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ASSESSMENT OF THE ADSORPTION KINETICS, EQUILIBRIUM AND THERMODYNAMICS FOR THE POTENTIAL REMOVAL OF NI^{2+} FROM AQUEOUS SOLUTION USING WASTE EGGSHELL

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Abstract. In this study, Ni^{2+} sorption onto the waste eggshell was investigated under different operational conditions. Results indicated that the eggshell could be successfully used to remove Ni^{2+} ions from the water. Quick sorption process reached to equilibrium in about 2 hours with maximum sorption at pH 7.0. Based on the experimental data, Langmuir isotherm model with the q_m value of 1.845 mg Ni^{2+}/g eggshell was observed. The pseudo-second-order model provided the best correlation coefficient in comparison with other models. The calculated q_e values derived from the pseudo-second-order for sorption of Ni^{2+} ions were very close to the experimental (q_{exp}) values. Such thermodynamic parameters as ΔG°, ΔH°, and ΔS° were determined in order to predict the nature of adsorption. Results indicated that the adsorption of Ni^{2+} onto the eggshell was endothermically supported by the increasing adsorption of Ni^{2+} ions with temperature.

Keywords: adsorption isotherms, eggshell, nickel, thermodynamics.

Introduction

Heavy metal pollution of water sources is one of the most important problems. Various industries – such as mining and smelting of metalliferrous, electroplating, battery manufacture, textile production, refineries, and petrochemical factories etc. – produce wastewater that contains metals (Celekli, Bozkurt 2011) which is discharged to the water bodies after treatment. As heavy metals are non-biodegradable water pollutants, they tend to accumulate in living organisms (Gupta *et al.* 2010; Celekli, Bozkurt 2011).

In this experimental study, nickel was selected as an adsorbate, because nickel compounds have widespread application in many industrial processes, such as metal plating, silver refineries, zinc base casting and storage battery industries, and its concentration in industrial wastewaters range from 3.40 to 900 mg/L (Erdogan *et al.* 2005). Although low concentrations of nickel may be beneficial to organisms as a component in a number of enzymes and stimulate the activation of microorganisms (Aslan, Gurbuz 2011), an exceeded permissible exposure level of nickel causes various health problems such as unintentional weight loss, heart and liver damage, renal edema, lung and pulmonary fibrosis, skin dermatitis, and gastrointestinal discomfort (Bar-Sela *et al.* 1992; Celekli *et al.* 2010; Gupta *et al.* 2010; Kumar *et al.* 2011; Pahlavanzadeh *et al.* 2010).

Nickel (II) is one of the toxic pollutants in the industrial effluent wastewaters. Maximum contaminant limits of Ni (II) set by the EU and WHO as 0.02 mg/L and 0.07 mg/L, respectively (EU 2011; WHO 2005). Recommended limits for Ni (II) in reclaimed water for irrigation are 0.2 mg/L and 2.0 mg/L for the short and long-term usage (USEPA 2012).

Due to the accumulation of heavy metals in the food chain and persistence in the ecosystem, it causes the toxicity for living organisms. The wastewaters containing heavy metals are required to be properly treated prior to discharge into the receiving waters (Bhatnagar, Minocha 2010). Such conventional methods as the chemical precipitation, filtration, ion exchange, evaporation, reverse osmosis, solvent extraction, electrochemical treatment, membrane technologies, and adsorption could be applied in order to remove heavy metals from wastewater. Among these methods, adsorption is considered as an efficient and inexpensive method when the low concentration of heavy metal exists in the wastewater (Bermúdez *et al.* 2011; Ghazy *et al.* 2011; Kumar *et al.* 2011).

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Although the usage of activated carbon for sorption is an expensive method, commercially available activated carbon for the heavy metal removal from wastewater has been studied extensively (Erdogan *et al.* 2005). Consequently it is important to find new materials for removing by sorption of heavy metals from wastewaters.

In order to decrease the treatment cost of wastewater, researches have been focused on finding cheapest and effective sorbents. Among the numerous natural materials for removing nickel ions, biosorbents such as *Spirulina platensis* (Celekli, Bozkurt 2011), *Gracilaria caudata* and *Sargassum muticum* (Bermúdez *et al.* 2011), *Punica granatum* peel waste (Bhatnagar, Minocha 2010), cashew nut shell (Kumar *et al.* 2011), waste tea (Malkoc, Nuhoglu 2009; Shah *et al.* 2012) (*Camella cinencis)* (Aikpokpodion *et al.* 2010), acid–washed barley straw (Thevannan *et al.* 2011), Thespesia Populnea bark (Prabakaran, Arivoli 2012), activated locust bean husk (*Parkia biglobosa)* (Oladunni *et al.* 2012), *Sargassum filipendula* (Kleinubing *et al.* 2012), bael tree leaf powder (Kumar, Kirthika 2009), chitosan encapsulated *Sargassum sp.* (Yang *et al.* 2011), sugarcane bagasse pith (Krishnan *et al.* 2011), activated sludge (Liu *et al.* 2012), treated alga (*Oedogonium hatei*) (Gupta *et al.* 2010), *chlorella vulgaris* (Aksu, Donmez 2006), eggshell (Ghazy *et al.* 2011) have attracted attention as a low-cost sorbents from wastewater.

The aim of this study was to evaluate the adsorption capacity of the waste eggshell to remove Ni^{2+} ions in the synthetic waters. Effects of the initial pH, Ni^{2+} concentrations, temperature, contact time, and adsorbent dosage were determined in the batch experiments. The equilibrium isotherms; Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D – R) were determined by applying various Ni^{2+} concentrations. Adsorption kinetic models were used to analyze the kinetic and mechanisms of Ni^{2+} adsorption.

