Full Length Research Paper

Adsorption study on orange peel: Removal of Ni(II) ions from aqueous solution

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Adsorption of Nickel(II) ions from aqueous solution onto a low cost adsorbent-orange peel was investigated to evaluate the effects of pH, initial nickel ion concentration and adsorbent dose on the removal of Ni(II) systematically. The optimal pH value for Ni(II) adsorption onto the orange peel was found to be 5.0. Greater percentage of metal ion was removed with decrease in the initial concentration of metal ion and increase in amount of adsorbent used. Adsorption data was modeled using the Langmuir and Freundlich adsorption. The adsorption kinetics was found to follow pseudo-second-order rate kinetic model, with a good correlation ($r^2 > 0.99$) and intra-particle diffusion as one of the rate determining steps. Thermodynamic parameters ($\Delta G°$, $\Delta S°$ and $\Delta H°$) for sorption system was determined at five different temperatures.

Key words: Orange peel, heavy metal ion, adsorption, isotherms, kinetics.

INTRODUCTION

Inorganic effluents from the industries contain toxic metal ions which tend to accumulate in the food chain. The toxic heavy metal ions have high solubility in the aquatic environments and thus they can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metal ions may accumulate in the human body. If the metal ions are ingested beyond the permitted concentration, they can cause serious health disorders (Dadhaniya et al., 2009). Existence of heavy metal ion pollutants in water result in ecological problems even at very low concentration which increased the need for materials that can provide efficient complexing potential toward these metal ions (Essawy et al., 2004).

Nickel is a toxic metal, which may be present in waste-waters. Nickel salts are commonly used in metal plating and its concentration in industrial wastewaters range from 3.40 to 900 mg L^{-1}. Maximum permissible limit for nickel in bottled water has been fixed as 50 mg L^{-1} by European Economic Community (Demirbas et al., 2002). The chronic toxicity of nickel to humans and the environment is well known and high nickel concentration causes lungs and bone cancers. To solve this problem, many efforts has been made to produce an economically and technically attractive alternative to substitute the activated carbon as nickel adsorbent (Demirbas et al., 2002; Han et al., 2006; Paulino et al., 2005; Villora et al., 2004).

Considerable research has been carried out in developing nickel removal techniques. Conventional method such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, ion exchange, adsorption, membrane processing and electrolytic methods, have been traditionally employed for heavy metal removal from industrial wastewater (Tobin and Roux, 1998). However, the shortcomings of most of these methods are of high operational and maintenance costs, generation of toxic sludge and complicated procedure involved in the treatment. Comparatively, adsorption process is considered better in water treatment because of convenience, ease of operation and simplicity of design (Faust and Aly, 1987). Furthermore, this process can remove/minimize different type of pollutants and thus it has a wider applicability in water pollution control. Activated carbon is undoubtedly considered as universal adsorbent for effluent treatment

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and is commonly used for the removal of various pollutants from water (Bansal et al., 2005). However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost. A large variety of non-conventional adsor-bents have been examined for their ability to remove various types of pollutants from water and wastewater and have been reviewed extensively (Pollard et al., 1992; Miguel et al., 2006; Mohan and Pittman 2006, 2007; Ahmaruzzaman, 2008; Ngah et al., 2008; Sud et al., 2008; Lin and Juang, 2009; Bhatnagar and Sillanp, 2010; Rafatullah et al., 2010; Foo and Hameed, 2009). It has been found that various low-cost adsorbents developed from different origins show little or poor sorption potential for the removal of aquatic pollutants as compared to commercial activated carbon. Therefore, the search to develop efficient sorbents is still going on. From last few decades, biosorption process has emerged as a cost effective and efficient alternative for water and wastewater treatment utilizing naturally occurring and agricultural waste materials as biosorbents as these are cheaper, renewable and abundantly available. At present, biosorption field has been enriched by a vast amount of studies published in different journals. Various bio-sorbents have been examined for the removal of diverse type of pollutants from water (Srinivasan and Viraraghavan, 2010; Davis et al., 2003; Aksu, 2005; Romera et al., 2006; Volesky, 2007; Vijayaraghavan and Yun, 2008; Mathialagan et al., 2008; Gadd, 2009).

Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups responsible for metal ion adsorption (Wase, 1997). The abundant natural occurrence and presence of large amount of surface functional groups make various agri-cultural wastes good alternatives to expensive synthetic adsorbents (Bulut et al., 2007).

In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, and compost and leaves (Hasar, 2003). The use of orange peel as a biosorbent material presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicellulose and lignin. As a low cost, orange peel is an attractive and inexpensive option for the biosorption removal of dissolved metals. Ajmal et al. employed orange peel for metal ions removal from simulated wastewater (Wan Ngah et al., 2007; Ajmal et al., 2000). Some authors reported the use of orange waste as a precursor material for the preparation of an adsorbent by common chemical modifications such as alkaline, acid, ethanol and acetone treatment (Pérez et al., 2009; Li et al., 2007; Biswas et al., 2007; Liang et al., 2009; Liang et al., 2009).

The purpose of this present study was to assess the ability of orange peel to adsorb Ni(II) ions from aqueous solutions. The experiments were done in a batch system and nickel adsorption was investigated with respect to pH, initial metal ion concentration and adsorbent dose.

