Journal of Kerbala University , Vol. 13 No.3 Scientific . 2015

Kinetic and thermodynamic studies for the adsorption of Nickel (II) by Basil seeds in aqueous solutions

دراسة حركية وثرموديناميكية لامتزاز ايون النيكل الثنائي في المحاليل المائية بأستخدام بذور الريحان

[1]Elham M . AL-Rufaie and[2]Beidaa A.kadhim
[1,2]Department of chemistry , college of science , Bagdad university

Abstract :

Environmental pollution as a result of a heavy metal presence led to serious health problems. Inthis study, the adsorption by swollen Basil seeds were determined. The adsorption behavior of Basil seeds with respect to Nickel (II) has been studies by batch method to consider its application in this field.The effects of various experimental parameters like contact time, dosage of Basil seeds, initial concentration of the metal ion, pH of solution, and temperature have been investigated .The removal percentage is a pH dependent and decrease with increase in temperature, The best removal were at 20^0C. The equilibrium adsorption experimental data were found to fit Freundlich isotherms for Nickel (II). The pseudo-first and second order kinetic model both fitted the kinetic.The thermodynamic parameters, (Δ^0G) was found to be positive and become negative at low temperature (below 10^0C), Δ^0H is negative that means exothermic adsorption process and Δ^0S is negative also which indicate the increase in the order at the solid-solution interface.

Keywords :Heavymetals , pollution, thermodynamics, kinetics, isotherms, Adsorption, Nickel ion .

خلاصة :-

يؤدي التلوث البيئي الناتج من وجود الفلزات الثقيلة الى مشاكل صحية مختلفة في هذه الدراسة تم استخدام بذور الريحان كمادة مازة وقد تم دراسة تصرف الامتزاز لها بالنسبة لأيون النيكل بطريقة الوجبة، عينت الظروف الفضلى لعملية الامتزاز والتي تشمل, زمن التماس, وزن حبيبات بذور الريحان, التركيز الابتدائي للأيون الفلزي, الدالة حامضية للمحلول ودرجة الحرارة. وتبين من هذه النتائج أن عملية الامتزاز تعتمد على حامضية الوسط ودرجة الحرارة، وأن النسبة المئوية للإزالة R% تقل بزيادة درجة الحرارة. وكانت أفضل درجة حرارية للإزالة هي 20^0C.أن نتائج تجارب الامتزاز المتوازنة تم اختيارها على نماذج لنكماير وفريندلش ثابتة درجة الحرارة ومن قيم معامل التصحيح يظهر أن النتائج تتبع ايزوثيرماتفريندلش لعنصر النيكل. ومن تطبيق معادلات الحركية للرتبة الاولى والثانية وجد كلا المعادلتين ملائمة. ان الدوال الثرمديناميكية(Δ^0G), موجبة القيمة وتصبح سالبة عند درجة حرارة اقل من $10^0C,\Delta^0H$ سالبة وهذا يعني ان عملية الامتزاز باعثة للحرارة وΔ^0S سالبة وهذا يعني زيادة السطح البيني للطور سائل-صلب.

1.Introduction:

There are around thirty chemical elements that play a pivotal role in various biochemical and physiological mechanisms in living organisms, and recognized as essential elements for life. The intake of metal ions can be a double edged sword **[1].**

Majority of the known metals and metalloids are very toxic to living organisms and even those considered as essential can be toxic if present in excess. Concentration of several toxic metal and metalloids have been largely increased as a result of human activities.They can disturb important biochemical processes, constituting an important threat for the health of plant and animals **[2].**Nickel II is an environmental carcinogen, nephrotoxic and hepatotoxic heavy meta**l[3, 4]**.Its toxicity is dependent on the route of exposure and the solubility of its compound[**5]**.Ni(II) cannot be metabolized by the body, it accumulates especially in kidney and liver **[4, 6].**Removal of Nickel and other heavy metals can be accomplished by processes such as chemical precipitation, cementation, solvent extraction, reverse osmosis, ion-exchangeand adsorption**[7, 8]**.