1. Materials and methods

1.1. Preparation of adsorbent

After washing of the waste eggshell by tap and distilled waters, it was dried at 60 °C for 24 hours in an oven. The dry clean eggshells were crushed and screened through a set of sieves to get the size of 75–106 μm.

1.2. Sorption experimental studies

The synthetic waters were prepared by dissolving known masses of $NiCl_2 \cdot 6H_2O$ in the distilled water. A known amount of eggshell was used throughout the experiments and final volumes of the solution were 100 mL. Experimental studies were carried in 250 mL glass-stoppered Erlenmeyer flasks.

Experiments were performed at various initial concentrations of Ni^{2+} (5.0–50 mg/L) and waste eggshell amounts (0.1–1.0 g/L). Additionally, temperature and pH were tested for various levels to determine the optimal operational conditions. Kinetic constants were determined at the initial concentrations of 15–25–35 mg Ni^{2+}/L at the constant initial pH value and adsorbent dosage of ≅ 7.0 and 0.5 g/L, respectively. Kinetic experiments were also carried out at the temperature of 298–308–318 K. Batch experimental studies were performed in an orbital incubator shaker (Gerhardt) at a constant speed of 150 rpm.

1.3. Analytical methods

In order to get supernatant liquids, the samples were centrifuged at 4000 rpm for 10 min (NF800, NUVE). Concentrations of Ni^{2+} in the solutions were determined with a Merck photometer (PHARO100). A spectraquant analytical kit (Merck, 14785) was used to measure Ni^{2+} concentrations in the initial and final solutions.

1.4. Calculations

The following equation was used to determine the amount of Ni^{2+} adsorbed onto eggshell:

$$q_e(mg/g) = (C_0 - C_e)(mg/L) \times \frac{V}{M}(mL/g)\,. \quad (1)$$

Adsorption process was quantified by calculating the sorption percentage (E %) as defined by the Eq. 2:

$$Sorption(E)(\%) = \frac{C_0 - C_e}{C_0} \times 100\,, \quad (2)$$

where q_e (mg/g) is the maximum amount of Ni^{2+} adsorbed at equilibrium; the initial and equilibrium concentrations of Ni^{2+} in the solutions were shown as C_o and C_e (mg/L), respectively. M is the amount of eggshell (g), and V (mL) is the total solution volume in the Erlenmeyer flasks.

2. Results and discussion

Sorption experiments were performed in duplicate and the average values of samples were presented in the study. Blank samples (without Ni^{2+}) were used also to compare the results through all batch procedures. Data presented in the figures are mean values of standard deviation (≤7%) from the experiments.

2.1. Effect of contact time

Figure 1 shows the variation of Ni^{2+} uptake with mixing time at pH 7.0 using 0.5 g eggshell. As can be seen from the figure that the equilibrium time for the sorption of Ni^{2+} was about 120 min. At the equilibrium point, the highest Ni^{2+} sorption efficiency of about 50% and the adsorption value of 1.95 mg/g were obtained.

The active sites of sorbents availability and the highest driving force for mass transfer at the beginning of the experiments (zero to 20 min) caused rapid uptake of Ni^{2+} ions from the solution. Due to the occupancy of eggshell active sites and the lower concentrations of Ni^{2+} in the solutions, Ni^{2+} sorption was slower after passing 20 min of agitation times.

2.2. Effects of pH

Since the initial pH of solution not only affects the reactive groups present on the surface of adsorbents (protonation/deprotonation effects), but also influences solubility of metals and the competition ability of hydrogen ions with metal ions, the initial pH of solution is an important parameter for the evaluation of sorption performances (Bermúdez *et al.* 2011; Celekli, Bozkurt 2011; Chojnacka, 2005). The sorption of Ni^{2+} was investigated as the function of pHs in the range of 3.0 to 7.0 with an increment of 0.5 pH units. Experiments were not extended to pH value of higher than 7.0 because the precipitation of Ni^{2+} ions forming hydroxides. Precipitation of Ni^{2+} may be applied for recovery when the wastewater is not including other pollutants.

Polat and Aslan (2014) determined the temperature and pH effects on the release of Ca^{2+} and HCO^{-}_{3} from the eggshell. Because the eggshell was composed mainly of calcium carbonate, pH were increased during the experimental study. However, the level of solution pHs were lower than 8.0 at the end of the batch experimental studies.

Sorption of Ni^{2+} on the eggshell sorbents at various pHs are presented in Figure 2. As can be seen in figure that uptake of Ni^{2+} was a function of initial solution pH. The adsorption of Ni^{2+} ions increases with increase in the solution pHs. Significant sorption was not observed at the pH values of 3.0 and 3.5. The lowest Ni^{2+} adsorption efficiency of about 11% was observed at the initial pH value of 3.0. It could be attributed to the higher concentration of hydrogen ions in the solution competing with Ni^{2+} for binding sites on the eggshell. Similar observations were reported in the literature for the sorption of Ni^{2+} ions on the various adsorbents (Bermúdez *et al.* 2011; Celekli, Bozkurt 2011; Kumar *et al.* 2011). At low pH values, H^+ ions occupy most of the adsorption sites of eggshell surface and Ni^{2+} sorption could be limited due to the electric repulsion with H^+ ions on the eggshell surface (Kumar *et al.* 2011). Increasing the pHs values from 3.5 to 6.5, sorption capacities (q_e) and the removal efficiencies of Ni^{2+} were increased significantly from 0.67 mg/g to 2.02 mg/g and 17.5% to 50.4% respectively. It was assumed that because the adsorbent surface was more negatively charged at high pHs, the sorption of heavy metal ions by eggshell increased. The q_e value and removal efficiency decreases slightly when the initial pH of solution was increased to 7.0.

