Chemistry and Materials Research
ISSN 2224- 3224 (Print) ISSN 2225- 0956 (Online)
Vol.7 No.7, 2015 www.iiste.org

Removal of Ni(II) and Cd(II) from Their Aqueous by Bio Byproducts of Leaf Base (Petiole) and Fiber of the Date Palm as Low Cost Adsorbents

Mohammed T. Khathi
Chemistry Department \ College Of Science \ University Of Thi-Qar

Abstract

The present study included study of using the agricultural bio byproducts of leaf base (petiole) and fiber of the date palm as low cost adsorbents for removal of Ni(II) and Cd(II) from their aqueous solutions via preparation of activated carbon. The results showed that the adsorption equilibrium time was 40, 30 min. for Ni(II) by leaf and fiber respectively and 30 min for Cd (II) adsorption by both of byproducts. The obtained results indicated that over pH range (6.5–7.0) there is an increased optimum of adsorption for all metal ions. (0.5g) of adsorbent is very ideal to obtain the best adsorption for both studied metals ions . The capacity of the adsorbents to adsorb these metal ions were found to be Ni (II) >Cd (II). The isotherms obeyed Langmuir isotherm better than Freundlich isotherm for both metals. Fiber has the highest removal than petiole. Thermodynamic parameters (ΔG^o) , (ΔH^o) and (ΔS^o) have been found that the sorption process was feasible, spontaneous and exothermic. Calculated kinetic parameters showed that the pseudo first order model is best fit to the experimental data.

إزالة ايونات العناصر Ni(II) and Cd(II) من محاليلها المائية باستخدام المخلفات الزراعية لكرب وليف النخيل كمواد مازة واطئة الكلفة

محمد تركي خثي
قسم الكيمياء / كلية العلوم / جامعة بغداد

الخلاصة

من خلال Ni(II) , Cd(II) أجريت دراسة استخدام المخلفات الزراعية لكرب وليف النخيل كممتزات لإزالة الايونات الثنائية لعنصري
فكان زمن الاتزان لأمتزاز 40 و 30 دقيقة لكل من الكروم والنيكل بواسطة الكرب والليف على التوالي و 30 دقيقة تحضير الكاربون المنشط
غم) ضمن المدى (7-6.5) تعطي مثالية في كميات الامتزاز لكلا العنصرين. الدراسة بينت ان (pH 0.5للكادميوم باستخدام كلا المخلفين و أن قيم
كما ان Ni (II) >Cd (II)لوزن المادة المازة هو مثالي جدا للحصول على أفضل نسبة امتزاز ولكلا العنصرين ايضا . قابلية الامتزاز كانت
أيزوثرمات الامتزاز اكثر انطباقا لأيزوثرم لانكماير منه لأيزوثرم فرندلش. وعموما الليف يمتلك أعلى قابلية إزالة من الكرب .الثوابت
بينت ان عملية الازالة باعثة للحرارة و تلقائية ومنتظمة على التوالي , كما اثبت عمليا ان حركية (ΔS^o) و (ΔG^o) و (ΔH^o)الثرموداينميكية
الأمتزاز لكلا العنصرين المدروسين تنطبق عليها معادله المرتبة الأولى الكاذبة .

1-Introduction :

Different treatments and combinations of treatments are proposed to effectively manage the waste water. Classical techniques of heavy metal removal from solution included the following processes: metal salts precipitation this method require large quantities of chemicals, electrolytic methods, adsorption, ion exchange and evaporation(1). The problem of removing pollutants from water are growing with rapid industrialization the discharge of toxic metals into water causes serious pollution problems. The classical techniques that are utilized to remove pollutants have some of disadvantages, In the recent years many methods were followed the developments of effective and low cost adsorbent from natural materials(2) such as petiole and palm fiber.

Adsorption from solutions on a solid surface occurs as a result of one of two characteristic properties for a given solvent- solute- solid systems , or a combination of both systems (3).The process of adsorption from solution is even more difficult to treat theoretically than the corresponding gas-on-solid process. It appears, however ,that only a monolayer is formed, any further addition being strongly opposed by the solvating power of the solvent(4).

Toxic heavy metal ions get introduced to the aquatic streams by means of various industrial activities via mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc. which process a serious threat to environment(5). Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However the metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading to the health hazards and environmental pollution .Conventional methods for removal of metal ions from aqueous solutions include chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electro dialysis, ultra filtration etc (6). Conventional techniques have their own inherent limitations such as less efficiency, sensitive operating conditions, production of secondary sludge and further the disposal is a costly affair (7).

Another powerful technology is adsorption of heavy metals by activated carbon for treating domestic and industrial waste water. (8). However the high cost of activated carbon and its loss during the regeneration restricts its application. Since 1990's the adsorption of heavy metal ions by low cost renewable organic materials has gained momentum(9). The utilization of seaweeds, moulds, yeasts, and other dead microbial biomass and agricultural waste materials for removal of heavy metals has been explored (10). Recently attention has been diverted towards the biomaterials which are byproducts or the wastes from large scale industrial operations and agricultural waste materials(11).

The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of adsorbents and possibility of metal recovery(12).Agricultural materials particularly those containing cellulose show potential metal biosorption capacity. The basic components of the agricultural waste materials biomass include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, starch contain a variety of functional groups that facilitates metal complexation which helps for the sequestering of heavy metals (13).

