

Kinetic and Equilibrium Studies on Removal of Nickel Ions onto Pomegranate Peel

Safanah A. Farhan, Rasha M. Dadoosh and Ayad T. Mahmood*

Polymer Research Unit, College of Science, Mustansiriyah University, Baghdad-Iraq.

Abstract

In this work, pomegranate peel (PGP) was investigated as adsorbent for removal of nickel ions from aqueous solution. It was found that maximum adsorption occur at PH7. Their equilibrium data were fitted with the Freundlich and Langmuir isotherms. The adsorption kinetics data were best fitted with the pseudo-second order.

Keyword: Pomegranate peel, Isotherms, Kinetics, Adsorption.

Introduction

Industrial, agricultural and domestic waste pollute water bodies with heavy metals, which reach tissues through the food chain. The toxicity of heavy metals to aquatic organisms has been a subject of interest to biologist for many years. Adsorption of trace metals onto natural particulate matter can play an important role in determining trace metal speciation in many aquatic systems [1–4]. Among different types of pollution, the industrial waste constitutes the major source of various kinds of metal pollution in natural water [5]. The important toxic metals, i.e. Cd, Zn, Cr, Pb and Cu finds its way to the water bodies through wastewater from such industries as metal-plating industries of cadmium, nickel batteries, pigment, stabilizers, alloys [6].

Nickel is used in plating plants and is present in their wastewater [7]. About 40% of the nickel produced are used in steel factories, Ni batteries and in the production of some alloys[8]. Manifestation of dermatitis in some workers engaged in electroplating, polishing, paints and pigments may be attributed to nickel poisoning.

The conventional methods for heavy metal removal from wastewater includes reduction, precipitation, ion exchange, reaction with silica, electrochemical reduction, evaporation, reverse osmosis and direct precipitation. Most of these methods involve high capital cost with recurring expenses, which are not suitable for small-scale industries. Studies on treatment of effluents bearing heavy metals have revealed adsorption to be a highly effective, cheap and easy method among the physicochemical

treatment processes. Owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low-cost materials. Removal of nickel by adsorption using solid residue from olive mill products [9], *Mangifera indica* seed shell [10], humic acid type purifying agents [11], coal-based adsorbents [12], burned clay and root [13], furnace gas cleaning sludge [14], hydrous oxides of iron(II) [15] have been reported. The aim of this work is to study the ability of pomegranate peel to clean water from nickel, the pH of maximum adsorption and the effect of PGP concentration as well as the kinetic model that fit to the experimental data and the best isotherm that fitted to the experimental data will be investigated.

Experimental

Biomass

Pomegranate peel (PGP) was collected in the Baghdad district which was dried, then milled and sieved to particle size of 300–500 μm . The PGP was shake with distilled water for overnight then filtered, this process was repeated about ten times or until we get rid off all colored or soluble materials, then filtered and dried in an air oven at 80 °C for overnight.

Preparation of Nickel solution and analysis

A stock solution of Ni(II), 500 mg/L, was obtained by dissolving 2.272g of Ni(NO₃).6H₂O in 1L of deionized water, and the solution was used for further experimental solution preparation. The pH values were adjusted with 0.1 M HNO₃ or 0.1M NaOH. Analytical grade reagents were used throughout this study. The Ni(II) content in the

sorption solutions was determined by atomic absorption spectrophotometer type (phoenix-986).

Batch adsorption studies

Effect of pH

The initial pH values were adjusted to 5.0, 6.0, 7.0 and 8.0 with 0.1M HNO₃ and 0.1 M NaOH. The effect of initial pH on the Nickel ions adsorption onto PGP was determined using 0.1 g of adsorbent in 50 mL of Ni solution of 20 mg/L at 30° C for 90 minutes and 140 rpm agitation. The amount of Ni(II) adsorbed onto the PGP, q_e mg/g, was calculated using the following equation:

$$q_e = (C_i - C_e)V/W \dots\dots\dots(1)$$

where C_i and C_e are the initial and equilibrium liquid phase concentration of Ni(II) respectively. V is the volume of the solution (L) and W is the weight of the PGP used (g). the Nickel percent removal (R%) was calculated using the following equation:

$$R\% = C_i - C_e / C_i \times 100 \dots\dots\dots(2)$$

Kinetic studies

Kinetic studies were carried out at solution pH 7.0. Nickel solution of 20 mg/L agitated at 30 and 40°C. The samples were collected from duplicate flasks at different time intervals, filtered by filter paper, the filtrate was analyzed for residual Ni(II) concentration using atomic absorption spectrophotometer .