MATERIALS AND METHODS

Preparation of the adsorbent

Orange peel was from a local market. The collected biomaterial was extensively washed under tap water to remove any particulate, sprayed with distilled water. This biosorbent was cut into small pieces, ovendried at $100 \pm 2°C$, crushed and sieved through a 1.80 mm size before its use in adsorption experiments without any further treatment.

Orange waste consists mainly of cellulose, hemicellulose, pectin, limonene and many other low molecular weight compounds. Perez-Marín et al. (2008) studied orange peel for the removal of cadmium from aqueous solutions by adsorption. In this work, FTIR spectrum of the orange waste evidenced the presence of carboxyl and hydroxyl groups, which are important functional groups for metal uptake by biological materials (Perez-Marin et al., 2008).

Chemical

Ni(II) solutions were prepared by diluting 1000 ppm of $Ni(NO_3)_2 \cdot 6H2O$ (Merck) stock solution with deionized water to a desired concentration range between 10 and 200 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with diluted and concentrated H_2SO_4 and NaOH solutions, respectively. Insignificant decreases in the final equilibrium pH were recorded, so during the uptake pH was assumed constant.

Adsorption Studies

Batch adsorption experiments were carried out by agitating 0.2 g of the orange peel with 100 ml of nickel(II) solutions of desired concentrations and pH at room temperature using an orbital shaker operating at 200 rpm. The effect of pH was studied by adjusting the pH of the solutions using 1 N H_2SO_4 or 1 N NaOH solution. pH was measured using a pH meter. The effect of initial **metal ion** concentrations was carried out by shaking 100 ml nickel(II) solutions of desired concentrations (10, 25, 50, 75, 100, 125, 150 and 200 mg L^{-1}) with 0.2 g of the adsorbent. All the samples were adjusted to the optimum pH prior to the addition of the adsorbent. The samples were withdrawn from the shaker at pre-determined time intervals and nickel(II) solution was separated from the adsorbent by centrifugation at 4000 rpm for 5 min. Blank runs, with only the adsorbents in 100 ml of double-distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the adsorbents and adsorbed by glass containers.

All the investigations were carried out in duplicate to avoid any discrepancy in experimental results and metal solution controls were kept throughout the experiment to maintain quality control. The percentage of metal adsorption by the adsorbents was computed using the equation:

$$\text{Adsorption (\%)} = \left(\frac{C_i - C_e}{C_i} \right) \times 100 \tag{1}$$

Where, C_i and C_e are the initial and equilibrium concentration of metal ion (mg l^{-1}) in the solution. Adsorption capacity was calculated
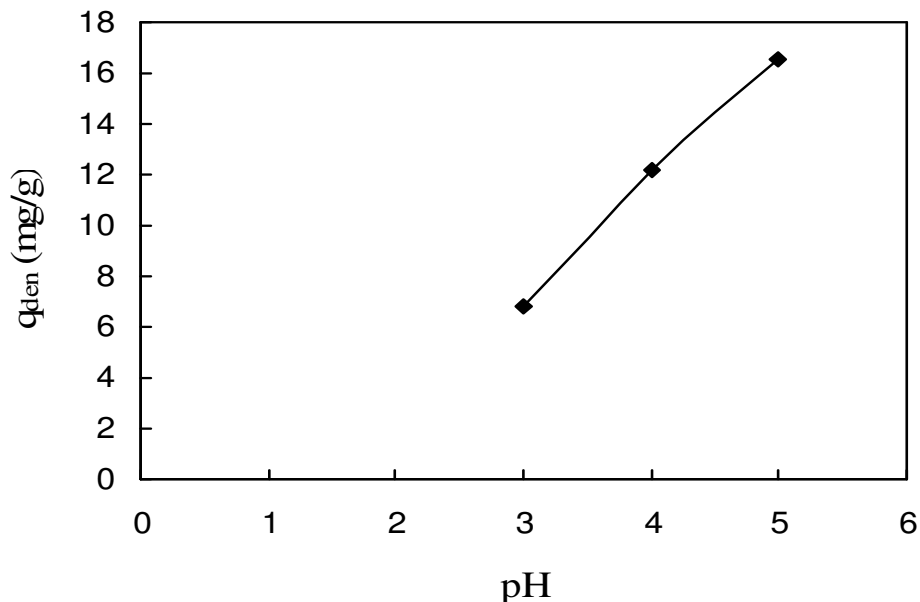
Figure 1. The effect of initial pH on the equilibrium Ni(II) sorption capacity of orange peel (T: 25°C; C_o: 100 mg l^{-1}; X: 2.0 g l^{-1}; agitation rate: 200 rpm).

by using the mass balance equation for the adsorbent:

$$q = \frac{(C_i - C_e)V}{W} \qquad (2)$$

Where, q is the adsorption capacity (mg g^{-1}), V is the volume of metal ion solution (L) and W is the weight of the adsorbent (g).