Agricultural waste materials being economic and ecofriendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation(119).Several studies reveal that various agricultural waste materials such as rice bran, rice husk, wheat bran, wheat husk, saw dust of various plants, bark of the trees, groundnut shells, coconut shells, black gram husk, hazelnut shells, walnut shells, cotton seed hulls, waste tea leaves, Cassia fistula leaves, maize corn cob, jatropa deoiled cakes, sugarcane bagasse, apple, banana, orange peels, soybean hulls, grapes stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, arjun nuts, cotton stalks etc has been tried (14).

The aims of this work is to investigate the key parameters and mechanism affecting the removal of Ni(II) and Cd(II) from aqueous solutions, using agricultural waste materials adsorbents leaf base and fiber of the date palm, not as nature form but after being modified to activated carbon for increasing their sorption capabilities using batch mode. The thermodynamic and kinetic parameters of removal process were also studied.

2- Experimental Part:

2-1 Cadmium standard solution:

An adsorbate standard solution of 100 mg/l of Cadmium was prepared by dissolving 0.1854g of $CdSO_4$ in 1000 ml of distilled water.The solution was served as stock solution for further applications.

2-2 Nickel standard solution:

An adsorbate standard solution of 100 mg/l of nickel was prepared by dissolving 0.2208g of $NiCl_2$ in 1000 ml of distilled water. The solution was served as stock solution for further applications.

2-3 The adsorbents:

Two types of adsorbents were used, *Leaf Base(Petiole)* and *Fiber of Palm* dates production. The adsorbents of date palm tree of type (Sukkary) was obtained from Nasiriya / Iraq.

Table (1) shows the main components of the ***Leaf Base (Petiole)*** and ***Palm Fiber*** according to Food and Agriculture Organization (FAO)(15). The pattern of sorption of metals on plant materials is attributable to the active groups and bond present on them (16). The active groups, such as amino, carbonyl and hydroxyl, present in the adsorbent are responsible for binding metal ions.

Table (1) The chemical analysis of leaf base and fiber of the date palm

Compound	***leaf base %***	***Palm Fiber%***
Cellulose	42.59	40.5
Hemi cellulose	21.30	20.0
Lignin	12.20	14.40
Ash	7.50	6.20
Proteins	1.29	1.2
Lipids	0.37	-
Loss in Ignition	14.63	16.33
Total%	99.88	98.63

2-4 Adsorption experimental procedure:

The base of the leaves were cutting and the external layer was removed completely. The leaf base (petiole) and fiber were divided into sections, dried at (110°C) for one day, left to cool at room temperature and kept in air light containers. The sections were ground to obtain a yellowish tint and brown powder respectively which is insoluble in water, acids, alkali hydroxides, and Ether. It swells with little amount of water. The BET surface area of the powders were measured before and after activated to petiole and fiber charcoal powders at 900°C Table (2).The adsorption capacity of carbon is strongly attributed to the chemical structure of its surface .

Table (2). The BET surface area of byproducts before and after activation

Adsorbates	**BET surface area before activation $m^2.g^{-1}$**	**BET surface area after activation $m^2.g^{-1}$**	**Mesh mm**
Petiole base	0.9	210	1-10

Palm Fiber	0.8	322	1-10

2-5 Adsorption isotherm

The adsorption isotherm for heavy metals solutions were determined by using Batch adsorption experiment :(25ml) of heavy metals solution of a known concentration ranged from (5mg/L) to (20mg/L) were added separately to volumetric flasks containing (0.5 g) of each adsorbents. At a certain temperature 25^{o}C and optimum pH, the flasks were shaken in a thermostatically controlled shaker incubator at a constant speed (10 cycler per minutes) for the required equilibrium time. The mixtures were then separated by centrifugation at (1500 rpm) for (10 minutes) and were filtered by using (No.42) Whatman filter paper. The metal Equilibrium concentrations were measured by using Atomic Absorption Spectrometer (AAS) and comparing the experimental data with the calibration curve. The amount of heavy metals adsorbed were calculated from the initial and final concentrations and the volume of solution according to the following equation(17):

$$Q_e = \frac{V(C_o - C_e)}{m}$$

Where :

V = Volume of solution (L) , C_o= initial concentration (mg/L)

C_e= equilibrium concentration (mg/L) , m = weight of adsorbent (g)

The amount of adsorption is expressed by (Q_e) which is defined as the quantity of adsorbate in (mg) held by weight of adsorbent in (1g).

2-6 Factors affecting adsorption of heavy metals by adsorbents:

The main investigated parameters that may influence metal sorption were: pH, temperature, adsorbent weight, contact time and heavy metal initial concentration .

2-6-1 pH effect:

An experiment was carried out at pH (4, 6, 7, 9) for heavy metal solution. The acidic and alkaline pH of the solution was adjusted by adding the required amounts of 0.1M hydrochloric acid and 0.1 M sodium hydroxide solutions.

2-6-2 Temperature effect:

The adsorption of heavy metals were studied at temperatures of 25°C, 30°C and 40°C with fixation of others factors.

2-6-3 Adsorbent weight effect:

The effect of different weight of adsorbents, that range from 0.01- 2g for adsorbent were assessed and the percentage of adsorption for different weights was determined by keeping all other factors constant.