The sorption capacities and removal efficiencies of Ni^{2+} were increased significantly from 0.43 to 2.02 mg Ni^{2+}/g.eggshell and 11% to 50.5%, respectively by increasing the pH from 3.0 to 6.5.

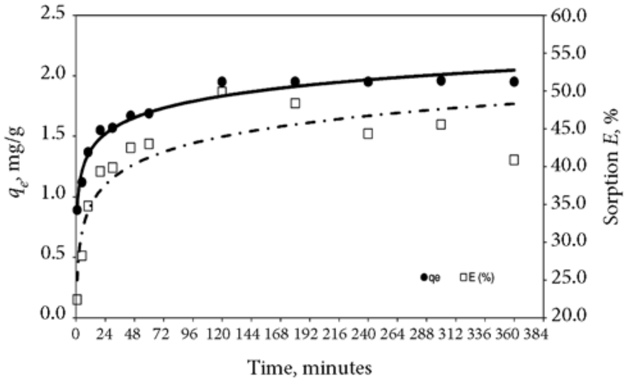

Fig. 1. Contact time effects on the sorption (C_0 = 20 mg Ni^{2+}/L)

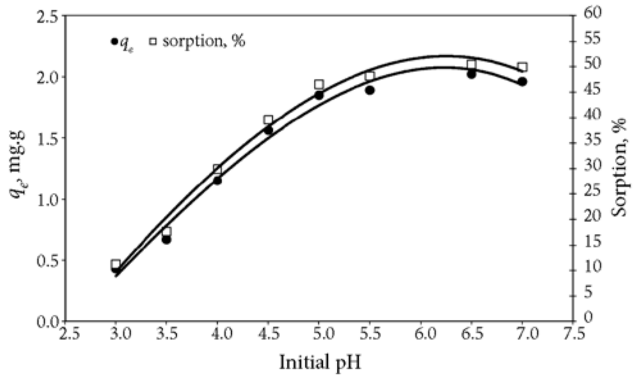

Fig. 2. Initial pH effects on the sorption of Ni^{2+}

2.3. Effect of temperature

The effect of temperature on Ni^{2+} uptake capacity of eggshell was studied and results are presented in Figure 3. As can be seen, Ni^{2+} ions uptake capacity of eggshell increased with increasing temperature up to 318 K. An increase in temperature from 298 to 318 K, increases the q_e values from 1.96 to 2.2 mg/g. Sorption efficiency achieved about 56% at the temperature of 318 K. The removal efficiencies of Ni^{2+} ions at equilibrium were about 50% and 56% at the temperature of 298 K and 318K, respectively. It was assumed that it was probably related with the increase of Ca^{2+} release from the eggshells at higher temperatures. Polat and Aslan (2014) reported that elevating the temperature from 25 to 50 °C, release of Ca^{2+} ions into the aqueous solution increased about two times. Rising temperature might create new active sites by releasing Ca^{2+} ions from the eggshell (Polat, Aslan 2014) and enlarge the pore size of adsorbent (Demirbas *et al.* 2009). Additionally, the collision frequency between adsorbent and Ni^{2+} ions is elevated at high temperatures.

Experimental results indicating that the adsorption of Ni^{2+} ions was favored at higher temperature and the sorption of Ni^{2+} is endothermic in nature. As a results the adsorption capacity of eggshell is improved at high temperature.

2.4. Effect of adsorbent amount

The adsorbent dosage is an important parameter in the sorption process. At a given equilibrium concentration of pollutants, the adsorbent takes up more pollutants at lower adsorbent amount than at higher amounts (Al-Homaidan *et al.* 2014). Effect of eggshell doses on the removal efficiency of Ni^{2+} and q_e values are shown in Figure 4. It was observed that the Ni^{2+} removal efficiency of the eggshell was a function of eggshell amounts in the solution. The percent removal of Ni^{2+} declined along with the decrease in eggshell amount.

It can be seen from the figure that initially the removal efficiency increases gradually with the increase in eggshell amount in the aqueous solution while the q_e values decreases. The maximum adsorption efficiency of Ni^{2+} ion onto the eggshell was found to be 75.1% at the dose of 10 g/L eggshell. The increase in sorption efficiency of heavy metal could be attributed to the increased number and exchangeable sites of adsorbent available for the adsorption (Kumar *et al.* 2011).