Analysis of Ni(II)

The concentration of residual Ni(II) in the adsorption medium was determined spectrophotometrically. 0.2 mL of 1% (w/v) sodium diethyl dithiocarbamate solution, and 20 mL of 1.5N NH_3 solution were added to the sample (1 mL) containing lower than 60 mg L^{-1} of nickel(II) ions and diluted to 25 mL with double-distilled water. The absorbance of the solution was read at 340 nm.

RESULTS

Effect of initial pH on Ni(II) adsorption

The removal of metal ions from aqueous solution by adsorption was depended on the pH of the solution since it affected adsorbent surface charge, degree of ionization of the functional groups, and metal ion speciation (Flaviane et al., 2010). Most researchers agreed that the optimal pH vary with diverse metal ions. At lower pH value, the H^+ ions compete with metal cation for the exchange sites in the system thereby partially releasing the latter. The heavy metal cations are completely released under circumstances of extreme acidic conditions. To find a suitable pH for the effective adsorption of Ni(II) ions, experiments were performed over a pH range

of 3.0 to 5.0. The variation of equilibrium metal ion uptake with initial pH is given in Figure 1 for an initial nickel(II) concentration of 100 mg L^{-1} at 25°C. The percent adsorption is minimum (q_{eq} = 6.82 mg g^{-1}) at pH 3 and increases as the pH is increased. The maximum adsorption occurs at pH 5 (q_{eq} = 16.60 mg g^{-1}). The minimum adsorption at low pH (3) may be due to the fact that high concentration and high mobility of H^+ ions, the hydrogen ions are preferentially adsorbed compared to Ni(II) ions.

Effect of contact time and concentration

The adsorbate concentration and contact time between adsorbent and adsorbate species play an important role in the process of removal of pollutants from water and wastewater by adsorption at a particular temperature and pH. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of the adsorbent for its use in wastewater treatment. In addition to this, the contact time is one of the factors for the development of surface charges at the solid solution interface. The initial concentration of adsorbate also plays an important role as a given mass of the adsorbent can adsorb only a fixed amount of the solute. The more concentrated the solution or effluent, the smaller is the volume of effluent that a given mass of adsorbent can purify. In high concentration range, the fractional adsorption is low.

The removal of the Ni(II) ions by orange peel increased from 1.05 to 29.04 mg g^{-1} by increasing the concentration of the metal ion from 10 to 200 mg L^{-1} at temperature 25 ± 1°C and pH 5.
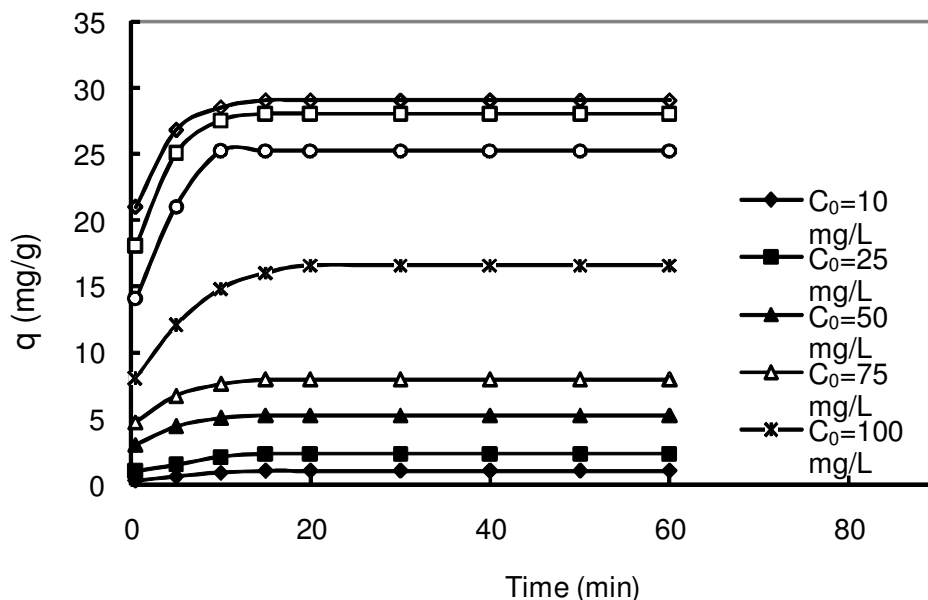
Figure 2. The effect of initial concentration on the equilibrium Ni(II) sorption capacity of orange peel (T: 25°C; pH: 5; X: 2.0 g l^{-1}; agitation rate: 200 rpm).

It is clear from Figure 2 that the extent of adsorption was rapid in the initial stages and became slow in later stages till saturation was attained. This is obvious from the fact that a large number of surface sites are available for adsorption at the initial stages and after a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phases. The time required to attain equilibrium in the case of adsorption of metal ion is 14 min. It can be seen from the figure that the equilibrium period remained unaltered with the change of initial concentration of the metal ion solution.

A series of contact experiments were undertaken for varying initial Ni(II) concentrations namely 10, 25, 50, 75, 100, 125, 150 and 200 mg L^{-1}. For low concentrations, there was a rapid uptake of metal ion due to surface mass transfer. The time variation curves for adsorption are simple, smooth and continuous, indicating the formation of monolayer coverage on the surface of adsorbent.