2-6-4 Contact time effect

The effect of period of contact time between the adsorbent and adsorbate on the removal of the metal ions was determined by keeping pH, temperature, weight and initial concentration constant(18).

2-6-5 Heavy metal initial concentration:

This experiment was conducted with several metal concentrations which were: 5, 10, 15, 20 and 25 mg.l^{-1}. All other factors were kept constant.

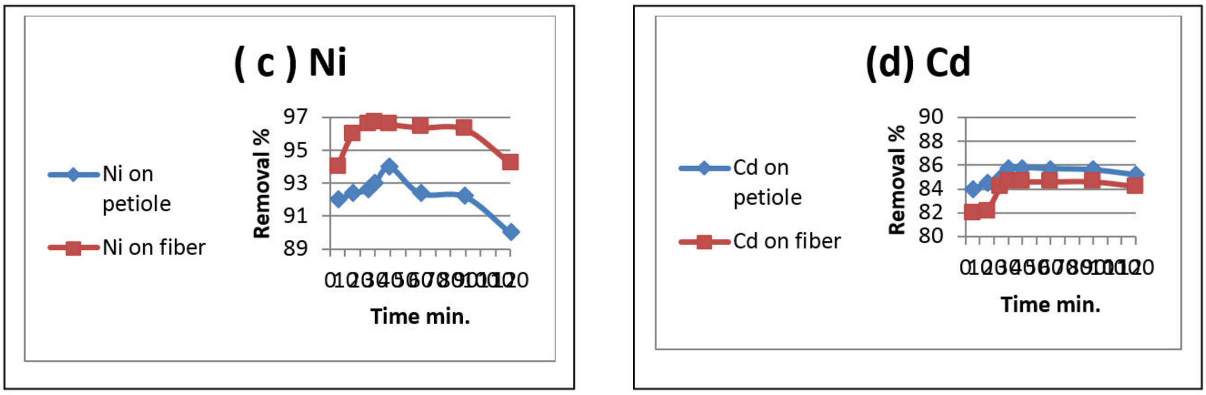
2-7 Removal of heavy metal by adsorbents from water :

The aim of this experiment was to test the ability of adsorbents for the removal of heavy metal from the water.

3- Result and discussion :

3-1 Effect of contact time

The equilibrium time was investigated as mentioned in(2-6-4). Figure (1a,b) represent rates of Ni(II) and Cd (II) removal by petiole base and fiber of palm with the contact time. The rate of uptake of metal ion was quite rapid, 40, 30 min. Ni(II) by leaf and fiber respectively and 30 min for Cd (II) adsorption by both of adsorbents.



Figures (1 a,b): Effect of contact time on rate of (a) Ni(II) and (b) Cd (II) removal by petiole base and fiber of palm at 25±2 °C , 0.5g and pH 7.

3-2 Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. These results indicated that in the pH range (6.5–7.0) figures (2a,b). There is an increase optimum of adsorption amounts for both element ions. However the adsorption amounts decrease at pH above (7) due to the decreases of the negative charge of the surface ,or caused by contamination which attributed to extended of metals ions to precipitation in base medium solutions (not precipitation may become significant mechanism in the metal removal process) .The change in adsorption capacity at different pH could be ascribed to the competitive adsorption between hydrogen ions and elements ions .

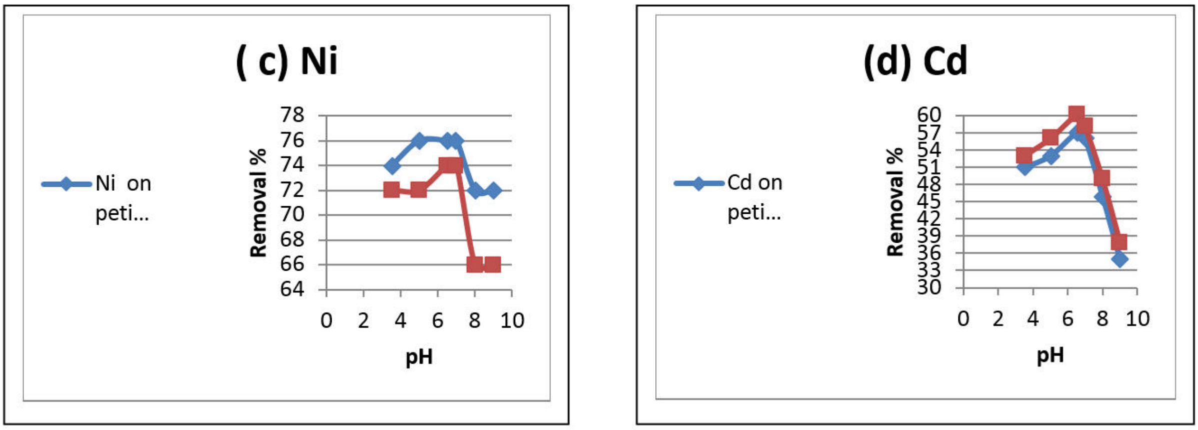


Figure (2a,b) : Effect of pH on rate of (a) Ni(II) and (b) Cd (II) removal for the petiole and fiber surfaces at 25 ± 2 °C.

3-3 Effect of the adsorbent weight change

The research work aimed to find the amount of adsorbent that is required to attain surface saturation at certain conditions. Figures (3a,b). It is very clear that the tested adsorbents doses (0.5g) of adsorbent weight was very ideal to obtain at best adsorption for all studied metals ions .

