

Research Article

Kinetics and Adsorption of Removal of Ni (II) ions by using Egg Shell Powder

K. Senthilkumar¹,*, V.Chitradevi¹, S. Mothil¹, M. Naveen Kumar¹, N. Sri Kokilavani²

 ¹Department of Chemical Engineering, Kongu Engineering College, Erode, Tamil Nadu – 638 060. India.
²Department of Chemical Engineering, Erode Sengunthar Engineering College, Erode, Tamil Nadu – 638 051. India.

*Corresponding author's e-mail: <u>uksen2003@gmail.com</u>

Abstract

The removal of Nickel (II) ions from wastewater by adsorption using eggshell powder was investigated. The adsorbent is cheap and easily available. The main parameters like solution pH, adsorbent dose, adsorbent size, initial concentration of metal ions, initial volume of effluent, agitation speed and temperatures influencing the adsorption process, were examined. The adsorption kinetics like Pseudo first order, pseudo second order, intra particle diffusion, fractional power and Elovich's equations were applied. The adsorption isotherms like Freundlich, Langmuir, Temkin and BET were also studied. Significant results on the removal of Ni (II) ions were achieved up to 90%. Fractional model and Temkin isotherm were applied and studied in this process.

Keywords: Adsorption; Eggshell; Nickel (II); Kinetics; Isotherm; Temkin; Fractional power model.

Introduction

Heavy metal pollutants in wastewater are increasing day by day because of the process industries. These pollutants are not biodegradable and can lead to bioaccumulation in living organisms causing health problems in animals, plants, and human life [1]. Recently, the application of a wide variety of low-cost adsorbent materials for the removal of heavy metals has raised considerable interest among researchers [2]. These pollutants can be readily absorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [3]. Metals are the main environmental concerns, because of their unique characteristics unlike organic pollutants; they are non-biodegradable and hence accumulated by organisms [4]. Due living to toxicity. incremental accumulation in the food chain and persistence in the ecosystem, wastewaters containing heavy metals are required to be properly treated prior to discharge into receiving waters [5].

Nickel was selected as adsorbate, because its compounds have widespread applications in many industrial processes such as non-ferrous metal, mineral processing, paint formulation, electroplating, batteries manufacturing, forging, porcelain enameling, copper sulfate manufacture, steam-electric power plants and dye industries, thus leading to relatively high concentrations in aquatic environment [6]. Nickel is one of the toxic heavy metals, which is quite common compared to other metal pollutants [4]. In humans, Nickel can cause serious problems, such as dermatitis, allergic sensitization, lungs, kidneys, skin and nervous system damages. It is also known as carcinogen [4]. It is important to treat industrial effluents polluted with Ni (II) ions before they are discharged into the receiving water bodies. Adsorption compared with other methods appears to be an attractive process in view of its efficiency and the ease with which it can be applied in the treatment of heavy metal containing wastewater [7].

It is necessary to have a low-cost material to treat large volumes of waste water. The use of egg shell powder as low-cost sorbents had been thoroughly investigated in this study. One of the cheap and easily available material having possibilities as a suitable sorbent for Ni (II) ions is eggshell. Due to their high calcium content, eggshells usually have no commercial importance. Disposal of eggshells is also a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs [9]. Since the eggshell is mainly composed of calcium carbonate i.e. calcite, it can be used as adsorbents [10], calcareous soil [11].

The hen eggshell mainly consists of two regions: the mammillary matrix (i.e., eggshell membrane) consisting of interwoven protein fibers and spherical masses, and the spongy matrix (i.e., calcified eggshell) made of interstitial calcite or calcium carbonate crystal [12, 13]. The by-product eggshell weighs approximately 10 % of the total mass (~ 60 g) of hen egg, representing a significant waste from the egg-derived products processor because it was traditionally useless and commonly disposed of in landfills without any pretreatment. This to describe the adsorption work aims characteristic of Ni (II) on eggshell concentrating on various operational parameters such as pH, adsorbent dosage, adsorbent size, initial concentration of effluent, initial volume of speed agitation and temperature. effluent. Experimental were analyzed by plotting adsorption isotherms and kinetics. Moreover, the cheap and effective powdered waste eggshell (ES) was used as inorganic sorbent for the removal of Ni (II) ions from industrial effluent.