Adsorption is a quite selective effective and is able to remove very low levels of heavy metal from aqueous solutions**[9]**.Agricultural byproducts have been widely studied for metal removal, these include peat, wood, pine bark, banana pith, peanut shells, rice husk, wool, orange peel, compost and leaves**[10].**Basil seeds can serve as a source of agriculturally-based exopolysaccharides. The seeds swell upon wetting and once swollen consist of a hard core with a porous swollen outer layer. The mucilaginous layer of the swollen seeds is a pectinous matrix, consisting of considerable amounts of unesterified galacturonic acid with a large capacity of hydration**[12] .**

The goals of this study isusing basil seeds as an adsorbent for the removal of nickel (II) from aqueous solution;study the influence of specific parameters such as, initial concentration of Ni(II), pH of solution,contact time, adsorbent dose andtemperature for the maximum removal of nickel from its aqueous solutions;determined the kinetic equation best describe the data obtained;calculated the activation energy for the practical application of basil seeds;determined the adsorption equation which best describe the equilibrium uptake and finally to calculate the thermodynamic parameters (Δ^oG, Δ^oH and Δ^oS) for the practical implementation of basil seeds.

2.Experimental :

2.1.Materials :

Basil seeds were purchased from the local market, the plants producing these seeds grown extensively in Iraq. Analytical grade nickel nitrate [$Ni(NO_3)_2.6H_2O$] was used for the preparation of metal stock solution of 500 mg/L, by dissolving 0.1g of Nickel nitrate in 200 mL of distilled water.

A series of solutions were prepared by fresh diluting of the stock solution**[11]**.The required quantity of seeds were washed with distilled water then allowed to swell for 30 min and directly used as adsorbentFigure(1):

Figure -1: Basil seeds a- dry seeds **Figure-1:b- socked in distilled water for 30 min .**

2.2.Methods :

The adsorption experiments were carried out by batch equilibrium method.Swollen seeds were taken in 250 ml round bottom flask containing 200ml of Nickelnitrate solution. The flasks were placed on a rotary shaker **(BS-11; Korea)** and shaken at 150 rpm at 20^{o}C.At the end of pre-determined time intervals, adsorbent was removed by centrifugation at 150 rpm and the super natant was analyzed for the residual Ni(II) concentration by atomic absorption spectrometer**[Perkin Elmer,model 500,US]**with air-acetylene flame.

Metal uptake by the adsorbent at equilibrium (q_e) was calculated using the following equation (1)**[3]**:

$$q_e = \frac{(c_0 - c_e)\,V}{w} \qquad (1)$$

Where: q_e is the amount of metal ion adsorbed in mg/g , c_o is the initial metal ion concentration in mg/l, c_e is the concentration at equilibrium in mg/l and V is the total volume of solution in Litre and w is the mass of the adsorbent (basil seeds) used in gram .

Removal percentage or adsorption percentage were calculated using equation (2)**[4]**:

$$(R\%) = \frac{(c_o - c_e)}{c_o} \times 100 \qquad (2)$$

Results and Discussions :

Characteristics of the adsorbent :

The chemical nature and pore structure of the adsorbent generally determines the sorption activity. The infrared spectrum of the dried mucilage part of basil seeds was tested using KBr technique. (figure-2), this figure shows the presence of the following groups (table-1) .