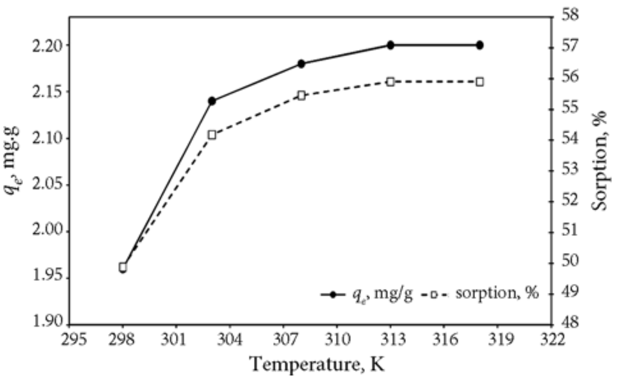

Fig. 3. Effects of temperature on the sorption of process

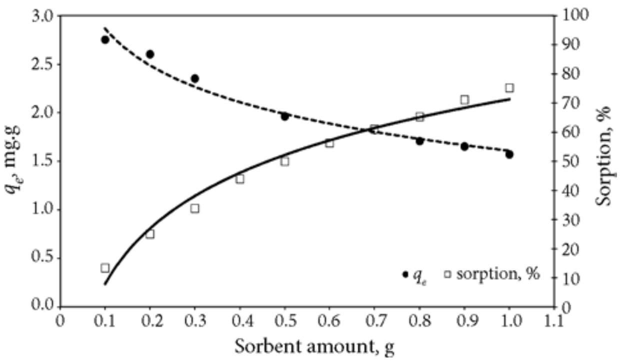

Fig. 4. Effects of eggshell amount on the Ni^{2+} ions sorption

2.5. Modeling of sorption equilibrium depending on Ni^{2+} concentrations

In order to understand the interaction between a sorbate and an adsorbent, it is important to establish the most appropriate correlation for the equilibrium curves. The experimental data were analyzed by applying the most commonly used equilibrium models namely Langmuir, Freundlich, Temkin, and D-R. The mathematical expressions are given in Table 1. Where q_m indicates the monolayer sorption capacity of adsorbate (mg/g). The constants b and E are the mean free energy and sorption per molecule of the sorbate, respectively. Sorption parameters for the isotherms are as follows; K_L (L/mg) Langmuir constant related to the energy of sorption, K_{Fi} (L/mg) Freundlich constant related to the sorption capacity of adsorbent, $q_{\max}$ (mg/g) is the maximum biosorption capacity of D–R. b_T and A_T (L/mg) Temkin isotherm parameters, R is the gas constant (8.314 joule.mol/K); T is the absolute temperature (K). The value of R_L indicates that the shape of the sorption process is; unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Kilic *et al.* 2011; Sljivic *et al.* 2009).

The constants of isotherms equation are presented in Table 2. The best fit was obtained by Langmuir model as compared with the other isotherm models due to determine the highest correlation coefficient value of 0.993. Langmuir model is suggesting that the Ni^{2+} ions were adsorbed onto the eggshell in a monolayer. The maximum monolayer adsorption capacity was found to be 1.845 mg Ni^{2+}/g for the eggshell. The essential characteristic of the Langmuir isotherm can be used to predict the affinity between the sorbent and sorbate using separation factor, "R_L". The R_L was determined to be 0.0119–0.107 for the concentrations of 5.0–50 mg Ni^{2+}/L which indicated that the sorption of Ni^{2+} by waste eggshell sample was favorable.

Previous experimental studies indicated that the pretreatment procedure increase the uptake capacity of sorbents (Ahmad *et al.* 2010; Gupta *et al.* 2010; Ewecharoen *et al.* 2009) and most of the organic materials (Gupta *et al.* 2006; Bhatnagar, Minocka 2010; Celekli, Bozkurt 2011) have higher q_e value than an inorganic materials (Otun *et al.* 2006; Bayat 2002; Rao *et al.* 2002). In order to justify the validity of eggshell as an adsorbent for Ni^{2+} adsorption, adsorption potential is compared with other adsorbents and summarized in Table 3.

2.6. Kinetics of sorption

Sorption kinetics of Ni^{2+} ions on the eggshell were analyzed using four kinetic models for fitting sorption kinetic data: pseudo-first-order, pseudo-second-order, intraparticle diffusion, and Elovich models. Equations for the kinetic models are presented in Table 1. Experiments were

Table 1. Equations of isotherm and kinetic models

	Equations	Plot	Parameters	References
Equilibrium models				
Langmuir	$q_e(mg/g) = q_m \frac{K_L C_e}{1+K_L C_e}$ $R_L = 1/(1+K_L \times C_0)$	C_e/q_e vs · C_e	q_m= 1/slope k_L= slope/intercept	Kilic *et al.* (2011); Sljivic *et al.* (2009)
Freundlich	$q_e(mg/g) = K_{Fi} C_e^{1/n}$	*log* q_e vs · *loq* C_e	k_F = exp (intercept) n = 1/(slope)	Tsai *et al.* (2008)
Temkin	$q_e(mg/g) = B \ln A_T + B\ \ln C_e$	Q_e vs lnC_e	q_e = slope A_t = exp(intercept)/(slope)	Kilic *et al.* (2011)
Dubinin-Radushkevich	$\ln q_e = \ln q_{\max} - \beta\varepsilon^2$ $\varepsilon = RT \ln\left(1+\frac{1}{C_\varepsilon}\right)$	*ln* q_e vs ϵ^2	q_0 = exp(intercept) b = –(slope)	Baig *et al.* (2010)
Kinetic models				
Pseudo first-order	$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$	*log* $(q_e – q_t)$ vs t	q_e = exp(intercept) k_1 = –(slope)	Chiou, Li (2002); Chairat *et al.* (2005)
Pseudo second-order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ $h = k_2 \times q_e^2$	t/q_t vs t	q_e = 1/(slope) k_2 = (slope)^2/(intercept)	Rao *et al.* (2002)
Intra particle diffusion	$q_t = k_{id} t^{1/2} + C$	q_t vs $t^{1/2}$	k_i = slope	Ghasemi *et al.* (2012)
Elovich	$q_t = \frac{1}{\beta}\ln\alpha\beta + \frac{1}{\beta}\ln t$	q_t vs lnt	b = slope a = 1/(slope) exp(intercept/slope)	Demirbas *et al.* (2009)

repeated for different initial eggshell amounts (15–25–35 mg/L) and temperatures (298–308–318 K).

Sorption capacities (q_e) and the calculated values (q_e, k_1, k_2, R^2, and h) from the models are presented in Table 4. Comparison the results of kinetic data, it can be concluded that the pseudo-second-order model provided the best correlation coefficient. In addition, the calculated q_e values derived from the pseudo-second-order were very close to the experimental (q_{exp}) values.