Materials and methods

Preparation of adsorbents

Initially, the raw egg shells used for this study were collected from nearby hotels. The samples were collected, washed with water and dried for 2 h in large trays in an oven maintained at 60°C, allowed to cool to room temperature, crushed, sieved and those with size (0.15 to 0.048 mm) were used in the experiments. The chemical composition (%, w/w) of by-product eggshell has been reported as follows: calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) [20, 21].

Preparation of stock solution

The synthetic stock solution of Ni (II) 1000 mg/l of Nickel (II) was prepared by dissolving 4.478 g of nickel sulphate (NiSO₄.H₂O) in 100 ml double distilled water.

Analysis of metal

Nickel (II) estimated was spectrophotometrically using Dimethyl Glyoxime (DMG). The solution containing less than 100 µg Ni (II) was transferred into 25 ml standard flask. 5 ml of 25 % sodium citrate was added to 10 ml of 0.5 N HCl and 1 ml of iodine solution (0.05 N) was also added in addition to 2 ml of dimethyl glyoxime (0.5 %) solution. The solution was made up to the mark with distilled water. The absorbance was measured using ELICO Bio UV Vis- Spectrophotometer after 20 min, at 470 nm against blank. A calibration graph with absorbance versus Nickel (II) concentration was prepared. The amount of Nickel (II) present was obtained from the calibration curve [14].

Procedure

Adsorption studies were performed in batch process. The concentrated stock solution was diluted by double distilled water to various concentrations like 500 ppm, 750 ppm and 1000 ppm. For the experimental study 500 ppm solution was accounted. The pH is varied from 2 to 12. For the different adsorbent dosage (0.5 to 1 gm/100 ml) the experiment was carried out. For different adsorbent size (0.15, 0.112 and 0.061 mm) batch adsorption process was carried out. The removal of Ni (II) was examined by varying the initial concentration from 500 ppm to 1000 ppm. The same process was carried out for various effluent volumes (50 ml, 150 ml and 200 ml), different agitation speeds (90 rpm, 120 rpm and 180 rpm) and also at different temperatures (50°C, 60°C and 70°C).

The percentage adsorption of Ni (II) ions from the solution was calculated by eq. 1.

% Adsorption = $(C_0 - C_r)/C_0 \times 10$ (1) Where C_i initial concentration of Ni (II) ions (mg/l); Cr residual concentration in the filtrate after shaking for a definite time period, (mg/l). The metal uptake at a particular time $q_t (mg/g)$ was calculated by eq. 2.

 $q_t = [(C_0 - C_r)/m] * V \dots (2)$

The amount of metal adsorbed at equilibrium, q_e (mg/g) was calculated by eq. 3.

 $q_e = [(C_0 - C_e)/m] * V \dots (3)$ Where, $C_e (mg l^{-1})$ is the concentrations of metal at equilibrium. Due to the inherent bias resulting from linearization of the isotherm model and kinetic model, the non-linear regression Root Mean Square Error (RMSE) test was employed as criterion for the quality of fitting [15] shown in eq. 4. The root mean square error of a model is evaluated by:

RMSE =
$$\sqrt{\frac{\sum (q_t - q_e)^2}{n - 2}}$$
(4)

Where, $q_t (mg/g)$ is the experimental value of uptake, q_e is the calculated value of uptake using a model (mg/g), and n is the number of observations in the experiment. The smaller RMSE value indicates the better curve fitting [15].

Results and discussions

Effect of pH

Initial pH is the important parameter for the protonation of the binding sites. Moreover, the adsorption of divalent nickel by Egg shell is also influenced by the surface properties of the adsorbent and nickel species present in effluent. In order to study the effect, pH of solution was varied from 2.0 to 12.0. It is well established that at pH < 8, the predominant species of nickel is Ni^{2+} . At pH > 8, nickel ion in the 2+ state seems to be capable of being hydrolyzed to $NiOH^+$, soluble Ni (OH) ₂ and Ni (OH) ₃ and solid Ni (OH)₂ [16, 17]. The powdered eggshell consists mainly of CaCO₃. When calcium carbonate (as sparingly soluble salt-type mineral) suspended with water, HCO_3^- , Ca_2^+ , was CaHCO₃⁺ and CaHO⁺ are formed as surfacecharged species and their presence is a function of solution pH [18].