Effect of adsorbent dose

The adsorption of nickel ions onto orange peel was studied by varying the adsorbent quantity (0.05, 0.1, 0.2, g/100 mL) in the test solution while keeping the initial **ion** concentration (100 mg L^{-1}), temperature (25 ± 1°C) and pH constant at all different time intervals. The percent adsorption was increased with adsorbent dosage (Figure 3). The adsorption increased from 9.67 to 33.14%, as the orange peel dosage was increased from 0.05 to 0.2 g/100 ml under the optimized conditions (Figure 3).

Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. But unit adsorption decreased with increase in adsorbent dose. For orange peel, unit adsorption was decreased from 19.37 to 16.60 mg g^{-1} as the adsorbent dose increased from 0.05 to 0.2 g/100 mL in the test solution.

This may be attributed to overlapping or aggregation of adsorbent surface area available to ion and an increase in diffusion path length.

Adsorption isotherms

The Freundlich and Langmuir models are the most frequently used models to describe the experimental data of adsorption isotherms. Here, both models were used to investigate how Ni(II) ions interact with adsorbents, the Langmuir and Freundlich models were applied to describe the isotherm data obtained at four temperatures.

The Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. It is represented as:

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \tag{3}$$

Where, k_F (Lg^{-1}) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Langmuir isotherm assumes a surface with homogeneous binding sites, equivalent sorption energies, and no interaction between adsorbed species.
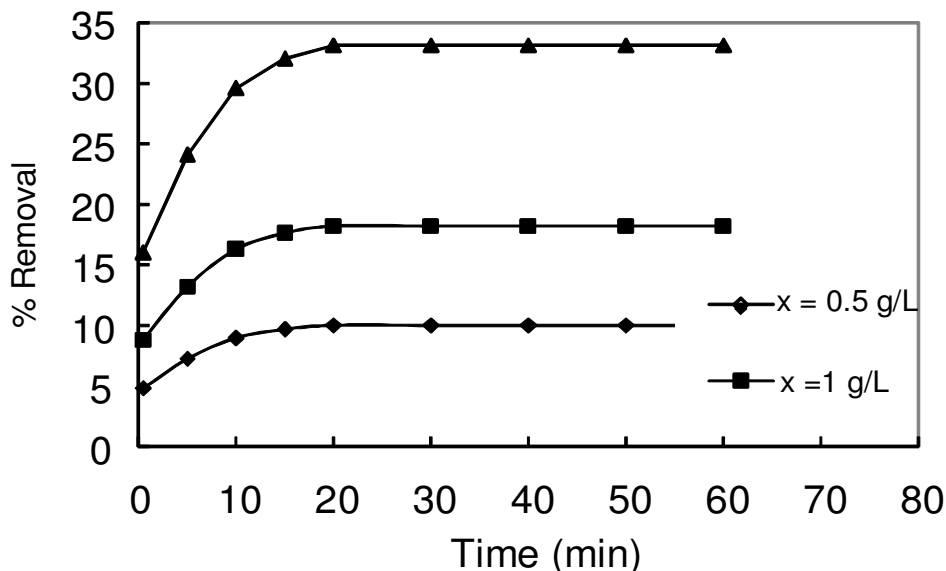
Figure 3. The effect of adsorbent dose on the equilibrium Ni(II) sorption capacity of orange peel ($C_o = 100$ mg l^{-1}; pH: 5; T = 25°C; agitation rate: 200 rpm).

Table 1. Parameters of Freundlich and Langmuir adsorption isotherm models for Ni(II) ions adsorbed by orange peel.

Temperature	Freundlich			Langmuir		
	k_F	n	ε (%)	q_{max} (mg/g)	k_L (L/g)	ε (%)
25	0.120	0.982	15.95	62.89	0.120	27.56
35	0.098	0.982	15.97	54.34	0.170	28.49
40	0.084	0.982	15.95	50.25	0.002	24.68
50	0.070	0.983	15.97	46.08	0.002	23.39

Its mathematical form is written as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max} k_L} \tag{4}$$

Where, q_{max} and k_L represent the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

The criteria for selection of the most suitable isotherm model were average percentage error and deviation from experimental value (Aksu and İşoğlu, 2005).

The corresponding Langmuir and Freundlich para-meters at different temperatures were obtained by non-linear regression analysis and listed in Table 1 along with the average percentage errors. The average percentage errors between the experimental and predicted values were calculated using Equation (5). In Equation (5), the subscripts 'exp' and 'calc' show the experimental and calculated values and N the number of measurements (Aksu and İşoğlu, 2005).

$$\varepsilon \% = \frac{\sum_{i=1}^{N} \left| q_{eq,i,exp} - q_{eq,i,calc} / q_{eq,i,exp} \right|}{N} \times 100 \tag{5}$$

Figures 4 and 5 show the comparison of experimental and predicted amounts of nickel(II) adsorbed on orange peel obtained from these adsorption models at the temperatures of 25, 35, 45 and 55°C.

Basically, if most of the data are distributed around the 45° line, this indicates that the model properly represent the experimental data of the system as shown in the figure.

Examination of the data (Table 1) showed that the two parameter Freundlich model described the adsorption of metal ions onto orange peel better than that of Langmuir model.