Result and Discussion

Effect of pH on Nickel(II) Adsorption

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution [16]. Plot of pH versus quantity of metal ion adsorbed on gram of adsorbent q_e was shown in Fig.(1). The optimum pH was found to be pH 7 .The maximum removal efficiency was 84.5%. At pH values higher than 6.0, insoluble Nickel hydroxide start precipitating from the solutions making true sorption studies impossible [17].

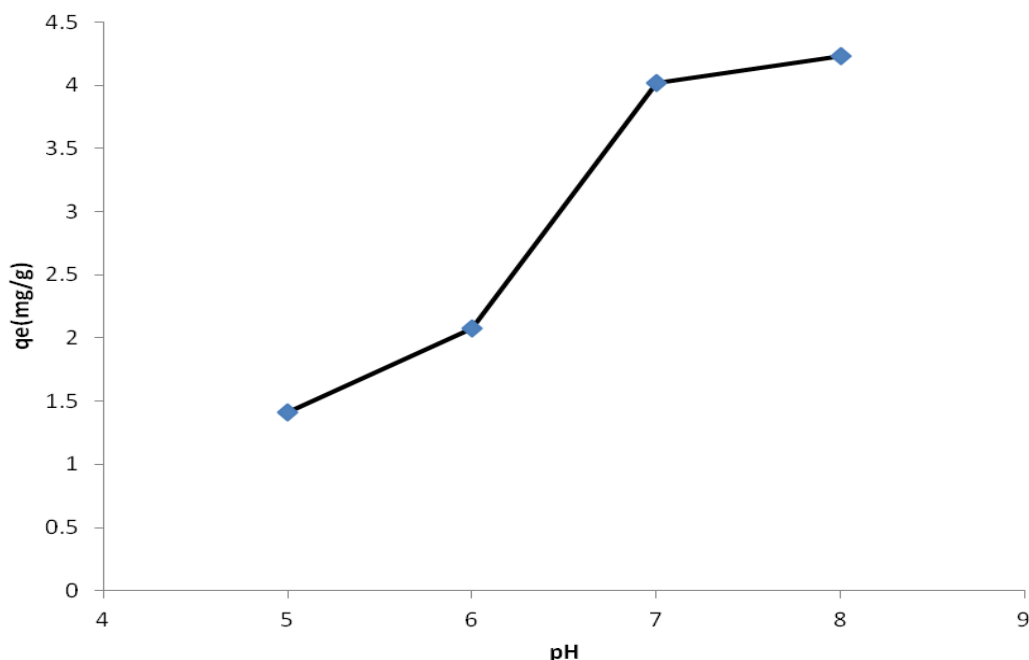


Fig .(1) pH versus quantity of metal ion (Ni^{+2}).

Effect of adsorbent concentration

The effect of PGP dosage on the adsorption of Ni(II) from aqueous solutions was investigated using four different adsorbent concentrations. The extent of adsorption is proportional to specific area, which can be defined as that portion of the total area that is available for adsorption. Concentrations of

PGP were varied from 2 to 16 g/L. The results are presented in Fig.(2) which indicate that the q_e decreased with increasing PGP concentration, while the R% increases with increasing PGP concentration . This result may be attributed to the fact that the higher sorbent doses provide the more sorbent surface area and pores volume which will be available

for adsorption [18]. On the other hand five experiments have been done to evaluate the effect of initial concentration of Ni(II) on the adsorption of Ni(II) onto PGP. This effect was

elucidated in Fig.(3) from the plot of q_e versus C_e . we can estimate the removal capacity of PGP which is about 28 mg/g.