At low pH values, H^+ ions compete with Ni (II) ions for the surface of the adsorbent which would hinder the Ni (II) ions from reaching the binding sites of the adsorbent caused by repulsive forces. Also, the lower removal of Ni (II) ions at pH= 3 may be attributed to the partial solubility of Egg shell sorbent used (consists mainly of CaCO₃). When pH is increased, the Ni (II) ions get precipitated due to increase in hydroxide anion forming a nickel hydroxide precipitates. For this reasons, the optimal pH was selected to be 4 with 120 min shaking for further experiment at studies. At the pH 4, the Ni (II) ions get maximum removal (Fig. 1).

Effect of adsorbent dosage

The effect of Ni (II) ions concentration on adsorbent dosage was calculated by varying the amount of adsorbent from 0.1 to 2.5 g. It was observed that the increase in the adsorbent dosage, leads to an increase of metal removal. As there is more surface area for the adsorption process, the more metal ions get adsorbed onto the surface of the powdered egg shell (Fig. 2).



Fig. 1. Effect of pH on removal of Ni (II)





Effect of adsorbent size

The effect of adsorbent size was calculated by varying the size of adsorbent from 0.15 mm, 0.112 mm, 0.061 mm. The study was carried out at the temperature of 30°C and at the optimum pH and adsorbent dosage for the metal. The process is carried out for 120 min. After certain time, the adsorption process attains equilibrium (Fig. 3). Very slow increase in removal of Ni (II) beyond an optimum dose may be attributed to attainment of equilibrium between adsorbate and adsorbent at the preferred operating conditions [19]. Higher adsorbent dose cause screening effect of dense outer layer of cells, blocking the binding sites from metal ions, resulting in lower metal removal per unit adsorbent [20,29,30].

Effect of initial concentration

The effect of initial concentration of effluent on Egg shell at room temperature by keeping the optimized value unchanged. These values are maintained constant for the further studies. The rate of adsorption increases with increase in initial concentration. But after the process reached equilibrium, i.e, after 120 min there was no increase in the metal removal. At 500 ppm, the removal attained equilibrium (Fig. 4). This result show that the removal of metal ions on egg shell powder depends on initial concentration of effluent. Moreover, with increasing Ni (II) concentration in the synthetic solution, the diffusion of Ni (II) ions in the boundary layer increases resulting in higher sorption by egg shell powder [31].



Fig. 3. Effect of adsorbent sizes on removal of Ni (II) (a - 0.15 mm, b - 0.112 mm & c - 0.061 mm)



Fig. 4. Effect of initial concentrations on removal of Ni (II) (a–500 ppm, b–750 ppm & c–1000 ppm)

Effect of initial volume

Adsorption of Ni (II) for different initial volume of effluent (50 ml, 150 ml and 200 ml) on Egg shell powder was conducted. As there are more ions for adsorption, the optimized amount of dosage adsorbs more ions till equilibrium was attained. The increase in the effluent volume tends to more rate of adsorption. Maximum removal was attained at maximum volume (Fig. 5).



Fig. 5. Effect of initial volumes on removal of Ni (II) (a - 50 ml, b - 150 ml & c - 200 ml)

Effect of temperature

temperature The studies were investigated by carrying out batch studies at the optimal conditions and different temperatures [21,32]. The temperature was varied from 30 to 60°C by keeping all the optimized parameters unchanged. The influence of temperature in the adsorption of Ni (II) on Egg shell powder was noted. Pure adsorption kinetics in the range of 30 to 60°C, also follows pseudo second order rate equation. The equilibrium amount absorbed increases linearly with increase also in temperature. This may be due to the movements of the accelerated metal ions. These ions get easily adsorbed on the surface of the adsorbate (Fig. 6).



