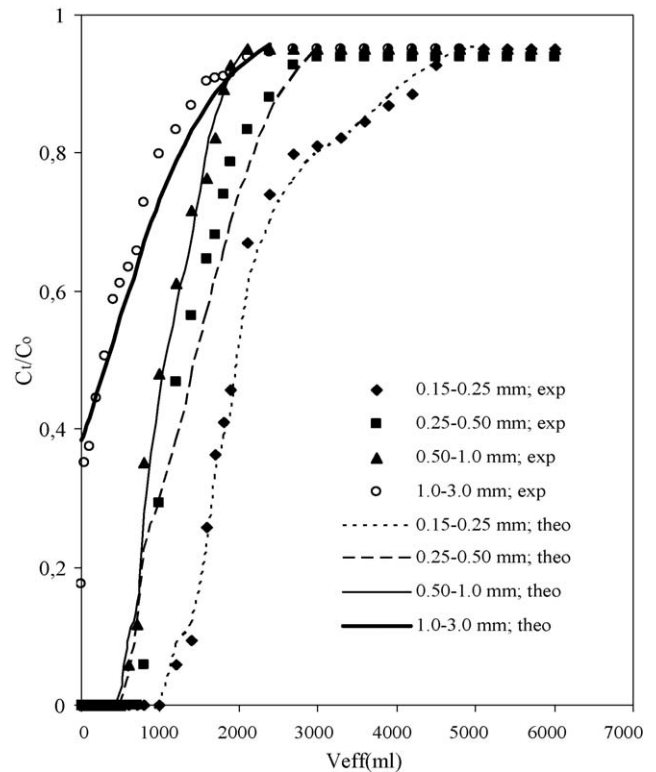


Fig. 10. The measured and modeled breakthrough curves for adsorption of Ni(II) onto waste tea at different particle sizes ($Q = 10$ mL/min, bed depth = 10 cm, pH 4.0, $C_0 = 100$ mg/L).

removal percentage values decreased with increasing particle sizes.

The correlation coefficients between the experimental and modeled values using Thomas model for all tested particle sizes were between 0.845 and 0.929. The calculated q_{eq} values from Thomas model are similar to experimental q_{eq} values. The values of q_{eq} obtained from the Thomas model and k_{TH} were 19.14, 13.2, 11.83, 9.41 mg/g and 0.00013, 0.00019, 0.00034 and 0.00015 L/mg h at 0.15–0.25, 0.25–0.50, 0.50–1.0 and 1.0–3.0 mm particle size, respectively. As shown Fig. 10, the experimental breakthrough curves were very close to calculated according to Thomas model.

4. Conclusion

Fixed-bed adsorption of a heavy metal, nickel(II), from aqueous solutions using waste of tea factory was experimentally and theoretically studied. The following results were obtained:

- These studies show that tea factory waste is an effective and inexpensive adsorbent for nickel(II) removal from aqueous solutions.
- From FTIR study, –OH, C=O, secondary amine group and CH_3 and SO_3 groups were the main functional groups of waste tea participate in metal binding.
- The adsorption capacity is strongly dependent on the flow rate, inlet nickel(II) ion, and bed height. As the flow rate increased,

the breakthrough curve became steeper, the break point time and adsorbed ion concentration decreased.

- Both breakthrough time and exhaustion time increased with increasing bed height. The rate constant, K_a , calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase and the computed N_0 and K_a were 12000 mg/L and 0.089 L/mg min, respectively.
- Equilibrium metal uptake (q_{eq}) of Ni(II) decreased with the increase in the initial feed Ni(II) concentration.
- In Ni(II) adsorption on waste tea, the highest maximum bed capacity and the longest breakthrough time is obtained at pH 4.0.
- It is showed that increasing the size of adsorbent particles reduces the maximum bed capacities and breakthrough time.
- Thomas model for the waste of tea factory on Ni(II) adsorption was used to predict the breakthrough curves under varying experimental conditions. As seen in Figs. 7–10, this model gave good agreement between experimental and calculated breakthrough curves. This model was also successfully used for the prediction.

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