As can be seen from the Table 4 that the equilibrium adsorption capacity, q_e, increases as the initial Ni^{2+} concentration, C_i, increased from 15 to 35 mg/L. However, it was found that the rate constant of pseudo-second-order (k_2) seem to have a decreasing trend with increasing the initial Ni^{2+} concentrations. Similar trends were also observed by applying pseudo-second-order model at various temperatures. For example, the values of q_e increased from 1.96 mg/g to 2.22 mg/g at the temperature of 298 K and 318 K, respectively. The reason for this situation might be attributed to the less competition for the sorption surfaces sites at lower concentration. At higher concentrations, the competition for the surface active sites is high and consequently lower sorption rates are achieved (Kumar *et al.*

Table 2. Correlation coefficient and adsorption parameters for the models

Model	Sorption Parameters	
Freundlich	R^2	0.688
	n	4.63
	K_F	1.061
Langmuir	R^2	0.993
	R_L	0.033
	q_m	1.845
	K_L	1.665
Temkin	R^2	0.690
	B_T	0.282
	$A_T(L/g)$	29.96
R-D	R^2	0.946
	q_0 (mg/g)	1.83
	β (mol^2/j^2)	0.519
	E (kj/mol)	0.98

2011). These results confirmed that the chemisorption mechanisms may play an important role for the sorption of Ni^{2+} on the eggshell.

2.7. Adsorption thermodynamics

In order to determine the thermodynamic parameters – such as free energy ($\Delta G°$, Kj/mol), entalphy ($\Delta H°$, Kj/mol), and entropy ($\Delta S°$, j/mol/K) – change of Ni^{2+} adsorption onto the eggshell, the batch experiments were performed at different temperatures of 298, 303, 308, 313, and 318 K. The thermodynamic parameters are calculated using the following equations (Mezenner, Bensmailli 2009):

$$\Delta G° = -RT \cdot \ln K_d; \quad (3)$$

$$\text{Ln } K_d = -(\Delta H°/RT) + (\Delta S°/R), \quad (4)$$

where K_d is the distribution coefficient for the adsorption.

Table 3. Comparison of maximum monolayer adsorption on Ni (II) ions onto various adsorbents

Adsorbents	q_m (mg/g)	K_L (ml/g)	References
Pomegranate peel	69.4	24.10^3	Bhatnagar, Minocka 2010
Spirulina platensis	69.04	0.0019	Celekli, Bozkurt 2011
Irradiation-grafted activated carbon	55.7	0.009	Ewecharoen *et al.* 2009
Acid-treated alga	44.247	0.063	Gupta *et al.* 2010
Activated carbon	44.1	0.005	Ewecharoen *et al.* 2009
Untreated alga	40.983	0.060	Gupta *et al.* 2010
Modified activated carbon II	37.175	0.091	Hasar 2003
Modified activated carbon I	30.769	0.025	Hasar 2003
Cashew nut shell	18.868	0.071	Kumar *et al.* 2011
Calcined phosphate	15.53	0.299	Hannachi *et al.* 2010
Clarified sludge	14.3	0.222	Hannachi *et al.* 2010
Red mud	13.63	0.102	Hannachi *et al.* 2010
Anode dust	8.64	$6.50 \cdot 10^{-3}$	Strkalj *et al.* 2010
Powdered eggshell	7.0	0.281	Otun *et al.* 2006
Smectite clay	6.68	0.586	Mbadcam *et al.* 2012
Sawdust	4.6	38.14	Bozic *et al.* 2009
Sepiolite	3.44	0.24	Sanchez *et al.* 1999
eggshell	2.36	0.478	Ghazy *et al.* 2011
eggshell	1.84	1.665	This study
Bael tree leaf powder	1.527	0.0622	Kumar, Kirthika 2009
Fly ash (Seyitomer)	1.160	1.839	Bayat 2002
Fly ash (Afşin-Elbistan)	0.787	2.092	Bayat 2002
Fly ash	0.249	0.0684	Agarwal *et al.* 2013
Fly ash	0.03	0.08	Rao *et al.* 2002
Bagasse	0.001	0.48	Rao *et al.* 2002

Table 4. Parameters of adsorption kinetics of Ni2+ by eggshell

Ni^{2+} (mg/L)	q_e (exp) (mg/g)	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion			Elovich		
		q_e	k_1	R^2	q_e	k_2	R^2	h	k_p	R^2	α	β	R^2
15	1.6	0.035	0.453	0.823	1.62	0.49	0.996	1.29	0.055	0.629	775	7.813	0.723
25	1.94	0.028	0.782	0.795	1.97	0.112	0.997	0.434	0.096	0.904	15.38	4.74	0.910
35	2.28	0.021	1.183	0.919	2.32	0.0613	0.993	0.33	0.141	0.918	2.76	3.14	0.986
Temperature (K)													
298	1.96	0.0138	0.723	0.685	1.71	0.304	0.999	0.89	0.09	0.797	20.07	5.21	0.955
308	2.39	0.0253	0.991	0.848	2.44	0.082	0.993	0.488	0.126	0.678	6.32	3.24	0.848
318	2.22	0.035	1.167	0.947	2.29	0.080	0.997	0.419	0.143	0.825	2.45	2.96	0.967

The calculated values of thermodynamic parameters are presented in Table 5. The value of Δ*G*° is small at 298 K and negative with increase in temperature. It indicates that the adsorption process leads to an increase in Gibbs energy. The negative Δ*G*° value means the Ni^{2+} sorption onto the eggshell is feasible and spontaneous in the nature. The value of Δ*H*° (13.66 kj/mol) and Δ*S*° (0.136 Kj/mol/K) were determined from the data. The positive values of Δ*H*° and Δ*S*° suggests the endothermic nature of process and randomness at the eggshell – solution interface during the sorption (Katal *et al.* 2012).