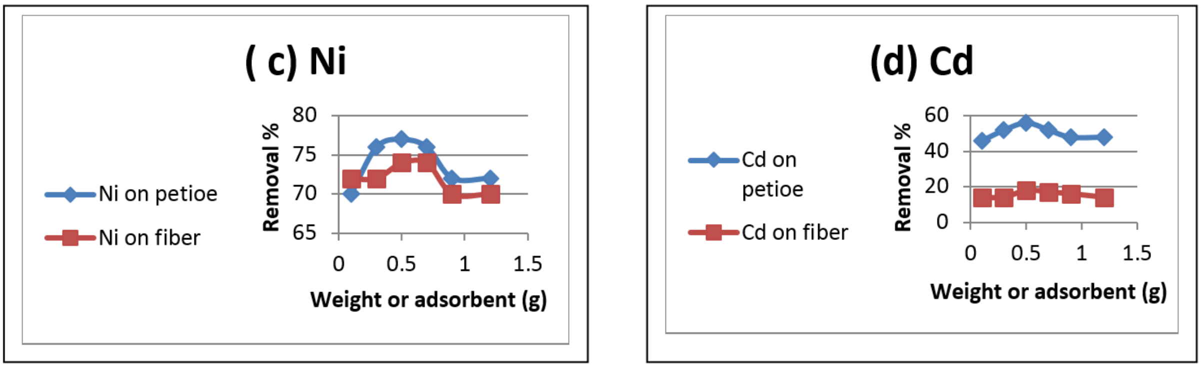
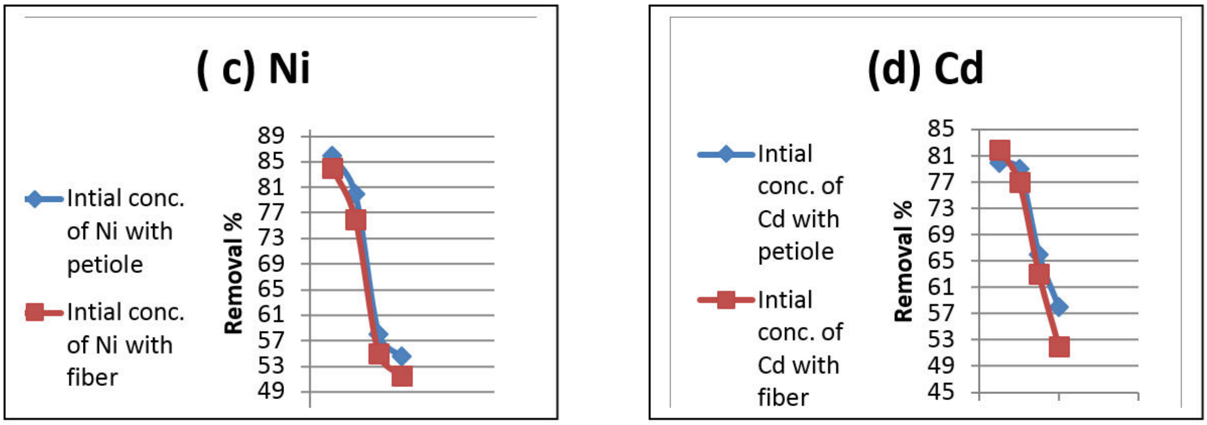


Figure (3a,b) : Effect of the adsorbent weight change on rate of (a) Ni(II) and (b) Cd (II) removal for the petiole and fiber surfaces at 25 ± 2 °C. , pH 7 and contact time 30 min.

3-4 : Effect of initial metal concentration

The effect of initial metal concentration on rate of both ions was studied by batch adsorption experiments, which were carried out at 25±2◦C using different initial metal ion concentrations in the range (5, 10, 15 and 20 mg/l) at optimum pH and are shown in figures (4a,b) which indicate that the percentage removal decreases with the increase in the initial ion concentration , this is because there were no more adsorption sites on the adsorption surface of the adsorbent material. The maximum removal percentage of Ni using petiole was 86% and the maximum removal percentage of Cd using fiber was 82% at a metal concentrations 5mg/l for all heavy metals under study. This optimum concentration was used in all experiments.