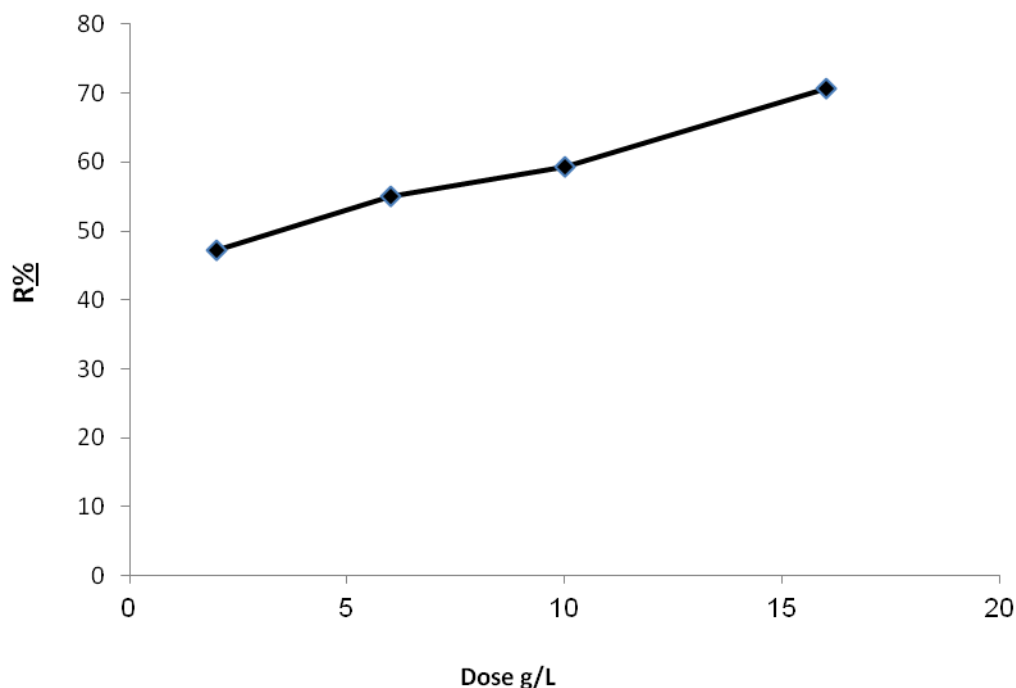


Fig.(2) Adsorbent dose versus Nickel percent removal (R%).