Fig. 6. Effect of temperatures on removal of Ni (II) $(a - 40^{\circ}C, b - 50^{\circ}C \& c - 60^{\circ}C)$

Effect of agitation time

Agitation speed is an important parameter to be considered. For the various agitation speeds like 90 rpm, 120 rpm and 180 rpm the adsorption studies was carried out in room temperature with optimized value. With increase in the agitation speed the metal removal was found to increase, which may be due to forces between the molecules, resulting with more metals gets bind to the surface of the adsorbate. There is no further increase in the removal after the equilibrium was attained (Fig. 7). Increase in the removal was due to the decrease in the boundary layer thickness.



Agitation speed rpm

Fig. 7. Effect of agitation speed on removal of Ni (II)

Kinetics of adsorption

In order to examine the mechanism of adsorption, suitable kinetic model is necessary to analyze the rate data. The dynamics of adsorption describes the rate of Ni (II) uptake on egg shell powder and this rate controls the equilibrium time. In order to study the mechanism of sorption and potential rate determining steps, different kinetic models have been used to test experimental data obtained from two different process variables (Different initial concentration and different temperatures). The adsorption dynamics of the Ni (II) on egg shell were tested with the Lagergren pseudo-first order [25], the chemisorptions pseudo-second order [26], Elovich kinetic model [23], the intraparticle diffusion model [22], and Fractional power model [26].

Pseudo first order

The adsorption kinetics may be described by a pseudo first-order equation. The linear pseudo first-order equation is given by eq. (5).

$$\log (q_{e} - q_{i}) = \log q_{e} - \frac{k_{I} t}{2.303} \qquad \dots (5)$$

Where q_e and q_t are the amounts of metal ions adsorbed (mg/g) at equilibrium and at time *t*, respectively, and k₁ is the equilibrium rate constant of pseudo first-order adsorption, (min⁻¹). The linear plot of log (q_e – q_t) versus *t* shows the appropriateness of the above equation and consequently, the first-order nature of the process. At various temperatures and for different concentrations experiments were conducted. The theoretical q_e values found from the first-order kinetic model did not give any reasonable values. This suggests that this adsorption system is not a first-order.

Pseudo second order

The linear pseudo second-order equation is given by eq. (6).

 $t/q_t = 1/k_2 q_e^2 + 1/q_t * t$ (6)

Where k_2 the equilibrium is rate constant of pseudo second-order adsorption (g/mg.min). The slopes and intercepts of plots t/q_t versus t were used to calculate the second-order rate constants k_2 and q_e . The plot of t/qt versus t did not show any good agreement of experimental data with the second-order kinetic model for different temperatures and initial concentrations (Table 1 and Table 2). The obtained regression coefficients for the second order kinetic model were not in acceptable value. This shows that this model not suits for the adsorption of Ni (II) ions.

Fractional power model

The adsorption kinetics can also be described by power function equation. The linear power function equation is given by eq. (7).

 $\ln q_t = \ln k + \mu \ln t \qquad \dots (7)$

The plot ln q and ln t should give linear relationship from which μ and k can be determined from the slope and intercept of the plot respectively. For different temperatures and concentrations, the model was checked to fit. The results indicated that the power function model described the time-dependent. The kinetic of Ni (II) ion adsorption can be satisfactory described by power function model. Power model describes rates of adsorption (as in the common Freundlich model). However, the regression coefficient R² was very high (<0.99) (Table 2) which indicates that power function is the best model to correlate kinetic data.

Intra particle diffusion

The rate parameters for intraparticle diffusion at different initial concentrations are determined using the following eq. (8).

$$q_t = k_{int} t^{1/2} \dots (8)$$

Where k is the intraparticle diffusion rate (mg/g.min). The mechanism constant, of adsorption is complex but that intraparticle diffusion is important in the early stages. In this case, the first linear portions observed at different temperatures and concentrations may be due to intraparticle diffusion effects. The slopes of these linear portions can be defined as a rate parameter and characteristic of the rate of adsorption in the region where intraparticle diffusion occurs. Initially, within a short-time period, it was postulated that the ion was transported to the external surface of the egg shell powder through film diffusion and its rate had been very fast. After saturation of the surface, the ion entered into the egg shell powder by intraparticle diffusion through pore and interior surface diffusion until equilibrium was

attained which was represented by the second straight.