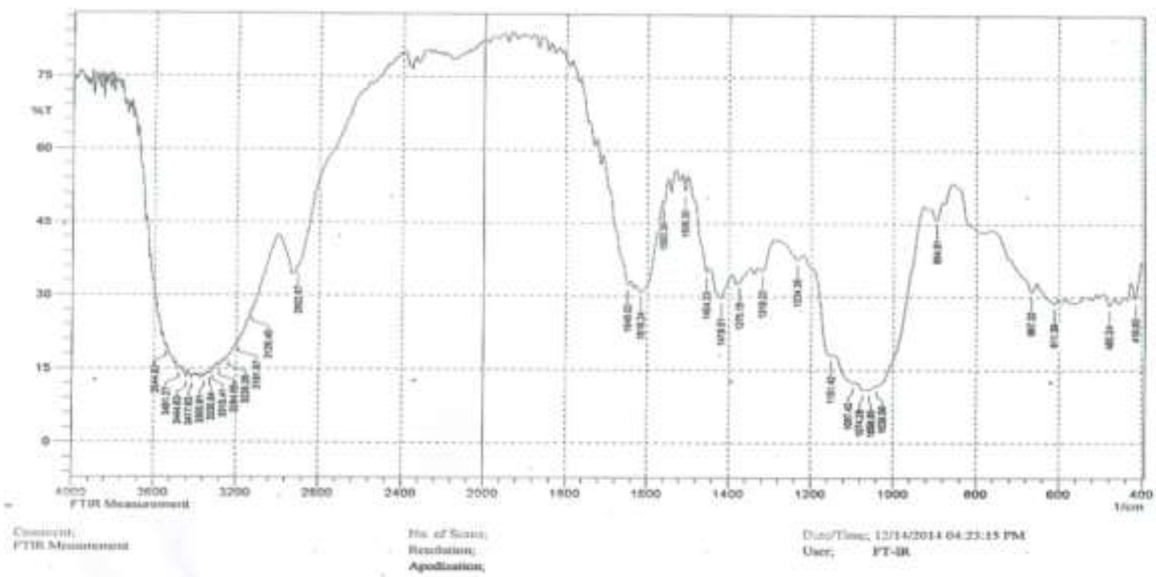

Figure - 2: Infrared spectra of dried mucilage of Basil seeds .

Table -1: Main functional groups observed with IR-

Wave number cm^{-1}	Vibration type
3191-3481	Stretching vibration of OH
2902	Symmetric α Asymmetric stretching vibration of C-H
1616-1649	Vibration of C=O and C-N (amide I)
1560	Stretching vibration of C-N and deformation vibration of N-H (amide II)
1454	Deformation vibration of CH_2
1419	Stretching vibration of C=O
1234	Deformation vibration of C=O
1151	Stretching vibration C-O-C (polysaccharide)
1039-1079	Stretching vibration of OH

3.2.Effect parameters of Adsorption:

3.2.1.Effect of contact time :

The mixture of Basil seeds (0.5 g) and (200mL) volume solution withinitial concentration of Nickel(20ppm) were agitated 20^{o}C for different time (5, 10, 15, 20, 30, 40, 50, 60, 70 and 80 min), and centrifuged. Nickel concentration were determined as above the effect of the contact time on the adsorption of Nickel (II) are shown in figure -3.The equilibrium was attained aftershaking for 40 min therefor 40 min was accepted as optimal time for adsorption of Ni(II) on Basil seeds , further increase in contact time did not show any increase in adsorption due to a saturation in a surface sites**[12]**.

3.2.2.Effect of adsorbent dose :

Initial Ni(II) concentration of(20 mg/l) were used in conjunction with different amount of swollen Basil seeds of (0.1, 0.2, 0.3, 0.5, 0.7, 0.9, 1, 1.1, 1.2 and 1.3) g,the other parameters were kept constant; contact time 40 min,agitation speed 150 rpm; temperature 20^{o}C, and pH = 6.22. Nickel uptake was found to increase with increase in B.S dosage up to 1.3 g. The higher dose cause screen effect of dense outer layer, blocking the binding sites for metal ions , resulting in lower metal removal**[13]**.Therefore optimum B.S. dose was chosen as 1.3g for the subsequent experiment.

3.2.3.Effect of initial metal concentration :

The experimental values for adsorption of different concentration of nickel ion (2, 4, 6, 8, 10, 12, 14, 16, 18, and 20) mg/l are shown in figure -5.As the concentration of metal ion increase, more and more surface sites are covered and hence at higher concentration, the capacity of the adsorbent get exhausted due to non-availability of the surface sites **[11].**

3.2.4.Effect of pH :

Nickel ion uptake was found to depend on pH of the solution; shown infigure–6, solutions were pH adjusted at(2,3, 4, 6, 8, 9, 10 and 12).Nickel uptake was found to be maximum atpH= 6**[14]**

4.2.5.Effect of temperature :

Experiments were carried out at different temperature 20, 25, 30, 35, and 40°C in conjunction with the optimum other parameters, contact time 40 min, adsorbent dose 1.3 g, agitation speed 150rpm and pH =6.

figure -7 shows that at 20°C there are the best Removal % and so this temperature was chosen for further experiments .