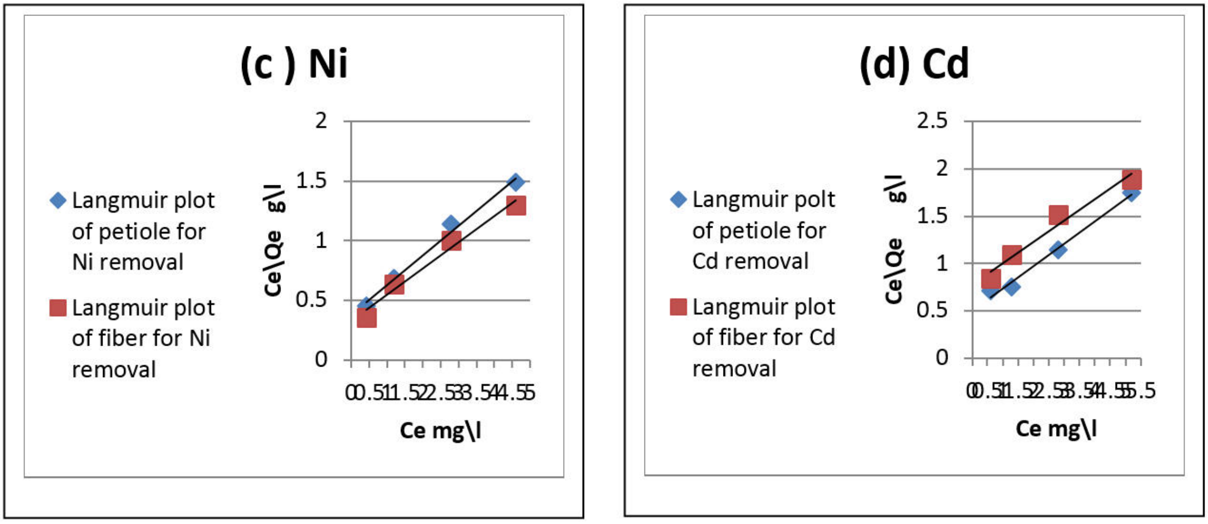


Figures(4a,b):Effect of initial concentration on rate of (a) Ni (II) (b) Cd (II) removal for petiole and fiber at 25±2 oC

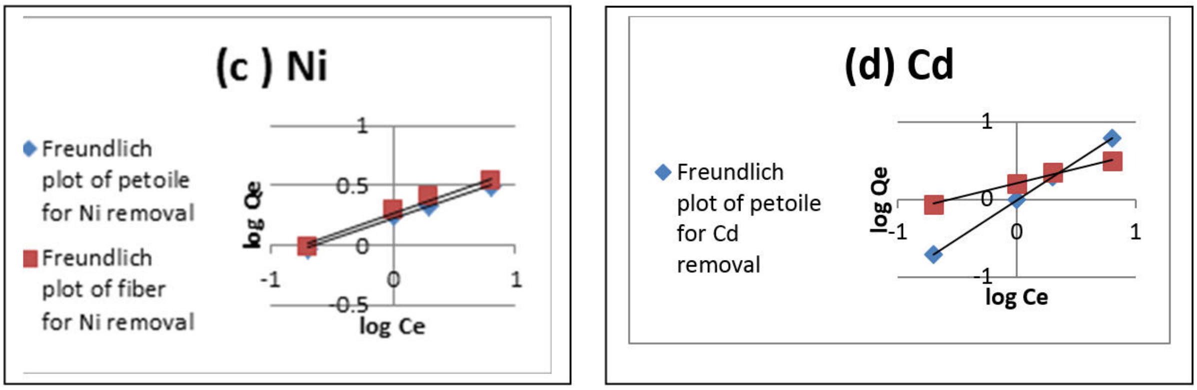
The capacity of the adsorbents to adsorbate for these metals was Ni (II) > Cd (II).

3-5 Adsorption isotherms

Linear plots of Ce/Qe versus Ce and log Ce versus log Qe are shown in Figures (5a,b) (6a,b). The adsorption of metals ions on two adsorbents seems to follow the Langmuir isotherm as well as Freundlich isotherm.



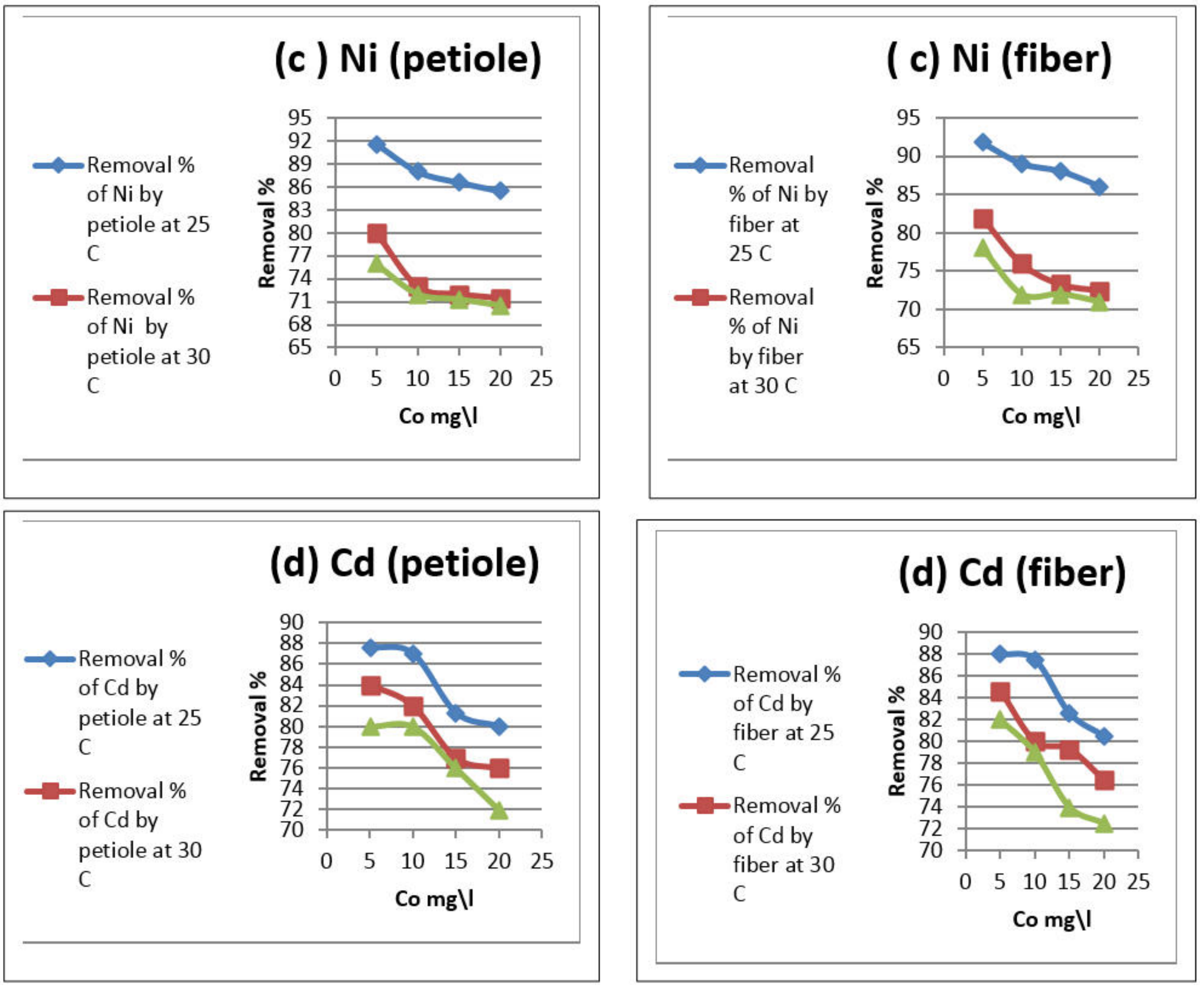
Figures (5a,b) Langmuir plot of petiole for (a) Ni and (b) Cd removal at 25±2^{o}C.