Elovich equation

The linear Elovich equation is given by equation 9,

 $q_t = 1/\beta * \ln (\alpha \beta) + 1/\beta * \ln t$ (9)

Where α is the initial sorption rate (mg/g.min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg). The Elovich equation describes predominantly chemical adsorption on highly heterogeneous adsorbents, but the equation does not propose any definite mechanism for adsorbate-adsorbent interaction. The experiment was conducted for various temperatures and different concentrations. This kinetic data also not fit for this adsorption process, because of the low regression coefficient value (0.907).

Models	Doromotors	Concentration at	Concentration	Concentration 1000
WIGUEIS	r ai aiiletei s	500 ppm	at 750 ppm	ppm
	R^2	0.772	0.671	0.695
Pseudo first order	K (g/mg.min)	0.055	0.0552	0.046
	$q_e (mg/g)$	11.023	7.838	5.349
Pseudo second order	\mathbb{R}^2	0.835	0.908	0.987
	K (g/mg.min)	0.00007	0.0001	0.0002
	$q_e (mg/g)$	21.73	26.315	34.48
	R^2	0.99	0.816	0.815
Fractional power	Κ	0.0009	4.859	16.726
	Ν	2.099	0.291	0.123
Intra particle	\mathbb{R}^2	0.972	0.857	0.878
diffusion	Κ	3.696	1.317	0.927
	R^2	0.902	0.768	0.794
Elovich	α_{e}	0.445	2.200	162.14
	β _e	0.071	0.201	0.285
RMSE	-	18.18	7.937	5.525

Table 1. Kinetic parameters for the adsorption of Ni (II) at different concentration

Adsorption isotherms

Equilibrium isotherm was described by a sorption isotherm, characterized by certain constants whose values express the surface properties and affinity of the adsorbent sorption equilibrium was established when the concentration of sorbate in the bulk solution was in dynamic balance with that at the sorbent interface. In order to quantify the affinity of Egg shell powder for the metal studied, i.e. Ni (II), four widely used isotherm models (Langmuir, Freundlich, Temkin and Brunauer-Emmett-Teller isotherm models) were used to analyze the

data obtained from the adsorption process [27,28,33,34].

Langmuir adsorption isotherm

The monolayer coverage of the sorbate on a sorbent surface at a constant temperature was represented by the Langmuir isotherm. The basic assumption is that the forces exerted by chemically unsaturated surface atoms do not extend further than the diameter of one sorbed molecule. The Langmuir isotherm is given by eq. (10).

 $C_e/q_e = [1/K_d q_m] + [1/q_m]C_e$ (10)

Where, q_e is the amount of Ni (II) adsorbed at equilibrium per mass of Egg shell powder (mg/g); C_e is the concentration of the metal in aqueous phase at equilibrium (mg/l); K_d is the sorption equilibrium constant; q_m (mg/g) is the monolayer capacity. The monolayer coverage is

obtained from a plot of C_e/q_e versus C_e . For different temperatures and different concentrations the equation is checked to fit. The slope and the intercept of the linear graph obtained from this plot give the value of q_m and K.

Table 2. Kinetic parameters	for the adsorption of Ni (II)	at different concentration
ruele 2. Hindhe purumeters		at annotone concentration

Models	Parameters	Temperature at 30°C	Temperature at 40°C	Temperature at 50°C	Temperature at 60°C
Pseudo first order	\mathbb{R}^2	0.772	0.811	0.894	0.851
	K (g/mg.min)	0.055	0.05	0.08	0.025
	q _e (mg/g)	11.023	9.66	13.105	4.495
Pseudo	\mathbf{R}^2	0.835	0.89	0.490	0.921
second	K (g/mg.min)	0.00007	0.0004	0.00005	0.00046
order	q _e (mg/g)	21.73	13.33	71.42	31.25
Fractional power	R^2	0.99	0.983	0.933	0.972
	Κ	0.0009	0.01	0.392	1.9
	Ν	2.099	1.594	0.859	0.491
Intra	R^2	0.972	0973	0.911	0.957
particle	Κ	3.696	3.512	2.63	1.839
diffusion					
Elovich	\mathbb{R}^2	0.902	0.907	0.972	0.927
	α_{e}	0.445	0.474	0.708	0.929
	β_e	0.071	0.074	0.092	0.138
RMSE	-	18.18	17.01	10.88	9.74

Freundlich isotherm

Freundlich equation assumes that the uptake of metal ions occurs on heterogeneous surface by multilayer adsorption. Linear form of Freundlich equation is given by eq. (11).

log $q_e = \log k_f + 1/n \log C_e$ (11) Where q_e - adsorption capacity (mg/g), C_e - final concentration (mg/l), n= empirical constant. The experiment is conducted for various temperatures and different concentrations. The Freundlich coefficients *n* and K_f are obtained from the plots of $\ln q_e$ versus $\ln C_e$. From the below graph it was observed that this adsorption process not followed Freundlich isotherm.