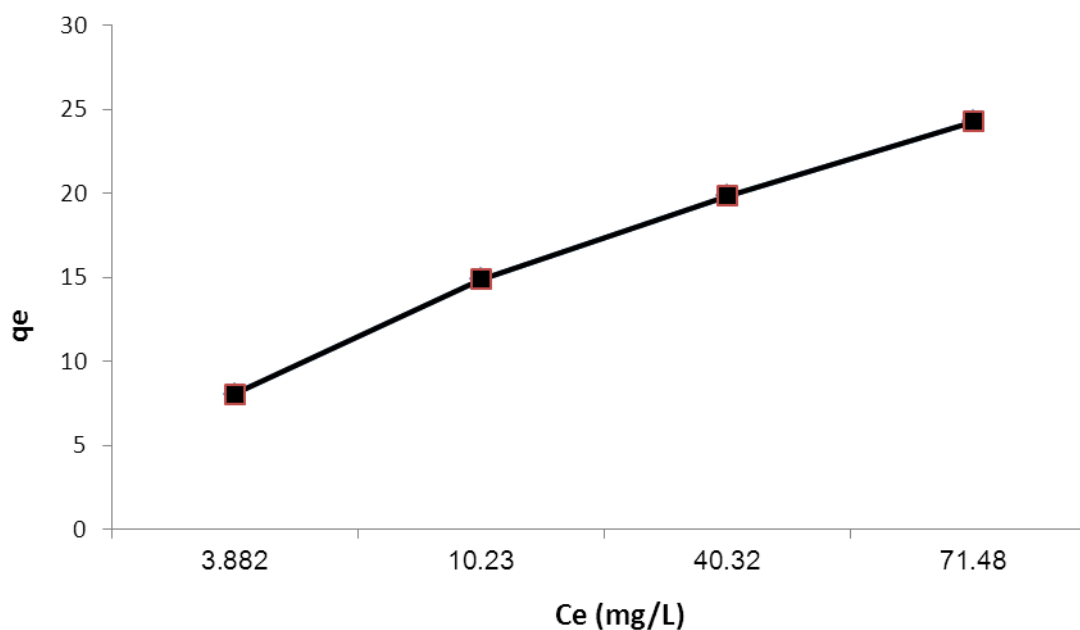


Fig.(3) The amount of Ni (II) adsorbed at equilibrium liquid phase concentration.

Adsorption kinetic

The study of adsorption kinetic describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of

Ni(II) adsorption on the PGP were analyzed using pseudo first-order and pseudo second-order. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2)

and the coincidence between the experimental and calculated q_e . A relatively high (R^2) value indicates that the model successfully describes the kinetics of Ni(II) adsorption.

The pseudo first-order equation [19] is generally expressed in its linear form as follows:

$$\text{Log}(q_e - q_t) = \text{Log}q_e - (k_1 / 2.303) t \dots\dots\dots(3)$$

The linear form of pseudo second-order adsorption kinetic equation is expressed as [20]:

$$t / q_t = 1 / k_2 q_e^2 + 1 / q_e (t) \dots\dots\dots(4)$$

Where k_1 and k_2 are the rate constants of Pseudo-first-order and Pseudo-second-order kinetics, q_e and q_t are the adsorption capacity

at equilibrium and time t respectively. From the plot of first-order kinetic, $\text{log}(q_e - q_t)$ versus time, the rate constants and the adsorption capacity q_e can be calculated which was presented in Table (1). It is obvious from the correlation constants and the calculated q_e that the adsorption process did not follow the first-order kinetic. When the experimental data were applied to the second-order kinetic it was obvious from Fig.(4) and Table (1) that the calculated q_e in good agreement with experimental one, and the correlation coefficient was higher than that of the first order kinetic.

Table (1)
Kinetic parameters of 1st-order and 2nd-order models at 40&50 °C.

| <i>Pseudo-first-order kinetic</i> | <i>40°C</i> | <i>50°C</i> |
|-----------------------------------|-------------|-------------|
| $q_e(\text{exp.})$ | 7.355 | 8.34 |
| $q_e(\text{cal.})$ | 2.154 | 5.144 |
| k_1 | 0.024 | 0.025 |
| R^2 | 0.961 | 0.7488 |

| <i>Pseudo-second-order kinetic</i> | <i>40°C</i> | <i>50°C</i> |
|------------------------------------|-------------|-------------|
| $q_e(\text{cal.})$ | 7.496 | 8.562 |
| k_2 | 0.028 | 0.011 |
| R^2 | 0.9995 | 0.9877 |