Table 5. Thermodynamic parameters for the adsorption of Ni^{2+} onto eggshell

	Δ*H*° (kj/mol)	Δ*S*° (kj/mol/K)	Δ*G*° (kj/K.mol)				
			298 K	303 K	308 K	313 K	318 K
Ni^{2+}	13.66	0.136	0.013	−0.422	−0.561	−0.610	−0.629

Conclusions

As can be seen from the experimental results, the waste eggshells might be used for nickel removal from aqueous solution. Following conclusions could be drawn from the study:

1. The maximum sorption capacities were determined at the pH value of 6.5. Adsorption of Ni^{2+} was highly temperature dependent.
2. The Ni^{2+} ions were adsorbed onto the eggshell in a monolayer due to the highest correlation coefficient (0.9995) was determined using the Langmuir model comparing with the other models.
3. The sorption perfectly complies with pseudo-second order reaction than the others (pseudo first order kinetics, intraparticle diffusion, and Elovich models) and the sorption of Ni^{2+} onto the eggshell appeared to be controlled by the chemisorption process.
4. Of the thermodynamic point of view, the sorption mechanisms of Ni^{2+} ions onto the eggshell was endothermic.

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References

Ahmad, R.; Kumar, R.; Haseeb, S. 2010. Adsorption of Cu^{2+} from aqueous solution onto iron oxide coated eggshell powder: evaluation of equilibrium, isotherms, kinetics, and regeneration capacity, *Arabian Journal of Chemistry* 5(3): 353–359. http://dx.doi.org/10.1016/j.arabjc.2010.09.003

Aikpokpodion, P. E.; Ipinmoroti, R. R.; Omotoso, S. M. 2010. Biosorption of nickel (II) from aqueous solution using waste tea (Camella cinencis) materials, *American – Eurasian Journal of Toxicological Sciences* 2(2): 72–82 [online], [cited July 2014]. Available from Internet: http://www.idosi.org/aejts/aejts2(2)10.htm

Agarwal, A. K.; Kadu, M. S.; Pandhurnekar, C. P.; Muthreja, I. L. 2013. Removal of nickel (II) ions from aqueous solution using thermal power plant fly ash as a low cost adsorbent, *International Journal of Environmental Protection* 3(3): 33–43 [online], [cited July 2014]. Available from Internet: http://www.ij-ep.org/paperInfo.aspx?ID=200

Aksu, Z.; Donmez, G. 2006. Binary biosorption of cadmium(II) and nickel(II) onto dried Chlorella vulgaris: co-ion effect on mono-component isotherm parameters, *Process Biochemistry* 41: 860–868. http://dx.doi.org/10.1016/j.procbio.2005.10.025

Al-Homaidan, A. A.; Al-Houri, H. J.; Al-Hazzani, A. A.; Elgaaly, G.; Moubayed, N. M. S. 2014. Biosorption of copper ions from aqueous solutions by Spirulina platensis biomass, *Arabian Journal of Chemistry* 7: 57–62. http://dx.doi.org/10.1016/j.arabjc.2013.05.022

Aslan, S.; Gurbuz, B. 2011. Influence of operational parameters and low nickel concentrations on partial nitrification in a submerged biofilter, *Applied Biochemistry and Biotechnology* 165: 1543–1555. http://dx.doi.org./10.1007/s12010-011-9374-0

Baig, J. A.; Kazi, T. G.; Shah, A. Q.; Kandhro, G. A.; Afridi, H. I.; Khan, S.; Kolachi, N. F. 2010. Biosorption studies on powder of stem of Acacia nilotica: removal of arsenic from surface water, *Journal of Hazardous Materials* 178: 941–948. http://dx.doi.org/10.1016/j.jhazmat.2010.02.028

Bar-Sela, S.; Levy, M.; Westin, J. B.; Laster, R.; Richter, E. D. 1992. Medical findings in nickel-cadmium battery workers, *Israel Journal of Medical Sciences* 28: 51–53 [online], [cited July 2014]. Available from Internet: http://www.ncbi.nlm.nih.gov/pubmed/1428813

Bayat, B. 2002. Comparative study of adsorption properties of Turkish fly ashes I. The case of nickel(II), copper(II) and zinc(II), *Journal of Hazardous Materials* B95: 251–273. http://dx.doi.org/10.1016/S0304-3894(02)00140-1

Bermúdez, Y. G.; Rico, I. L. R.; Bermúdez, O. G.; Guibal, E. 2011. nickel biosorption using Gracilaria caudata and Sargassum muticum, *Chemical Engineering Journal* 166: 122–131. http://dx.doi.org/10.1016/j.cej.2010.10.038

Bhatnagar, A.; Minocha, A. K. 2010. Biosorption optimization of nickel removal from water using Punica granatum peel waste, *Colloids and Surfaces B: Biointerfaces* 76: 544–548. http://dx.doi.org/10.1016/j.colsurfb.2009.12.016

Bozic, D.; Stankovic, V.; Gorgievski, M.; Bogdanovic, G.; Kovacevic, R. 2009. Adsorption of heavy metal ions by sawdust of deciduous trees, *Journal of Hazardous Materials* 171: 684–692. http://dx.doi.org/10.1016/j.jhazmat.2009.06.055

Celekli, A.; Bozkurt, H. 2011. Bio-sorption of cadmium and nickel ions using Spirulina platensis: kinetic and equilibrium studies, *Desalination* 275: 141–147. http://dx.doi.org/10.1016/j.desal.2011.02.043

Celekli, A.; Atmaca, M.; Bozkurt, H. 2010. An ecofriendly process: predictive modelling of copper adsorption from aqueous solution on Spirulina platensis, *Journal of Hazardous Materials* 173: 123–129. http://dx.doi.org/10.1016/j.jhazmat.2009.08.057

Chairat, M.; Rattanaphani, S.; Bremner, J. B.; Rattanaphani, V. 2005. An adsorption and kinetic study of lac dyeing on silk, *Dyes and Pigments* 64: 231–241. http://dx.doi.org/10.1016/j.dyepig.2004.06.009