Temkin isotherm

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent - adsorbate interactions, and that the adsorption was characterized by a uniform distribution of the bonding energies, up to some maximum binding energy. The Temkin isotherm is given by eq. (12).

$$X = a + b \ln C \qquad \dots (12)$$

Where, C - concentration of adsorbate in solution at equilibrium (mg/l), X -amount of metal adsorbed per unit weight of adsorbent (mg/g), a and b are constants related to adsorption capacity and intensity of adsorption and related to the intercept and slope of the plots of ln C against X [27]. For different temperatures and concentrations the given equation was checked to fit.

BET adsorption isotherm

BET isotherm was developed by Brunauer, Emmett and Teller as an extension of Langmuir isotherm, it assumes that first layer of molecules adhere to the surface with energy comparable to heat of adsorption for monolayer sorption and subsequent layers have equal energies. Equation in linearized form is expresses by eq. (13).

 $C_f/(C_s - C_f)q=1/Bq_{max}-(B-1/Bq_{max})(C_f/C_s)..(13)$ Where C_s is the saturation concentration (mg/l) of the solute, C_f is solute equilibrium concentration. For different temperatures and concentrations the given equation is checked to fit. B and q max are two constants and can be evaluated from the slope and intercept [28]. The fitting of data, values obtained from the adsorption of Ni (II) on egg shell powder, to the 4 isotherm models showed that the linearity of the Temkin isotherm models (0.998) was higher than that of the other isotherm models (Table 3,

4). This shows that the adsorption of Ni (II) on egg shell powder was more of monolayer sorption rather than adsorption on a surface having heterogeneous energy distribution.

Isotherm	Parameters	Temperature at 30°C	Temperature at 40°C	Temperature at 50°C	Temperature at 60°C
Freundlich isotherm	\mathbb{R}^2	0.767	0.833	0.905	0.903
	K _f	0.001	0.0009	0.0002	0.00004
	n	1.848	1.364	0.810	0.561
	\mathbf{R}^2	0.654	0.772	0.905	0.945
Langmuir isotherm	Q_{o}	1.25	2.381	5.555	8.772
	b	0.007	0.008	0.012	0.016
	R _L	0.222	0.2	0.142	0.111
Temkin isotherm	R^2	0.955	0.959	0.964	0.961
	a	71.61	69.46	62.65	55.8
	b	11.16	10.73	9.316	7.84
BET isotherm	R^2	0.908	0.895	0.508	0.961
	В	5.297	4.801	3.785	3.842
	q_{max}	0.162	0.032	0.039	0.013
RMSE	-	18.18	17.01	10.88	9.74

Table 3. Adsorption isotherm data for different temperatures on the removal of Ni (II)

Table 4. Adsorption isotherm data for different concentrations on the removal of Ni (II)

Models	Parameters	Concentration for	Concentration for	Concentration for
		500 ppm	750 ppm	1000 ppm
Freundlich isotherm	R^2	0.767	0.988	0.996
	K_{f}	0.001	0.00001	0.00002
	n	1.848	1.113	0.732
	R^2	0.654	0.984	0.997
Langmuir isotherm	Q_{o}	1.25	8.13	16.66
	b	0.007	0.004	0.005
	R_L	0.222	0.25	0.167
Temkin isotherm	\mathbb{R}^2	0.955	0.997	0.998
	a	71.61	133.4	155.7
	b	11.16	19.38	21.01
BET isotherm	\mathbb{R}^2	0.908	0.925	0.896
	В	5.297	2.409	2.251
	q_{max}	0.162	0.007	0.012
RMSE	-	18.18	7.937	5.525