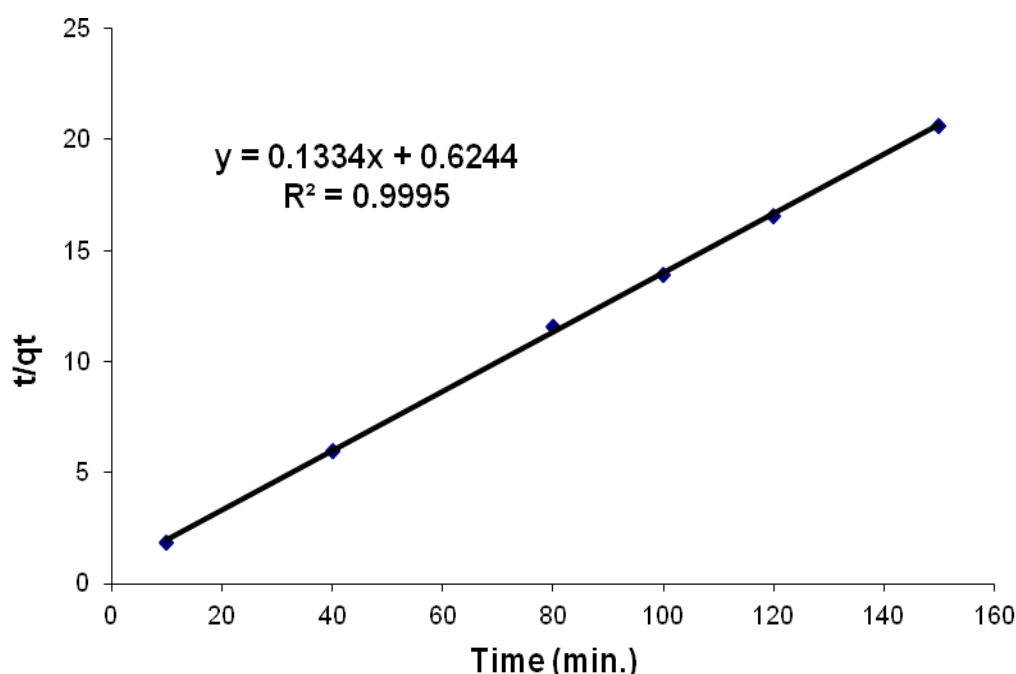


Fig.(4) *2nd-order kinetic at 40 °C.*

Adsorption isotherm

Adsorption isotherms are essential for the description of how metal ion concentration will interact with the adsorbent surface and are useful to optimize the adsorbent for the removal of Ni(II) ions . Isotherms are one of the most important data to understand the mechanism of the sorption. Several isotherm equations are available and two important isotherm are selected in this study. They are namely the Langmuir, and Freundlich models. The **Langmuir equation** equation is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, the linear form can be written as follow [21]:

$$C_e/q_e = (1/Q_m b) + (1/Q_m) C_e \dots\dots\dots(5)$$

Where Q_m is the theoretical maximum adsorption capacity ($mg\ g^{-1}$), b is the Langmuir adsorption constant ($L\ mg^{-1}$). Plot of C_e/q_e versus C_e is presented in Fig.(5). The values of Langmuir isotherm constants and correlation coefficients are found in Table (2). The

correlation coefficients of the isotherm were found to be linear over the whole concentration indicating that the Langmuir isotherm is applicable. The Q_m value is presented in table 2 and found to be 26.8 mg/g. The **Freundlich isotherm** [22] is derived by assuming a heterogenous surface with a non-uniform distribution of heat of sorption over the surface , the linear form is :

$$\text{Log } q_e = \text{log}K_F + 1/n \text{log}C_e \dots\dots\dots(6)$$

Where K_F ($L\ mg^{-1}$) and n are isotherm constants indicate the capacity and intensity of the adsorption respectively. The linear plot of $\text{log } q_e$ versus $\text{log}C_e$ indicate that the adsorption of Ni(II) onto PGP also follows Freundlich equation Fig.(6), the Freundlich constants and correlation coefficients are listed in Table (2). The value of $1/n$ was found to lie between zero and one, indicating that the Ni(II) is favourably adsorbed by PGP at the studied temperature[23]. On the other hand, the value of (n) are higher than one indicating that the adsorption may be physical [24].

Table (2)
Isotherms Constant of adsorption Ni⁺² onto PGP at 30 °C.

| | | |
|-------------------|-----------------------------|---------------|
| Langmuir | Q_{max} | 26.8 |
| | b | 0.103 |
| | R² | 0.9906 |
| Freundlich | K_F | 5.55 |
| | n | 2.833 |
| | R² | 0.9413 |