Adsorption kinetic study

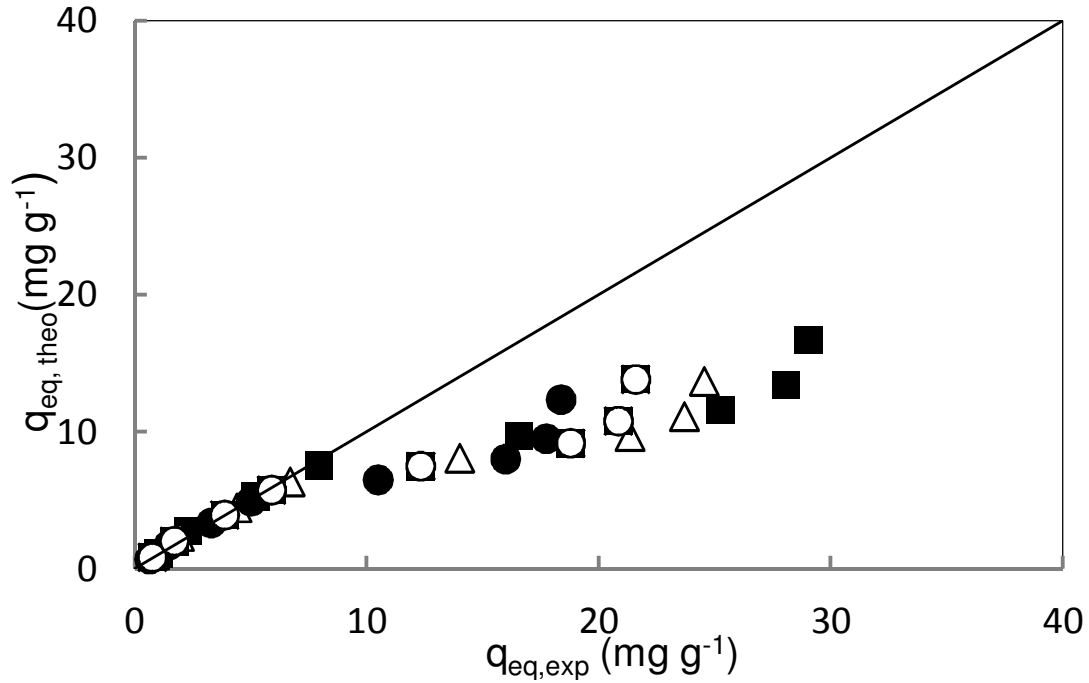Adsorption kinetic is important from the point of view to

Figure 4. Experimental and theoretical q_{eq} values obtained from the Langmuir model at different temperatures for nickel(II) adsorption. ■:25°C; ○:35°C; ●:40°C; Δ:50°C.
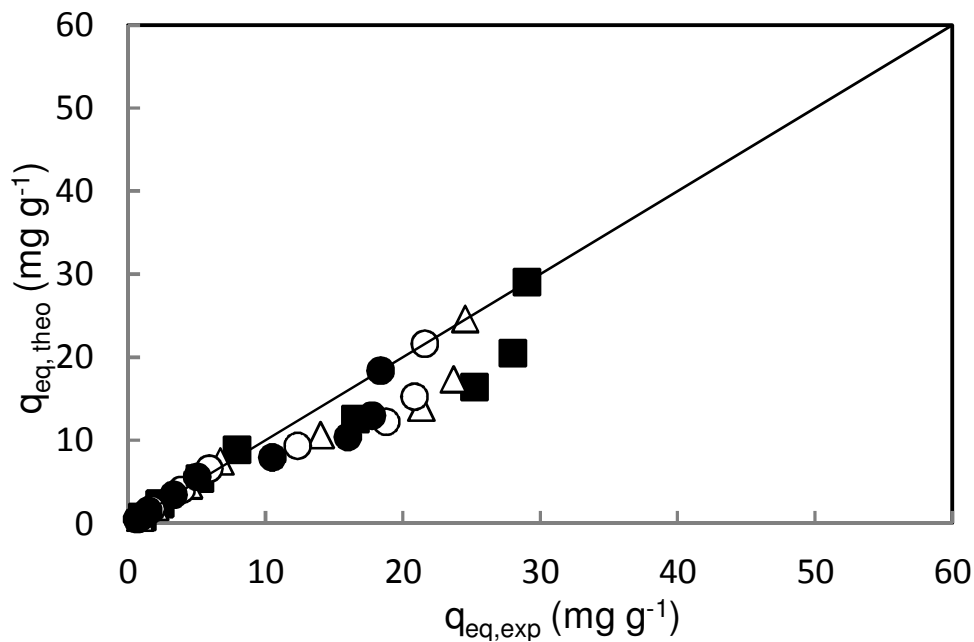

Figure 5. Experimental and theoretical q_{eq} values obtained from the Freundlich model at different temperatures for nickel(II) adsorption. ■:25; ○:35; ●:40; Δ:50°C.

control the process efficiency. The adsorption of a solute by a solid in aqueous solution is a phenomenon with often complex kinetics. The adsorption rate is strongly influenced by several parameters related to the state of the solid, generally having very heterogeneous reactive surface, and to the physico chemical conditions under which adsorption is carried out. Various kinetic models have been used by various researchers, where the

Table 2. Pseudo-second order kinetic model and intra particle diffusion model parameters for the adsorption systems in this study.