Figures (6a,b) . Freundlich plot of petiole for (a) Pb Ni and (b) Cd removal at 25± 2 ^{o}C.

3- 6 The Adsorption isotherm of metals ions on petiole and fiber at different temperature

The adsorption of Ni(II) and Cd(II) on the petiole and fiber surfaces were studied at (25^{o}C) as well as at the other two temperatures (30 and 40)^{o} C, the initial concentration of heavy metals ,adsorbents dosage and pH were fixed to 5 mg\l ,0.5 g and 6.5-7 respectively. The quantity (Q_e) was plotted versus the equilibrium concentration (C_e) to obtain the general shape of the adsorption isotherms as shown in figures (7a,b) and (8a,b) which represents the isotherms of both ions on the petiole and fiber at different temperatures.



Figures(7a,b) and **(8a,b): Removal % of Ni(II0 and Cd(II) ions by petiole and fiber surfaces at different temperatures**

A decrease in the amount of metals ions which was removed on petiole and fiber with the increase of temperature was noticed , that adsorption process appeared to be exothermic(19). The low temperatures are the favorite for adsorption of metals ions on petiole and fiber. The decrease in adsorption of metals ions with the increase of temperature could be explained by the fact that the thickness of the boundary layer decreases with the rise in the solution temperature , due to the increased tendency metals ions to desorbed from the solid phase to the liquid phase(20) .It is well understood that lignocelluloses materials such as petiole are not pure polymers. Their main constituents are cellulose, lignin, hemi cellulose and extractives(21),where chemical and physical forces interact with the ionic lead to the result complexity. Consequently, the removal of metals ions can be governed by any four basic processes ; adsorption , absorption , ion exchange and chelating . However this change in removal rate of metals ions could be attributed to one or more of these different processes , the most effected method may be ions exchange and adsorption.

3-7 Thermodynamic studies

Thermodynamic parameters such as the free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes during adsorption can be evaluated from the equations (1,2 and 3) where Kc is the equilibrium constant, Ce is the equilibrium concentration in solution (mg.L^{-1}) and C_{Ae} is the solid-phase concentration at equilibrium(mg.L^{-1}). ΔG^o , ΔH^o and ΔS^o are changes in Gibbs free energy (kJ.mol^{-1}), enthalpy (kJ.mol^{-1}) and entropy (J.mol^{-1}K^{-1}), respectively. R is the gas constant (8.314 J.mol^{-1}.K^{-1}) and T is the temperature in (K). A plots of log K_c versus 1/T enable as to calculate the values of ΔH^o from the slope and ΔS^o from the intercept resulted from plots . The ΔG^o values were obtained using Equation (2). (22)

$$K_c = \frac{C_{Ae}}{C_e} \qquad \text{------------------------------------} \qquad -1$$

$$\Delta G^o = -RT\ln K_c \qquad \text{------------------------------------} \qquad -2$$

$$\log K_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \qquad \text{- - - - - - - - - - - - - - - - -} \qquad -3$$

Table (3a): Effect of temperature on the thermodynamic equilibrium constant for adsorption of metals ions on the petiole surface .

Metals ions	T (^{o}C)	T (^{o}K)	Inverse Temp (^{o}K^{-1})10^{-3}	b	Q_m	R2
Ni(II)	25	298.15	3.356	1.557	15.02	0.9953
	30	303.15	3.297	2.597	11.846	0.9942
	40	313.15	3.358	1.345	14.832	0.9944
Cd (II)	25	298.15	3.354	0.059	13.263	0.9907
	30	303.15	3.296	1.421	11.876	0.9936
	40	313.15	3.193	1.335	10.312	0.9932

Table (3b) : Effect of temperature on the thermodynamic equilibrium constant for adsorption of metals ions on the fiber surface .