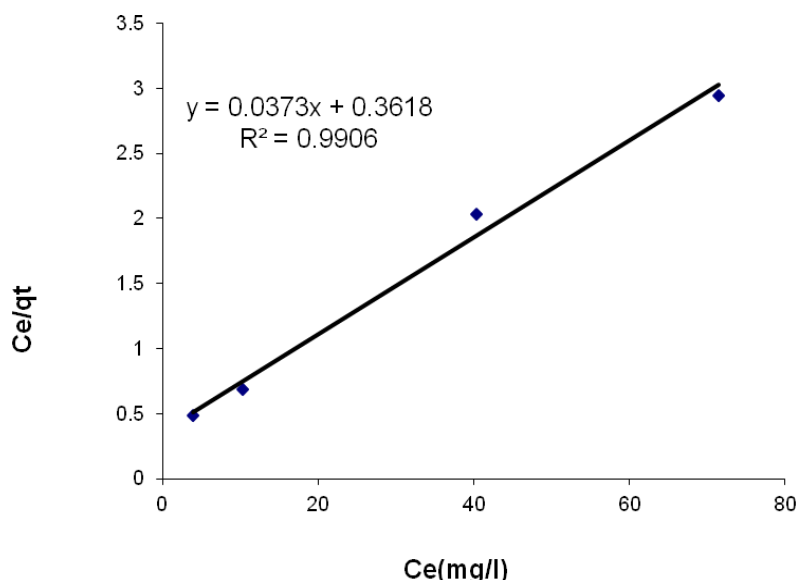


Fig.(5) Adsorption isotherm from Langmuir equation.

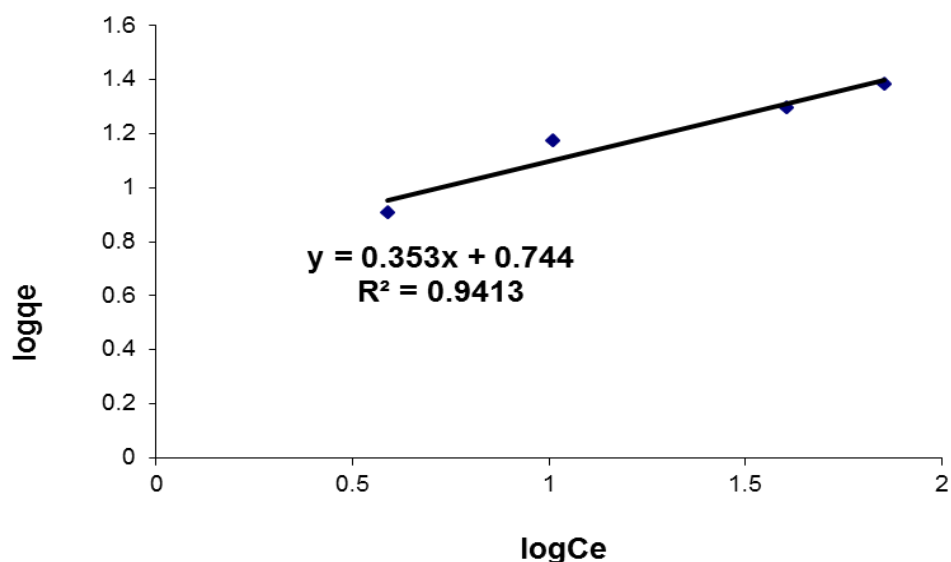


Fig.(6) Adsorption isotherm from Freundlich equation at 30 °C.