C_o (mg l^{-1})	Pseudo-second-order model				Intra-particle diffusion model		
	$q_{e,exp}$ (mg/g)	$q_{e,calc}$ (mg/g)	k_2(g/mgmin)	r^2	k_i (mg/g min$^{1/2}$)	c_i	r^2
10	1.05	1.09	0.567	0.998	0.240	0.114	0.989
50	5.23	5.28	0.424	0.999	0.722	2.611	0.969
100	16.57	16.95	0.001	0.999	2.589	6.257	0.995
200	29.04	29.16	0.165	0.999	2.602	19.85	0.940

pseudo-first-order (Ho and McKay, 1999, Ho et al., 2000) and pseudo-second-order models were studied (Aharoni et al., 1970).

The second-order kinetic model (McKay and McKay, 1999) is expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q e_2} + \frac{t}{q_e} \qquad (6)$$

Where, k_2 is the second-order rate constant (g/mg min), by plotting of t/q versus t is a linear relationship. Values of k_2 and q_e were calculated from the intercept and slope of the plots of t/q versus t. Adsorption kinetic data was further used to determine whether the intra-particle diffusion was rate limiting and also to find the diffusion rate constant, k_i (mg/g min$^{0.5}$).

Weber et al. (1963) intraparticle diffusion model is characterized by the relationship between specific adsorption and the square root of time, according to the following equation:

$$ki = \frac{q_t}{t^{0.5}} \qquad (7)$$

The pseudo-second order and intra-particle diffusion kinetic models are employed in this work. The obtained parameters for all of kinetic models are given in Table 2. As seen from this table, the pseudo-second order rate equation and intra-particle diffusion kinetic models for adsorption of Ni(II) ions onto orange peel agreed well with the data for $r^2 > 98$ and $r^2 > 93$ in turn. The correlation coefficients calculated for all models, i.e., r^2, and the other parameters are shown in Table 2. Also, as seen from this table, it was observed that correlation coefficient, r^2, for the intra-particle diffusion kinetic model was much lower than for the pseudo-second order rate equation. For the second- order model, $q_{e,calc}$, values are close to $q_{e,exp}$ for all the initial concentration and temperatures. For this model, the linear regression analysis gave high values ($r^2 \geq 0.98$). In addition, due to the porous nature of the orange peel, diffusion of Ni(II) ions was also expected at the surface. Therefore, the plots of q_t versus $t^{1/2}$ according to intra-particle diffusion kinetics were obtained. The constants of intra-particle transport

(k_i) and the c values were calculated from the slopes and intercepts of the linear portions of the plots at various contact times (Table 2). The r^2 values obtained from intra-particle diffusion model and pseudo-second order model was very high. From these results, it is seen that the intra-particle diffusion model and pseudo-second-kinetic model are applicable for adsorption system. The applicability of both models showed that adsorption process is complex and involves more than one mechanism.

Thermodynamics of Ni(II) adosorption

Thermodynamic analysis provides valuable information on the mechanism of adsorption. The thermodynamics of Ni(II) adsorption onto orange peel were studied using the free energy change, $\Delta G°$, according to Equation (8):

$$\Delta G° = RT \ln K \qquad (8)$$

The plot of ln K vs. 1/T gives a straightline and the values of $\Delta S°$ and $\Delta H°$ can be obtained from its intercept and slope, respectively. The calculated values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ are presented in Table 3.

Values of $\Delta G°$ were between 2.168 and 3.266kJ/mol, indicating that a chemical sorption process occurred under the experimental conditions. The negative value of $\Delta H°$ indicates an exothermic biosorption reaction while negative $\Delta S°$ confirms the decreased randomness at the solid–solution interface during biosorption (Aksu and Işoğlu, 2005).

DISCUSSION

The fruit peel of orange is a low-cost adsorbent which is abundantly available in Turkey as waste material. It can be used as an effective adsorbent for the removal and recovery of Ni(II) from waste water.

In this study, the adsorption behavior of Ni(II) onto orange peel was investigated in the batch experiments. The adsorption was found to be drastically dependent on pH, adsorbent dosage, and initial metal ion concentration. The optimum pH for the adsorption of Ni(II) ion was found

Table 3. $\Delta G°$, $\Delta H°$ and $T\Delta S°$ values at various temperatures.