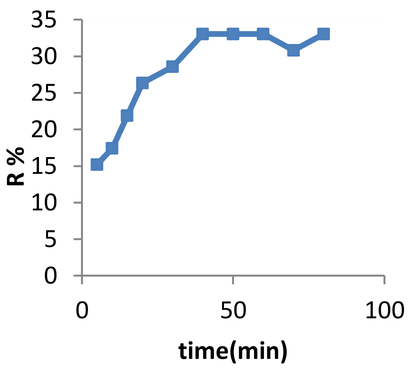

Figure -3 : effect of contact time on adsorption of Nickel (II) onto Basil seeds

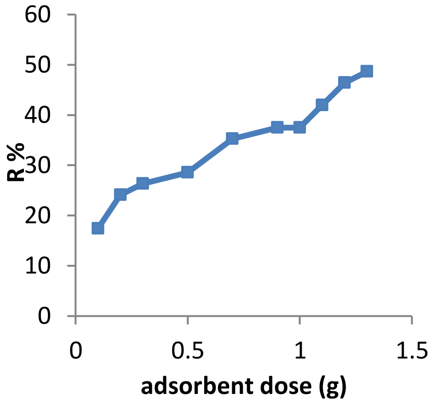

Figure – 4 : Effect of adsorbent dose on adsorption of Nickel (II) onto Basil seeds .

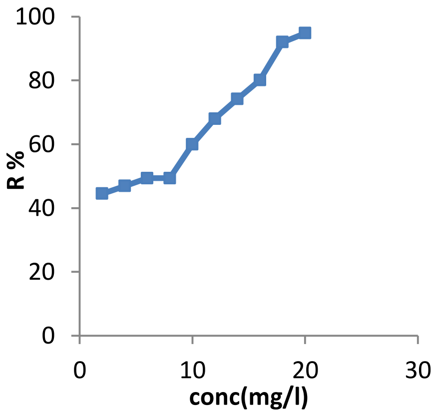

Figure -5: Effect of initial ion concentration on adsorption of Nickel (II) onto Basil seeds .

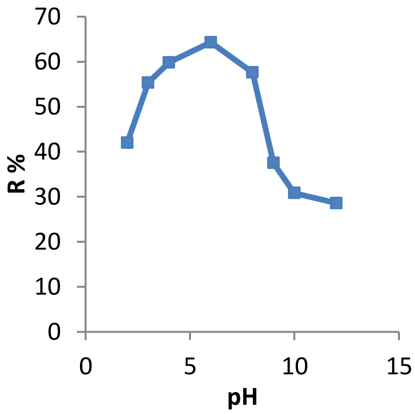

Figure – 6 :Effect of pH on adsorption of Nickel (II) onto Basil seeds .

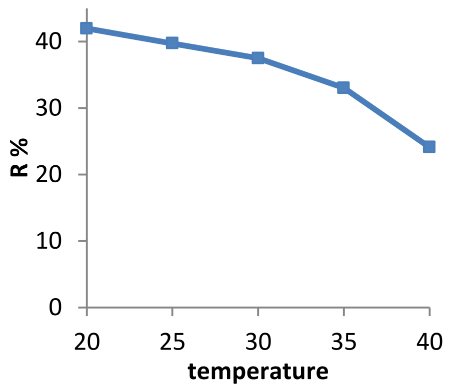

Figure (7) :Effect of temperature on the removal of Nickel (II) onto Basil seeds .

3.3.Adsorption isotherms :

To determine the adsorption capacity and potential for selecting theadsorbent for the removal of metal ions, the study of adsorption isotherm is essential in selecting the adsorbent. From all the batch experiment carried out, the optimum parameters selected were; pH 6 ,Basil seeds dose 1.3g, contact time 40 min and agitation speed 150rpm **[15].**Adsorption isotherm study was carried out by five different temperature which were 20, 25, 30, 35 and 40°C.Two most common isotherm models were employed for describing the adsorption data, which were Langmuir and freundlich isotherm. The equilibrium values obtained are depicted in table -2.