Metals ions	T (^{o}C)	T (^{o}K)	Inverse Temp (^{o}K^{-1})10^{-3}	b	Q_m	R2
Ni(II)	25	298.15	3.316	1.425	18.453	0.9853
	30	303.15	3.298	1.55	10.909	0.9333
	40	313.15	3.158	1.49	10.009	0.9766
Cd (II)	25	298.15	3.016	0.066	16.155	0.9771
	30	303.15	3.297	2.36	12.543	0.9002
	40	313.15	3.1358	1.62	22.621	0.9478

Table (4a): Values of thermodynamic functions for the adsorption of metals ions on the petiole surfaces at different temperatures.

Metals ions	*T* ^oC	*ΔG°* (*kJ. mol^{-1}*)	*ΔH°* (*kJ. mol^{-1}*)	*ΔS°* (*J. mol^{-1}.K^{-1}*)
Ni(II)	**25**	**-68.27**	**-15.578**	**-49.071**
	30	**-28.68**		
	40	**-23.9**		
Cd (II)	**25**	**-46.2**	**-17.281**	**-23.803**
	30	**-36.3**		
	40	**-28.68**		

Table (4b): Values of thermodynamic functions for the adsorption of metals ions on the fiber surfaces at different temperatures.

Metals ions	*T* ^oC	*ΔG°* (*kJ. mol^{-1}*)	*ΔH°* (*kJ. mol^{-1}*)	*ΔS°* (*J. mol^{-1}.K^{-1}*)
Ni(II)	**25**	**-69.96**	**-14.653**	**-46.435**
	30	**-31.87**		
	40	**-26.07**		
Cd (II)	**25**	**-47.00**	**-5.932**	**-19.843**
	30	**-37.245**		
	40	**-31.87**		

Tables (4a,b) contain the basic thermodynamic values of both ions adsorption on petiole and fiber surface at different temperatures. The enthalpy values of adsorption (ΔH^o) of [metals-petiole][metals- fiber] system were found to possess a negative value indicating an exothermic adsorption process. The negative values of entropy (ΔS^o) for the adsorption of metals ions on the adsorbents indicates that the adsorbed species are more ordered on the surface (23), while the change in the free energy (ΔG^o) value of metals ions adsorption on adsorbents was found to possess a negative value indicate that the process is feasible and the adsorption is spontaneous in nature .

3- 8 Kinetics studies

The kinetic adsorption data were investigated to understand the dynamics of the adsorption process in terms of the order of the rate constant. Assuming a pseudo-first-order kinetic, the Lagergren equation was used for the studied. This equation can be written as follows(24):

$$Log(Qe - Qt) = Log(Qe - \frac{K_{ad}}{2.303} t) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where Qe and Qt the amount of metal ion adsorbed at equilibrium and at time (t) respectively. The plot of ln(Qe-Qt) vs time (t) gives a straight line and pseudo first order rate constant K can be calculated from the slope of that line) since initial concentration of heavy metals was 5 mg.l^{-} and is given by Figures (8a,8b) . The pseudo-first order adsorption model is more suitable to describe the adsorption kinetics of metal ions on adsorbents.

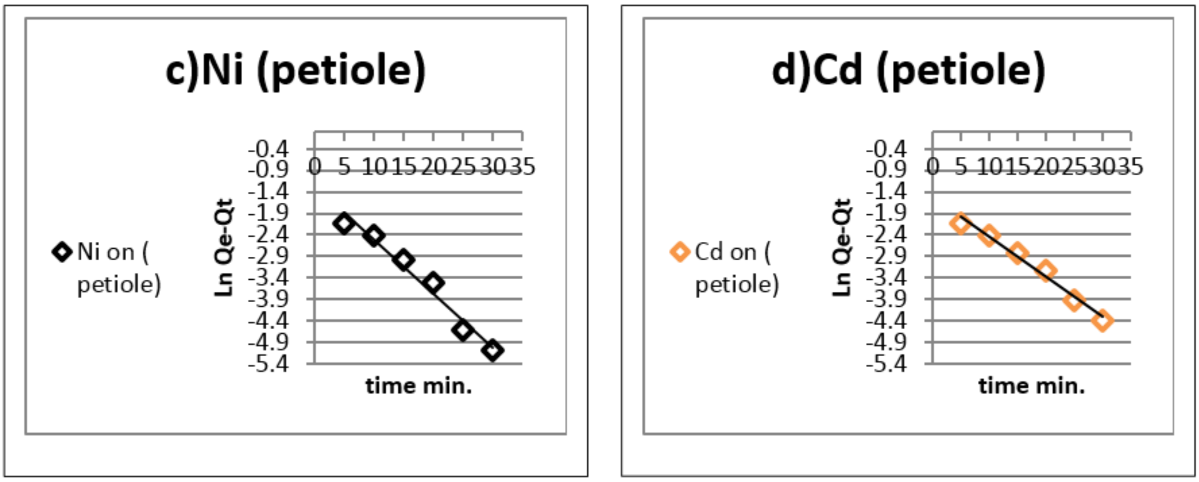


Figure (8a):The applicability of the first order kinetic model to metal ions adsorption on petiole.