T(K)	$\Delta G°$ (kj/mol)	$-\Delta H°$ ((kj/mol)	$-T\Delta S°$ (kj/mol K^{-1})
298	2.168	10.918	13.086
303	2.387	10.918	13.306
308	2.607	10.918	13.525
313	2.827	10.918	13.744
323	3.266	10.918	14.184

to be 5. The rate of adsorption of this metal ion was rapid. The nickel-orange peel system attained equilibrium in 14 min. According to the Langmuir model, the maximum Ni(II) biosorption capacity of biosorbent was 62.3 mg g^{-1} at 25°C. The Ni(II) biosorption capacity of orange peel was compared to the adsorption capacities of some other adsorbents, reported in literature. Differences of Ni(II) uptake are due to the properties of each adsorbent such as structure, functional groups and surface area (Alper and Işoğlu, 2005). Malkoç and Nuhoğlu studied the biosorption of Ni(II) by waste tea and found a 15.26 mg g-1 maximum metal ion uptake capacity (Malkoç and Nuhoğlu, 2005). Kumar et al. (2011) examined the biosorption of the biosorption of Ni(II) by cashew nut shell and determined the maximum biosorption capacity of the sorbent as 18.87 mg g^{-1}. Parab et al. (2006) studied with the coir pith for the biosorption of Ni(II); the biosorption capacity of biosorbent was 15.95 mg g^{-1}. The comparison of results of this work with the other works found in the literature showed that orange peel has a high adsorption capacity for Ni(II) ion.

The adsorption process rate and dynamic behaviour of the system are very important factors for the process design and operation control. The negative value of ΔH indicates an exothermic biosorption reaction while $\Delta S°$ confirms the decreased randomness at the solid-solution interface during biosorption.

The rate of diffusion may be valid in many realistic situations. In order to test the adsorption kinetics pseudo second-order kinetic models was used. It was shown that the adsorption of Ni(II) onto orange peel could be fitted by the second-order model. An intraparticle diffusion model developed by Weber and Morris was used to find intraparticle diffusion rate constants.

Thermodynamic constants were also evaluated using equilibrium constants changing with temperature. The positive values of $\Delta G°$ showed the endothermic nature of Ni(II) adsorption.Orange peel showed significant adsorption capacity for Ni(II) ion under suitable experimental conditions and hence will serve as an useful adsorbent. Orange peels are abundantly available and are inexpensive too. Its binding capacity of Ni(II) ion is appreciably high. The data may be useful for designing and fabricating an economically cheap treatment process using batched or stirred tank flow reactors for the removal of Ni(II) ion from dilute industrial wastewaters in the future.

ACKNOWLEDGEMENT

REFERENCES

Ahmaruzzaman M (2008). Adsorption of phenolic compounds on low-cost adsorbents: a review. Adv. Colloid Interface Sci. 143: 48–67.

Aharoni C, Tompkins FC, Eley DD, Pines H, Weisz PB (Eds.) (1970). Kinetics of adsorption and desorption and the Elovich equation, Advance in Catalysis and Related Subjects. Vol. 21. Academic Press. New York.

Ajmal M, Rao, Ahmad RAKR, Ahmad J (2000). Adsorption studies on *Citrus reticulata* (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. J. Hazard. Mater. B79: 117–131.

Aksu Z (2005). Application of biosorption for the removal of organic pollutants: a review. Process Biochem. 40: 997-1026.

Aksu Z., İşoğlu A (2005). Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. Process Biochem. 40: 3031-3044.

Bansal RC, Goyal M (2005).Activated Carbon Adsorption. CRC press.

Bhatnagar A, Sillanp M (2010). Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment—a review. Chem Eng J 157: 277–296.

Biswas B. K, Inoue K, Ghimire KN, Ohta S, Harada H,. Ohto K, Kawakita, H (2007).The adsorption of phosphate from an aquatic environment using metal-loaded orangewaste. J. Colloid Interface Sci. 312: 214–223.

Bulut Y, Tez Z (2007). Adsorption studies on ground shells of hazelnut and almond. J. Hazard. Mater. 149: 35–41.

Dadhaniya PV, Patel AM, Patel MP, Patel RG (2009). A new cationic poly[1-vinyl-V3-ethyl imidazolium iodide], P(VEII) hydrogel for the effective removal ofVchromium (VI) from aqueous solution. J. Macromol. Sci. Part A: Pure Appl. Polym. Chem. 46: 447–454.

Davis TA, Volesky B, Mucci A (2003). A review of the biochemistry of heavy metal biosorption by brown algae. Water Res. 37: 4311-4330

Demirbas E, Kobya M, Oncel S, Sencan S (2002). Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Bioresour. Technol. 84: 291–293

Essawy HA, Ibrahim HS (2004). Synthesis and characterization of poly(vinylpyrrolidone- co-methylacrylate) hydrogel for removal and recovery of heavy metal ions from wastewater. React. Funct. Polym. 61: 421–432.

Faust SD, Aly OM (1987). Adsorption Process for Water Treatment. Stoneham: Butterworths Publishers.

Flaviane VK Leandro VA, Laurent GF (2010). Removal of Zn from aqueous single metal solutions and electroplating wastewater with wood sawdust and sugar cane bagasse modified with EDTA dianhydride(EDTAD). J. Hazard. Mater. 176: 856-863.

Foo KY, Hameed BH (2009). Utilization of rice husk ash as novel adsorbent: a judicious recycling of the colloidal agricultural waste. Adv. Colloid Interface. 152: 39-47.

Gadd GM (2009). Biosorption: Critical Review of Scientific Rationale, Environmental Importance and Significance for Pollution Treatment. J Chem. Technol. Biotechnol. 84: 13-28.

Han RP, Zou WH, Zhang Z.P, Shi J, Yang JJ (2006). Removal of copper (II) and lead (II) from aqueous solution by manganese oxide coated sand (I) Characterization and kinetic study J Hazard. Mater. 137: 384-395.