Table -2: Equilibrium parameters for the adsorption of Nickel (II) onto Basil seeds .

Ni(II) C_O(mg/L)	Temperature °C									
	20		25		30		35		40	
	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)	Ce(mg/L)	Qe(mg/g)
2	1.22	0.120	1.29	0.109	1.31	0.106	1.41	0.091	1.53	0.072
4	2.45	0.239	2.59	0.217	2.63	0.211	2.84	0.178	2.98	0.157
6	3.59	0.371	3.91	0.321	3.96	0.314	4.29	0.263	4.58	0.218
8	4.98	0.465	5.23	0.426	5.29	0.417	5.76	0.345	6.11	0.291
10	6.24	0.578	6.41	0.552	6.64	0.517	7.29	0.417	7.67	0.358
12	7.51	0.691	7.93	0.626	7.98	0.619	8.98	0.465	9.22	0.428
14	8.68	0.818	9.28	0.726	9.46	0.699	10.29	0.571	10.62	0.52
16	10.15	0.9	10.64	0.825	10.86	0.791	11.88	0.634	12.41	0.552
18	11.66	0.975	12.17	0.897	12.22	0.889	13.39	0.709	13.83	0.646
20	12.96	1.220	13.56	0.991	13.91	0.937	14.58	0.834	15.66	0.668

3.3.1.Langmuir isotherm :

The Langmuir isotherm is valid for monolayer adsorption on to a surface with a finite number of identical sites. It is based on assumption of adsorption homogeneity, such as equally available adsorption sites, monolayer surface coverage and no interaction between adsorbed species**[12].** According to the Langmuir adsorption isotherm, the adsorption process can be expressed as **:[12]**.

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{K_d}{q_m} \tag{3}$$

Where C_e (mg/l) is the equilibrium concentration of Ni(II) in solution, $Q_e(mg/g)$is the amount adsorbed per unit weight at equilibrium, $q_m(mg/g)$ the maximum adsorption capacity andK_d is the effective dissociation constant .

The linear plots of C_e/Q_e VS C_e suggest the applicability of the Langmuir isotherm; (figure - 8) .The values of q_m and K_d were calculated from the slope and intercepts of the plots are listed inTable-3. Langmuir constants relates to the adsorption capacity and rate of adsorption , respectively .

Table -3 : Langmuir and , freundlich isotherm modelparameters and their correlation coefficient for the adsorption of Nickel (II) onto Basil seeds.

Temperature C^0	Langmuir isotherm Results			Freundlich isotherm Results			Dimension less separation factor R_L
	q_m	K_L	R^2	k_f	n	R^2	Metal ionC_0(20mg/L)
20	8.9686	0.0112	0.4994	0.0944	1.076	0.9959	0.817
25	6.4977	0.0134	0.8091	0.0887	1.0630	0.9976	0.789
30	5.7339	0.0147	0.8832	0.0854	1.0691	0.998	0.773
35	4.2955	0.0149	0.6421	0.0676	1.0944	0.9968	0.770
40	3.8834	0.01295	0.458	0.0512	1.0464	0.996	0.794

The essential characteristic of the Langmuir isotherm can be expressed by a dimensionless separation factor (R_L) , and were determined by the following equation**[16]** .

$$R_L = \frac{1}{1 + K_d C_o} \tag{4}$$

Where: K_d is the Langmuir constant (L/mg).C_o is the initial concentration (mg/l).The value of R_L indicates the shape of the isotherm to be either unfavorable (R_L >1), linear (R_L=1), favorable (0<R_L< 1) or irreversible (R_L= 0). Since R_L values lies between 0 and 1 for all the five temperature studied, it indicates that the adsorption is favorable, favorable sticking of adsorbate to adsorbent-physisorption mechanism predominant**[17].**

3.3.2.Freundlich isotherm :

Batch isotherm data fitted to the linear form of the freundlich isotherm which is commonly expressed by the following equation **[18].**