Conclusion

The powdered eggshell was used as a cheap and effective inorganic adsorbent for the removal of Ni (II) ions from aqueous solutions. The adsorption was found to occur mainly at the surface of the solid egg shell powder and slightly by the internal pores. The adsorption data was well described by Temkin model over the concentration range and different temperature. The adsorption process followed Fractional power model for different concentrations and different temperatures. The adsorption occurs, depending on the solution pH, through ion exchange, adsorption of hydrolytic species, Ni $(OH)^+$ ions, and/or the precipitation of nickel hydroxide onto egg shell powder adsorbent. The pH value of 4, adsorbent dosage of 2.5 g and agitation speed of 120 rpm were optimized for the further studies. From this study it was proved that Ni (II) ions can be removed up to 90% from effluents using ecofriendly material like egg shell powder.

Conflicts of interest

Authors declare no conflicts of interest.

References

- Ajmal M, Ali Khan Rao R, Anwar S, Ahmad J, Ahmad R. Adsorption studies on rice husk: Removal and recovery of Cd (II) from wastewater. Bioresource Technology. 2003;86(2):147-149.
- [2] Bailey SE, Olin TJ, Bricka RM, Adrian DO, A review of potentially low-cost sorbents for heavy metals. Water Research. 1991;33(11):2469-2479.
- [3] Lin SH, Lai SL, Leu HG. Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process. Journal of Hazardous Materials. 2000;76:139-153.
- [4] Malkoc E.Ni (II) removal from aqueous solutions using cone biomass of Thujaorientalis. Journal of Hazardous Materials. 2006;137(2):899-908.
- [5] Bhatnagar A Minocha AK. Biosorption optimization of nickel removal from water using *Punicagranatum* peel waste. Colloids and Surfaces B. 2010;76 (2):387-584.
- [6] Ghazy SE, Asmy AAHE, Nokrashy AME. Batch removal of Nickel by Eggshell as a Low Cost Sorbent. International Journal for Industrial Chemistry. 2011;2(4):242-252.
- [7] Umesh K, Garg MP, Kaur MP, Garg VK, Sud D. Removal of Ni (II) from aqueous solution by adsorption on agricultural waste biomass using a response surface methodological approach. Bioresource Technology.2008;99(5):909 – 1502.
- [8] Patterson JW. Industrial Waste Water Treatment Technology. 2nd edition Butter-worth's Publishers USA. 1985.
- [9] Ozcan AS, ErdemB, Ozcan A. Adsorption of Acid Blue 193 from aqueous solutions onto BTMA-bentonite. Colloids and Surface A. 2005;266:73-81.
- [10] Vander Weijden RD, MeimaJ,Comans RNJ. Sorption and Sorption reversibility of cadmium on calcite in the presence of phosphate and sulfate. Marine Chemistry. 1997;57(1-2):119-132.
- [11] Wenming D, Zhijun G, Jinzhou D, LiyingZ, Zuyi T. Sorption characteristics ofZinc (II) by calcareous soil-radiotracer

study. Applied Radiation and Isotope. 2001;54 (3):371-375.

- [12] Tsai WT, Yang JM, Lai CW, Cheng YH, Lin CCYeh CW. Characterization and adsorption properties of eggshells and eggshell membrane. Bioresource Technology. 2006;97(3):488-493.
- [13] Tsai WT, Hsien KJ, Hsu HC, Lin CM, Lin KY Chiu CH. Utilization of ground eggshell waste as an adsorbent for the removal of dyes from aqueous solution. Bioresource Technology. 2008;99(6):1623-1629.
- [14] Patel Niyati S, Desai H. Potential of MoringaOleifera seeds, leaves and bark for removal of hexavalent chromium from aqueous solution with reference to adsorption isotherm. International Journal of Water Resources and Environment Management. 2011;2(1):41-57.
- [15] Sahmoune MN, Louhab K, Boukhiar A, Addad J, Barr S. Kinetic and equilibrium models for the biosorption of Cr (III) on *Streptomycesrimosus*. Toxicological and Environmental Chemistry. 2009;91:1291-1303.
- [16] Baes CF, Mesmer RE. The Hydrolysis of Cations. 3rd edition, John Wiley & Sons New York; 1976.
- [17] Tremaine PR, Leblanc JC. The solubility of magnetite and hydrolysis and oxidation of Fe2+ in water to 300°C. Journal of Chemical Thermodynamics. 1980;12:521-538.
- [18] Somasundran P, Agar GE. The zero point of charge of calcite. Journal of colloid and Interface Science. 1967;24(4):433-440.
- [19] Rao M, Parvate AV, Bhole AG. Process Development for removal of copper and lead from aqueous solution by low cost material. Journal of Environmental Pollution. 2002;22(1):17-25.
- [20] Bishnoi NR, Pant A, Garima P. Biosorption of Cu (II) from aqueous solution using algal biomass. Journal of Scientific Industrial Research. 2004;63:813-816.
- [21] Al-Asheh S, Banat F. Study of the sorption of divalent metal ions on to peat. Adsorption Science and Technology. 2001;19(1):25-43.