Chiou, M. S.; Li, H. Y. 2002. Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads, *Journal of Hazardous Materials* B93: 233–248. http://dx.doi.org/10.1016/S0304-3894(02)00030-4

Chojnacka, K. 2005. Biosorption of Cr (III) ions by eggshells, *Journal of Hazardous Materials* B121: 167–173. http://dx.doi.org/10.1016/j.jhazmat.2005.02.004

Demirbas, E.; Dizge, E.; Sulak, M. T.; Kobya, M. 2009. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon, *Chemical Engineering Journal* 148: 480–487. http://dx.doi.org/10.1016/j.cej.2008.09.027

Erdogan, S.; Onal, Y.; Basar, C. A.; Erdemoglu, S. B.; Ozdemir, C. S.; Koseoglu, E.; Icduygu, G. 2005. Optimization of nickel adsorption from aqueous solution by using activated carbon prepared from waste apricot by chemical activation, *Applied Surface Science* 252: 1324–1331. http://dx.doi.org/10.1016/j.apsusc.2005.02.089

EU. 2011. *European and National Drinking Water Quality Standards*. Northern Ireland Environment Agency, Department for Regional Development, October 2011.

Ewecharoen, A.; Thiravetyan, P.; Wendel, E.; Bertagnolli, H. 2009. Nickel adsorption by sodium polyacrylate-grafted activated carbon, *Journal of Hazardous Materials* 171: 335–339. http://dx.doi.org/10.1016/j.jhazmat.2009.06.008

Ghasemi, Z.; Seif, A.; Ahmadi, T. S.; Zargar, B.; Rashidi, F.; Rouzbahani, G. M. 2012. Thermodynamic and kinetic studies for the adsorption of Hg(II) by nano-TiO_2 from aqueous solution, *Advanced Powder Technology* 23: 148–156. http://dx.doi.org/10.1016/j.apt.2011.01.004.

Ghazy, S. E.; El-Asmy, A. A.-H.; El-Nokrashy, A. M. 2011. Batch removal of nickel by eggshell as a low cost sorbent, *International Journal of Industrial Chemistry* 2(4): 242–252 [online], [cited July 2014]. Available from Internet: http://www.ijichem.org/FCKUploaded/file/Archive%20Issue/2011/2/4/article_7.pdf.

Gupta, V. K.; Rastogi, A.; Saini, V. K.; Jain, N. 2006. Biosorption of copper(II) from aqueous solutions by Spirogyra species, *Journal of Colloid and Interface Science* 296: 59–63. http://dx.doi.org/10.1016/j.jcis.2005.08.033

Gupta, V. K.; Rastogi, A.; Nayak, A. 2010. Biosorption of nickel onto treated alga (Oedogonium hatei): application of isotherm and kinetic models, *Journal of Colloid and Interface Science* 342: 533–539. http://dx.doi.org/10.1016.j.jcis.2009.10.074

Hannachi, Y.; Shapovalov, N. A.; Hannachi, A. 2010. Adsorption of nickel from aqueous solution by the use of low-cost adsorbents, *Korean Journal of Chemical Engineer* 27(1): 152–158. http://dx.doi.org/10.1016.j.jcis.2009.10.074

Hasar, H. 2003. Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from almond husk, *Journal of Hazardous Materials* B97: 49–57. http://dx.doi.org/10.1007/s11814-009-0303-7

Katal R.; Baei, M. S.; Rahmati, H. T.; Esfendian, H. 2012. Kinetic, isotherm, and thermodynamic study of nitrate adsorption from aqueous solution using modified rice husk, *Journal of Industrial Chemistry* 18: 295–302. http://dx.doi.org/10.1016/j.jiec.2011.11.035

Kilic, M.; Varol, E. A.; Putun, A. E. 2011. Adsorptive removal of phenol from aqueous solutions on activated carbon prepared from tobacco residues: equilibrium, kinetics and thermodynamics, *Journal of Hazardous Materials* 189: 397–403. http://dx.doi.org/10.1016/j.jhazmat.2011.02.051

Kleinubing, S. J.; Guibal, E.; Silva, E. A.; Silva, M. G. C. 2012. Copper and nickel competitive biosorption simulation from single and binary systems by Sargassum filipendula, *Chemical Engineering Journal* 184: 16–22. http://dx.doi.org/10.1016/j.cej.2011.11.023

Krishnan, K. A.; Sreejalekshmi K. G.; Baiju, R. S. 2011. Nickel(II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith, *Bioresource Technology* 102: 10239–10247. http://dx.doi.org/10.1016/j.biortech.2011.08.069

Kumar, P. S.; Ramalingam, S.; Kirupha, S. D.; Murugesan, A.; Vidhyadevi, T.; Sivanesan, S. 2011. Adsorption behavior of nickel(II) onto cashew nut shell: equilibrium, thermodynamics, kinetics, mechanism and process design, *Chemical Engineering Journal* 167: 122–131. http://dx.doi.org/10.1016/j.cej.2010.12.010

Kumar, P. S.; Kirthika, K. 2009. Equilibrium and kinetic study of adsorption on nickel from aquous solution onto Bael Tree leaf powder, *Journal of Engineering Science and Technology* 4(4): 351–363 [online], [cited July 2014]. Available from Internet: http://jestec.taylors.edu.my/Vol%204%20Issue%204%20December%2009/Vol_4_4_351_363_P.%20Senthil%20Kumar.pdf

Liu, D.; Tao, Y.; Li, K.; Yu, J. 2012. Influence of the presence of three typical surfactants on the adsorption of nickel (II) to aerobic activated sludge, *Bioresource Technology* 126: 56–63. http://dx.doi.org/10.1016/j.biortech.2012.09.025