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \tag{5}$$

The values of K_f and n are calculated from figure (9) and the data are provided in Table -3.These are the indicators of the adsorption capacity and adsorption intensity, respectively.The linearity of the plots (0.996→ 0.998) at different temperature is evident from figure-9. This supports the applicability of freundlich adsorption isotherm indicating that the adsorption by swollen Basil seeds may be govern by physisorption. From the values of the regression coefficient R^2 listed in Table-3, Freundlich isotherm gave good and better fit to the experimental data than Langmuir

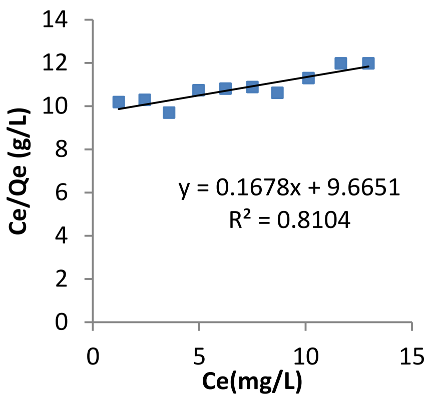

Figure -8: Langmuir adsorption isotherm for the adsorption of Nickel (II)in aqueous solution onto Basil seeds at 20C^0.

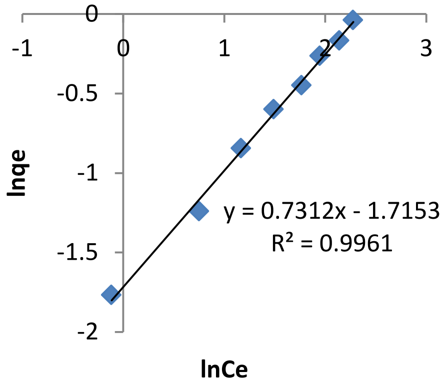

Figure -9 : freundlich adsorption isotherm for the adsorption of Nickel(II) aqueous solution onto Basil seeds at 20C^0 .

3.4.Adsorption thermodynamic :

Thermodynamic parameters, change in Gibbs free energy $\Delta^o G$, enthalpy change $\Delta^o H$, and entropy change $\Delta^o S$were calculated according to following equation:

$$\Delta G^0 = -RT \ln K_{eq} \qquad (6)$$

$$K_{eq} = Q_{solid}/C_{liquid} \qquad (7)$$

$$\ln K_{eq} = \frac{\Delta o_S}{R} - \frac{\Delta o_H}{RT} \qquad (8)$$

Where:

K_{eq} is the equilibrium constant, Q_e is the solid phase concentration at equilibrium (mg/g), C_e is the liquid phase concentration at equilibrium (mg/l) and T is an absolute temperature , and R is the gas constant **[19].**$\Delta^o H$and$\Delta^o S$ values were obtained from the slope and intercept of vant Hoff plots Figure (11) ,and are given in table- 4 .

Table- 4: thermodynamic parameters of Nickel (II) sorption onto Basil seeds.

Temperature (K)	K_{eq}	lnk_{eq}	$\Delta^o G(J.mol^{-1})$	$\Delta^o H(J.mol^{-1})$	$\Delta^o S(J.mol^{-1}.K^{-1})$
293	o.544	-0.61	1485..96	-24159.99	-87.19311
298	0.475	-0.745	1814.82		
303	0.438	-0.83	2021.88		
308	0.372	-0.99	2411.64		
313	0.277	-1.283	3125.39		

When the temperature of the system increase, the extent of adsorption decrease,this become obvious from the values of K_{eq} which decrease with increase in temperature, that means the process is exothermic, this is confirmed by the negative values of $\Delta^o H$. The negative value of entropy change $\Delta^o S$ suggest a high degree of the order at the solid-solution interface during the adsorption process .The positive value of $\Delta^o G$ indicate that the adsorption is non-spontaneous and become spontaneous at low temperature, at 10C^0 and below.