- [22] Weber WJ, Morris JC. Kinetics of adsorption on carbon from solution. Journal Sanitary Engineering Division Proceedings. American Society of Civil Engineering. 1963;89:31-60.
- [23] Chien SH, Clayton WR. Applications of Elovich Equation to the Kinetics of Phosphate Release and Sorption in Soils. Soil Science Society America Journal. 1980;44(2):265-268.
- [24] Ho YS, Ofomaja AE. Kinetics and Thermodynamics of Lead Ion Sorption on Palm Kernel Fiber from Aqueous Solution. Process biochemistry. 2005;40:3455-3461.
- [25] Lagergren S. Theorie der sogenannten adsorption gelöster Stoffe, Kungliga Svenska Vetenskapsakademiens. Handlingar, 1898;24(4):1-39.
- [26] Sahmoune MN, Louhab K, Boukhiar A. Studies of Chromium Removal Tannery Effluents by Dead Streptomyces rimosus.Chemical Product and Process Modelling. 2008;3(1):1934-2659.
- [27] Kannan K, Senthilkumar K, Akilamudhan P, Sangeetha V, Manikandan B. Studies on effectiveness of low cost adsorbents in continuous column for textile effluents. International Journal of Bioscience Biochemistry and Bioinformatics. 2012;6(2):398-402.
- [28] Senthilkumar K. Kinetic studies on the removal of Cr (VI) using natural adsorbent SSRG. International Journal of Chemical Engineering Research. 2017;4(1):29-54.
- [29] Kannadasan T, Sivakumar V, Basha C, Parwate A, Senthilkumar K. COD reduction studies of paper mill effluent using a batch recirculation

electrochemical method Polish. Journal of Chemical Technology. 2011;13(3):37-41.

- [30] Salihi IU, Kutty SRM, Isa MH. Adsorption of Lead ions onto Activated Carbon derived from Sugarcane bagasse. Materials Science and Engineering IOP conference series. 2017;201:012034 doi:10.1088/1757-899X/201/1/012034.
- [31] Somiyavilvanathan, Shanthakumar S. Column adsorption studies on nickel and cobalt removal from aqueous solution using native and biochar form of *Tectonagrandis*. Environmental Progress and Sustainable Energy. 2017;36(4) 1030-1038.
- [32] Wojciech K, Ewa M, Małgorzata A. Equilibrium and kinetics studies for the adsorption of Ni2+ and Fe3+ ions from aqueous solution by grapheneoxide. Polish Journal of Chemical Technology. 2017;19(3)120-129.
- [33] Igberase E, Osifo P, Ofomaja A. The Adsorption of Pb, Zn, Cu, Ni, and Cd by Modified Ligand in a Single Component Aqueous Solution: Equilibrium, Kinetic, Thermodynamic, and Desorption Studies. International Journal of Analytical Chemistry. 2017;15:Article ID: 6150209 doi.org/10.1155/2017/6150209.
- [34] Aamir A, Basim AA, Ihsanullah, Nadhir AH, Al-Baghli, Halim HR. Adsorption of Toluene and Paraxylene from Aqueous Solution Using Pure and Iron Oxide Impregnated Carbon Nanotubes: Kinetics and Isotherms Study. Bioinorganic Chemistry and Applications. 2017;11:Article 2853925. ID: doi:10.1155/2017/2853925.