Malkoc, E.; Nuhoglu, Y. 2009. Removal of Ni(II) ions from aqueous solutions using waste of tea factory: adsorption on a fixed-bed column, *Journal of Hazardous Materials* B135: 328–336. http://dx.doi.org/10.1016/j.jhazmat.2005.11.070

Mbadcam, K.; Dongmo, J. S.; Ndaghu, D. D. 2012. Kinetic and thermodynamic studies of the adsorption of nickel (II) ions from aqueous solution by smectite clay from Sabga-Cameroon, *International Journal of Current Research* 4(5): 162–167 [online], [cited July 2014]. Available from Internet: http://www.journalcra.com/article/kinetic-and-thermodynamic-studies-adsorption-nickel-ii-ions-aqueous-solutions-smectite-clay-

Mezenner, N. Y.; Bensmaili, A. 2009. Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste, *Chemical Engineering Journal* 147: 87–96. http://dx.doi.org/10.1016/j.cej.2008.06.024

Oladunni, N.; Agbaji, E. B.; Idris, S. O. 2012. Removal of Pb^{2+} and Ni^{2+} ions from aqueous solutions by adsorption onto activated locust bean (Parkia biglobosa) husk, *Scholars Research Library Archives of Applied Science Research* 4(6): 2308–2321. http://dx.doi.org/10.3923/jas.2006.2376

Otun, J. A.; Oke, I. A.; Olarinoye, N. O.; Adie, D. B.; Okuofu, C. A. 2006. Adsorption isotherms of Pb (II), Ni (II) and Cd (II) ions onto PES, *Journal of Applied Sciences* 6(11): 2368–2376. http://dx.doi.org/10.3923/jas.2006.2368.2376

Pahlavanzadeh, H.; Keshtkar, A. R.; Safdari, J.; Abadi, Z. 2010. Biosorption of nickel(II) from aqueous solution by brown algae: equilibrium, dynamic and thermodynamic studies, *Journal of Hazardous Materials* 175: 304–310. http://dx.doi.org/10.1016/j.jhazmat.2009.10.004

Polat, A.; Aslan, S. 2014. Kinetic and isotherm study of cupper adsorption from aqueous solution using waste eggshell, *Journal of Environmental Engineering and Landscape Management* 22(2): 132–140. http://dx.doi.org/10.3846/16486897.2013.865631

Prabakaran, R.; Arivoli, S. 2012. Adsorption kinetics, equilibrium and thermodynamic studies of Nickel adsorption onto Thespesia Populnea bark as biosorbent from aqueous solutions, *Scholars Research Library European Journal of Applied Engineering and Scientific Research* 1(4): 134–142 [online], [cited July 2014]. Available from Internet: http://scholarsresearchlibrary.com/archive.html

Rao, M.; Parwate, A. V.; Bhole, A. G. 2002. Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash, *Waste Management* 22: 821–830. http://dx.doi.org/10.1016/S0956-053X(02)00011-9

Sanchez, A. G.; Ayuso, E. A.; Blas, J. 1999. Sorption of heavy metals from industrial wastewater by low cost mineral silicates, *Clay Minerals* 34: 469–477. http://dx.doi.org/101180/000985599546370

Shah, J.; Jan, M. R.; Haq, A.; Zeeshan, M. 2012. Equilibrium, kinetic and thermodynamic studies for sorption of Ni (II) from aqueous solution using formaldehyde treated waste tea leaves, *Journal of Saudi Chemical Society* (in press). http://dx.doi.org/10.101016/j.jics.2012.04.004

Sljivic, M.; Smiciklas, I.; Plecas, I.; Mitric, M. 2009. The influence of equilibration conditions and hydroxyapatite physico-chemical properties onto retention of Cu^{2+} ion, *Chemical Engineering Journal* 148: 80–88. http://dx.doi.org/10.1016/j.cej.2008.08.003

Strkalj, A.; Rađenović, A.; Malina, J. 2010. Adsorption of Ni (II) ions from aqueous solution on anode dust: effect of pH value, *RMZ – Materials and Geoenvironment* 57(2): 165–172 [online], [cited July 2014]. Available from Internet: http://www.rmz-mg.com/letniki/rmz57/RMZ57_0165-0172.pdf

Thevannan, A.; Hill, G.; Niu, C. H. 2011. Kinetics of nickel biosorption by acid-washed barley straw, *The Canadian Journal of Chemical Engineering*, 89(1): 176–182. http://dx.doi.org/10.1016/j.biortech.2007.04.010

Tsai, W.-T.; Hsien, K.-J.; Hsu, H.-C. ; Lin, C.-M.; Lin, K.-Y.; Chiu, C.-H. 2008. Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution, *Bioresource Technology* 99: 1623–1629. http://dx.doi.org/10.1016/j.biortech.2007.04.010

USEPA. 2012. *Guidelines for Water Reuse* EPA/600/R-12/618, September. United States Environmental Protecction Agency [online], [cited July 2014]. Available from Internet: http://water.epa.gov/drink/contaminants/index.cfm

WHO. 2005. *Nickel in drinking-water*. Background document for development of WHO Guidelines for Drinking-water Quality, World Health Organization, Geneva, Switzerland [online], [cited July 2014]. Available from Internet: http://www.who.int/water_sanitation_health/gdwqrevision/nickel2005.pdf

Yang, F.; Liu, H.; Qu, J.; Chen, J. P. 2011. Preparation and characterization of chitosan encapsulated *Sargassum sp.* biosorbent for nickel ions sorption, *Bioresource Technology* 102: 2821–2828. http://dx.doi.org/10.1016/j.biortech.2010.10.038

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