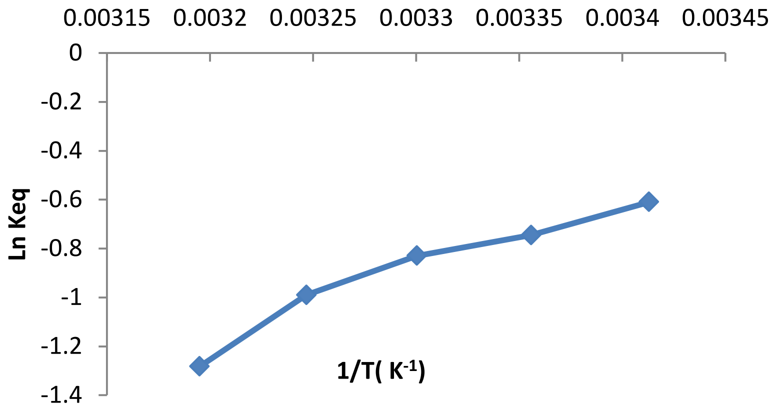

Figure -10 : vant-Hoff plot of $^{1}/_{T}$ VS ln K_{eq} for the adsorption of Nickel onto Basil seeds .

3.5.Adsorption kinetics:

In order to investigate the adsorption kinetics of Nickel ion onto swollen basil seeds, the pseudo – first order equation of lagergreen equation and,pseudo second order equation**[19].** were applied to the experimental data :

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (9)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

Where:q_e and $q_t$is the amount metal ion adsorbed at equilibrium and at time t respectively.k_1 is the first – order rate constant (min^{-1}).K_2 is the second –order rate constant (g/mg . min) and t is the time in min.The parameters obtained by the application of the two kinetic models were reported in Table-5.

Table - 5 : Parameters of kinetic models for adsorption of Nickel (II) onto Basil seeds at 20C^0.

Metal ion mg/L	Pseudo first order		Pseudo second-order	
	K_1	R^2	K_2	R^2
2	0.0405	0.8353	0.0427698	0.9668
4	0.0602	0.9099	0.0462443	0.9891
6	0.0558	0.9918	0.090149	0.9946
8	0.0458	0.9843	0.04780	0.9764
10	0.0429	0.9903	0.09558	0.9978

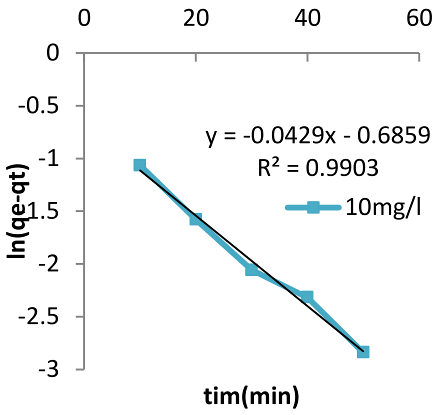

Figure-11: First-order kinetic equation model for adsorption of Nickel (II) onto Basil seeds at 20C^0.

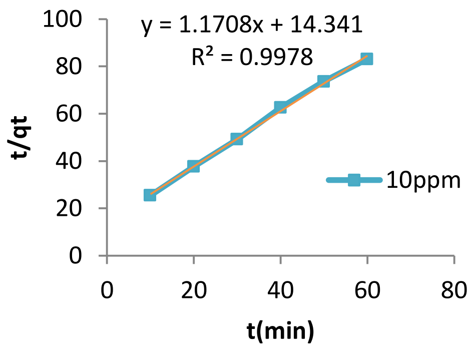

Figure-12: Second-order kinetic equation model for adsorption of Nickel(II) onto Basil seeds at 20C^0.

The value of the rate constant calculated from the first-order and second order kinetic equation are found to be similar, therefore any one of these kinetic equation can be employed to calculate the rate constant for the adsorption process of nickel(II) onto Basil seeds, Liner plots were obtained with high correlation coefficient (R^2), suggesting that the interaction between the adsorption and the metal ion follow the pseudo-second order mechanism.

4.Conclusions:

This study confirmed that Basil seeds can be used effectively for the removal of Nickel (II) from aqueous solution. The removal efficiency reaches 90% in some instances. the adsorption process based on solution pH and effect of temperature.

The process of adsorption was best fitted by Freundlich model, and pseudo-first and Second order model both fitted the kinetics. according to the results, Basil seeds is recommended as an available and safe Biosorbent to the removal of toxic metal ions.