References

- [1] Laxen D.P.H.; "Cadmium adsorption in freshwaters - a quantitative appraisal of the literature"; *Sci. Total Environ.* 29, 129–146, 1983.
- [2] Jenne E.A.; "Trace element sorption by sediments and soil-site and processes, in: Chappell W.R.; Peterson K.K. (Eds);" *Molybdenum in the Environment*" vol. 2 Marcel Dekker, New York, 1977, Chap. 5.
- [3] Florence T.M.;"The speciation of trace element in water", *Talanta* 29,345-364, 1982.
- [4] Oakley S.M.; Nelson P.O.; Williamson K.J.; "Model of trace metal partitioning in marine sediments"; *Environ. Sci. Technol.* 15, 474-480, 1981.
- [5] Harrison R.M.; Laxen D.P.H.;"Metals in the Environmental Chemistry"; *Br. vol.* 16, pp. 316–320, 1980.
- [6] Low K.S.; Lee C.K.; "Cadmium uptake by moss colympers delesertic, besch"; *Bioresour. Technol.* 38, 1-6, 1991.
- [7] Klein L.A.; Nash M; Kirschner N.; "Sources of metals in New York City wastewater"; *J. Water Pollution Control Fed.* 46, 2653–2662, 1974.
- [8] Friberg L.; Piscator M.; Nordberg G.F.; Kjellstorm T.; "Cadmium in the Environment" CRC Clevel, 1980.
- [9] Gharaibeh S.H.; Abu-El-Shair W.Y.; Al-Kofahi M.M.; "Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products"; *Water Res.* 32,498-502, 1998.
- [10] Ajmal M.; Mohammad A.; Yousuf R.; Ahmad A.; "Adsorption behaviour of Cd, Zn, Ni and Pb from aqueous solutions by *Mangifera indica* seed shell"; *Indian J. Environ. Health* 40, 15-26, 1998.
- [11] Guangju W.; Longgiang Z.; Cuncai C.; Shuisong T.; "Removal of nickel by adsorption using solid residue from olive mill products"; *Huanjing Kexue* 7 (3),35–38, 1986.
- [12] D.K. Singh; J. Lal; "Removal of toxic heavy metal ions from wastewater by coal based adsorbent"; *Pollut. Res.* 11,37–42, 1992.
- [13] Donali A.; Sietz M.; Moeselli L.; Zappoli S.; Ghedizzi A.; "Removal of nickel by adsorption using *Mangifera indica* seed shell";*Toxicol. Environ.Chem.*35, (1-2), 87–92, 1992.
- [14] Jallan G.; Pandey G.S.; "Blast furnace gas cleaning sludge as adsorbent of some toxic ions"; *Res. India* 37 (3) ,143-145, 1992.
- [15] Kanungo S.B.;" Adsorption of Cations on Hydrous Oxides of Iron: II"; *J. Colloid Interface Sci.* 162 (1),93-102, 1994.
- [16] Aksu Z.; "Application of biosorption for the removal of organic pollutants: a Review"; *Process Biochemistry* 40, 997-1026, 2005.
- [17] Antunes W.M.; Luna A.S.; Henriques C.A.; "An evaluation of copper biosorption by a brown seaweed under optimized conditions"; *Biotechnology*, 6, 174-184, 2003.

- [18] El Nemr, A; "Pomegranate husk as an adsorbent in the removal of toxic chromium from wastewater"; Chemistry and Ecology, 23(5),409-425, 2007.
- [19] Langergren, S.; and Svenska, B.K.; "Zur theorie der sogenannten adsorption geloester stoffe"; Veternskapsakad Handlingar, 24, 1-39, 1898.
- [20] Mckay, Ho. Ys.; Wase G.; DAJ and Foster,CF;" Study of the sorption of Divalent metal ions on to peat"; Adsorption Sci, Technol., 18, 639-650, 2000.
- [21] Langmuir I; "The constitution and fundamental properties of solids and liquids"; J.Am. Chem. Soc., 38, 2221-2295, 1916.
- [22] Freundlich HMF; Zeit, Phys. Chem. (Leipzig), 57A, 385-470, 1906.
- [23] Abdelwahab O.; "Kinetic and isotherm studies of copper(II) removal from wastewater using various adsorbent"; Egyption J. Aquatic Research, 33, 125-143, 2007.
- [24] Grini G; Peindy HN; Gimbert F; and Robert C;" Removal of C.I. basic green4 (Malachite Green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies"; Separation and Purification Technology, 53(1), 97-110. 2007.

الخلاصة

في هذا البحث تم استخدام قشور الرمان كماده امتزاز لازاله ايونات النيكل (II) من محاليل المائيه، ولقد وجد ان أفضل امتزاز يحصل عند (pH7). قيم التوازن الحراري تتفق مع معادلات فريندلش ولاينكمابير، حيث ان دراسه حركيه الامتزاز تتفق مع مرتبه التفاعل الثانيه الكاذبه.