Hasar H (2003). Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk. J. Hazard. Mater. 97: 49–57.

Ho YS, McKay G (1999). The sorption of lead (II) ions on peat. Water Res 33: 578–584.

Ho YS, Ng JCY, McKay G (2000). Kinetics of pollutant sorption by biosorbents: review. Separation Purif. Methods, 29(2): 189–232.

Kumar PS, Ramalingam S, Kirupha SD, Murugesan A, Vidhyadevi T, Sivanesan S (2011). Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design. Chem. Eng. J. 167:122–131.

Li X, Tang Y, Xuan Z, Liu Y, Luo F (2007). Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution. Sep. Purif. Technol. 55: 69–75

Liang S, Guo X, Feng N, Tian Q (2009). Adsorption of Cu2+ and Cd2+ from aqueous solution by mercapto-acetic acid modified orange peel Colloids Surf. B: Biointerfaces, 73: 10–14.

Liang S, Guo X, Feng N, Tian Q (2009). Application of orange peel xanthate for the adsorption of Pb^{2+} from aqueous solutions J. Hazard. Mater. 170: 425–429.

Lin SH, Juang RS (2009). Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: A review J Environ Manage 90: 1336-1349.

Malkoç E, Nuhoglu Y (2005). Investigations of nickel(II) removal from aqueous solutions using tea factory waste. J Hazard Mater B127: 120–128.

Mathialagan T, Viraraghavan (2008). Biosorption of chlorophenols: a review T. Int J Environ Pollut 34: 164-194.

McKay G, Ho YS (1999). Pseudo-second order model for sorption processes. Process. Biochem. 34: 451–465.

Miguel GS, Lambert, SD, Graham NJD (2006) A practical review of the performance of organic and inorganic adsorbents for the treatment of contaminated waters. J. Chem. Technol. Biotechnol. 81: 1685-1696.

Mohan D, Pittman Jr. CU (2006). Activated Carbons and Low-Cost Adsorbents for Remediation of Tri- and Hexavalent Chromium from Water: A Review," J. Hazard. Mater. B137: 762-811.

Mohan D, Pittman CU (2007). Arsenic removal from water/wastewater using adsorbents-a critical review. J. Hazard. Mater. 142: 1-53.

Ngah WSW, Hanafiah MAKM (2008). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresour. Technol. 99: 3935-3948.

Parab H, Joshi S, Shenoy N, Lali A, Sarma US, Sudersanan M (2006). Determination of kinetic and equilibrium parameters of the batch adsorption of Co(II), Cr(III) and Ni(II) onto coir pith. Process Biochem 41:609-615.

Paulino AT, Tessari JA, Nogami EM, Lenzi E, Nozaki J (2005). Lipid Increase Induced by Lead Accumulation in Tilapia *Oreochromis niloticus*. Bull. Environ. Contam. Toxicol. 75: 42–49.

Perez Marín A.B, Aguilar M I, Meseguer VF, Ortŭno JF, M. loŕens J. Śaez. (2008). Biosorption of chromium (III) by orange (Citrus cinensis) waste: Batch and continuous studies. Chem Eng J 155: 199–206.

Pérez-Marín AB, Ballester A , González F, Blázquez ML, Muñoz JA, Sáez J, Zapata VM (2008). Study of cadmium, zinc and lead biosorption by orange wastes using the subsequent addition method. Bioresour. Technol.99: 8101–8106

Pollard SJT, Fowler GD, Sollars CJ, Perry R (1992). Low cost adsorbents for waste and wastewater treatment: a review. Sci. Total Environ. 116: 31-52.

Rafatullah M, Sulaiman O, Hashim R, Ahmad A (2010). Adsorption of Methylene Blue on low-cost adsorbents: A review. J Hazard Mater 177: 70-80.

Romera E, González F, Ballester A, Blázquez ML, Muńoz JA (2006). Biosorption with Algae:A statistical review. Crit. Rev. Biotechnol. 26: 223-235.

Srinivasan A, Viraraghavan T (2010). Decolourization of ion wastewaters by biosorbents: A review. J. Environ. Manage. 91: 1915-1929.

Sud D, Mahajan G, Kaur, MP (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. Bioresour. Technol. 99: 6017–6027.

Tobin JM, Roux JC (1998). Mucor biosorbent for chromium removal from tanning effluents. Water Res. 32: 1407–1416.

Villora JM, Callejas P, Barba MF (2004). Influence of processing on the behaviour of ceramic materials as ion adsorbents in industrial waste waters Bull Spanish Glass Cer Soc. 43: 75–79.

Vijayaraghavan K, Yun YS (2008). Bacterial biosorbents and biosorption. Biotechnol. Adv. 26: 266–291.

Volesky B (2007). Biosorption and me. Wat.Res. 41: 4017-4029.

Wan Ngah WS, Hanafiah MAKM (2007). Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. Bioresour Technol 99: 3935–3948

Wase J, Forster C (1997). Biosorbents for Metal Ions. Taylor & Francis Ltd.

Weber WJ, Morris JC (1963). Kinetics of adsorption on carbon solution. J. Sanitary Eng. Division ASCE, 89: 31–60.