References:

1. Mudgal, V., N. Madaan, and A. Mudgal, *Heavy metals in plants: phytoremediation: Plants used to remediate heavy metal pollution.* Agriculture & Biology Journal of North America, 2010. 1(1).
2. Madaan, N. and V. Mudgal, *Differential Tolerance Behaviour of Safflower Accessions to Some Heavy Metals.* International Journal of Applied Environmental Sciences, 2009. 4(4).
3. Permenter, M.G., J.A. Lewis, and D.A. Jackson, *Exposure to nickel, chromium, or cadmium causes distinct changes in the gene expression patterns of a rat liver derived cell line.* PLoS One, 2011. 6(11): p. e27730.
4. Varga, I., Szebeni, Norbert and Kovács,*Determination of trace elements in human liver biopsy samples by ICP–MS and TXRF: hepatic steatosis and nickel accumulation.* Analytical and bioanalytical chemistry, 2005. 383(3): p. 476-482.
5. Coogan, T.P,Dorothy M Snow,Elizabeth TCosta, and Max, *Toxicity and carcinogenicity of nickel compounds.* CRC Critical reviews in toxicology, 1989. 19(4): p. 341-384.
6. Vyskočil, A., C. Viau, and M. Čížková, *Chronic Nephrotoxicity of Soluble Nickel in Rots.* Human & experimental toxicology, 1994. 13(10): p. 689-693.
7. Kaewsarn, P., *Biosorption of copper (II) from aqueous solutions by pre-treated biomass of marine algae Padina sp.* Chemosphere, 2002. 47(10): p. 1081-1085.
8. Dean, J.G., F.L. Bosqui, and K.H. Lanouette, *Removing heavy metals from waste water.* Environmental Science & Technology, 1972. 6(6): p. 518-522.

9. Pino, G.H., et al., *Biosorption of cadmium by green coconut shell powder.* Minerals engineering, 2006. 19(5): p. 380-387.
10. Fahn, A. and E. Werker, *Anatomical mechanisms of seed dispersal.* Seed Biology: Importance, Development, and Germination, 1972: p. 151-221.
11. Tiwari, D., H.-U. Kim, and S.-M. Lee, *Removal behavior of sericite for Cu (II) and Pb (II) from aqueous solutions: batch and column studies.* Separation and Purification Technology, 2007. 57(1): p. 11-16.
12. John, A.C, Ibironke,LO Adedeji, vector, Oladunni and Olafisoye,*Equilibrium and kinetic studies of the biosorption of heavy metal (cadmium) on Cassia siamea Bark.* American-Eurasian Journal of Scientific Research, 2011. 6(3): p. 123-130.
13. Shelke, RS.Madje, BR.Bharad, JV.Ubale and MB,*Adsorption of nickel (II), copper (II) and iron (III) from aqueous solution using Ashoka leaf powder.* Int J Chem Tech Res, 2009. 1: p. 1318-1325.
14. Das, B. and N. Mondal, *Calcareous Soil as a New Adsorbent to Remove Lead from Aqueous Solution: Equilibrium, Kinetic and Thermodynamic Study.* Universal Journal of Environmental Research & Technology, 2011. 1(4).
15. Gueu,S.Yao,*B.*Adouby,K.Ado,andG*, Kinetics and thermodynamics study of lead adsorption on to activated carbons from coconut and seed hull of the palm tree.* International Journal of Environmental Science & Technology, 2007. 4(1): p. 11-17.
16. Hameed, B., A. Ahmad, and K. Latiff, *Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust.* Dyes and Pigments, 2007. 75(1): p. 143-149.
17. Hameed, B. and A. Rahman, *Removal of phenol from aqueous solutions by adsorption onto activated carbon prepared from biomass material.* Journal of Hazardous Materials, 2008. 160(2): p. 576-581.
18. Dave, P.N., N. Subrahmanyam, and S. Sharma, *Kinetics and thermodynamics of copper ions removal from aqueous solution by use of activated charcoal.* Indian journal of Chemical technology, 2009. 16(3): p. 234.
19. Al Othman, Z.A., A. Hashem, and M.A. Habila, *Kinetic, equilibrium and thermodynamic studies of cadmium (II) adsorption by modified agricultural wastes.* Molecules, 2011. 16(12): p. 10443-10456.