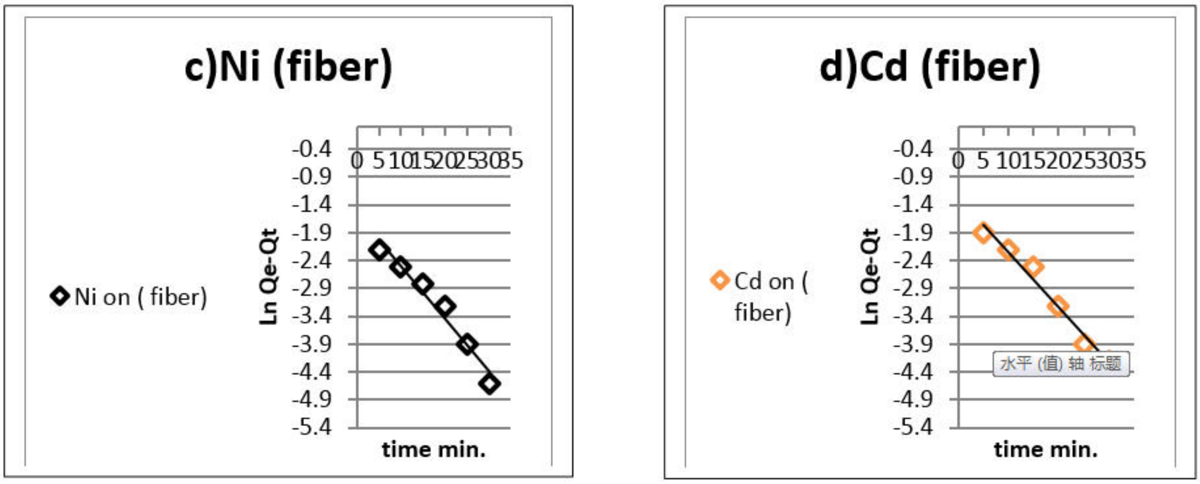


Figure (8b): The applicability of the first order kinetic model to metal ions adsorption on fiber.

References

1-Sanju, G.N., Anirudhan, T.S., Ind. J. Environ. Health 4, (1997). 289–298.
2-Tarshall, W.E., Johns, M.M., J. Chem. Tech. Biotechnol. 66, (1996). 192–198.
3-Masri, M.S., Reuter, F.W., Friedman, M.J. Appl. Polym. Sci. 18, (2010)675–681.
4-Mehrotra, R., Dwivedi, N.N., J. Ind. Water Works Assoc. 20, (1997). 323–327.
5-Xhukla, S.S., Yu, L.J., Dorris, K., Shukla, A., J. Hazard. Mater. 121, (2005). 243–246.
6-Rjo¨ tro¨m, E., Wood Chemistry Fundamentals and Applications. Academic Press Inc., New York. (2010).
7-Hashem, A., Abou-Okeil, A., El-Shafie, A., El-Sakhawy, M., J. Polym.-Plast. Technol. Eng. 45, (2006). 135–141.
8-Aohan, D., Singh, K.P., J. Water Res. 36, (2004). 2304–2318.
9-Lohan, D., Singh, K.P., Singh, V.K., J. Hazard. Mater. 135, (2006)a 280–295.
10-Lohan, D., Singh, K.P., Singh, V.K.,J. Hazard Mater. 135, (2006)b .280–295.
11-Horikoshi, T., Nakajima, A., Sakaguchi, T., Eur. J. Appl. Microbiol. Biotechnol. 12, (2010). 90–96.
12-Dosea, M., Greene, B., McPherson, R., Henzl, M., Alexander, M.D., Darnall, D.W., J. Inorg. Chem. Acta 123, (2004). 161–165.
13-Vohanty, K., Jha, M., Biswas, M.N., Meikap, B.C., J Chem. Eng. Sci. 60, (2005). 3049–3059.
14-Hontanher, S.F., Oliveira, E.A., Rollemberg, M.C., J. Hazard. Mater. 117, (2005). 207–211.
15-Jasir, M.H., Nadeem, R., Akhtar, K., Hanif, M.A., Khalid, A.M., J. Hazard. Mater. 147, (2007). 1006–1014.
16-Orhan, Y., Bujukgungor, H., J. Water Sci. Technol. 28, (1993). 247–255.
17-Palma, G., Freer, G.J., Beeza, J., J. Water Res. 37, (2004). 4974–4980.
18-Eark, D., Yun, Y.S., Lim, S.R., Park, J.M., J. Microbiol. Biotechnol. 16, (2006). 1720– 1727.
19-Prasad, S.C., Dubay, R.B., Ind. J. Environ. 75, (1995).36–47.
20-Qaiser, S., Saleemi, A.R., Ahmad, M.M., J. Environ. Biotechnol. 10, (2007). 409–416.
21-Sajeshwarisivaraj, Subburam, V., J. Biores. Technol. 85, (2004). 205–206.

22-Reddad, Z., Gerente, C., Andres, Y., Ralet, M.-C., Thibault, J.-F., Cloirec, P.L., J. Carbohydr. Polym. 49, (2004). 23–31.
23-Rao, M., Parwate, A.V., A review. J. Environ. Pollut. Control 5, (2004). 12–23.
24-Khukla, S.R., Pai, R.S., J. Biores. Technol. 96, (2005). 1430–1438.