



## Equilibrium Kinetic and Thermodynamic Adsorption of Ni and Cd Ions from Waste Water Using Orange Peel

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### Article information

#### Article history:

Received: July, 26, 2023

Accepted: August, 24, 2023

Available online: December, 14, 2023

#### Keywords:

Ni and Cd ions,  
Fresh orange peels (FOP),  
Adsorption

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#### DOI:

<https://doi.org/10.53523/ijoirVol10I3ID359>

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### Abstract

The aim of this study is to evaluate fresh orange peels as low cost available adsorbent for removing nickel and cadmium ions from laboratory solutions and record the adsorption capacity, which represents the amount of up take per amount of fresh orange peels (FOP). Fourier-Transform Infrared Spectroscopy (FTIR) analyses of FOP was carried out and comparing with the peaks of standard FTIR of cellulose matter to show functional groups and finger print that found in FOP formula. Batch experiments were carried out at different conditions: Ni and Cd ions initial concentration are (10, 20, 30, 40, and 50) ppm, FOP dosage (0.5, 0.75, 1, and 1.5) g, pH (3.5, 5, and 6), contact time (30 to 240) min and temperature (28, 35, and 45) °C where recorded. The results showed that the removal percentage of Ni and Cd increased with increasing FOP dosage. Initial Ni and Cd concentration, pH, and contact time. The best Ni and Cd Removal% where 64% and 80%, respectively at optimum conditions with FOP dosage of 1 g, pH of 6, initial concentration of 50 ppm and contact time of 120 min, where the calculated adsorption capacity was 2.9 mg/g for Ni and 4 mg/g for Cd. In case of the thermal study, best result was obtained at 45 °C with removal% of 65% for Ni and 78% for Cd and adsorption capacity of 2.8 mg/g and 3.7 mg/g for Ni and Cd, respectively.

### 1. Introduction

Rapid industrial development is causing environmental pollution with heavy metals. Industries such as leather tanning, textiles, electroplating, and mining can leak a large amount of water contaminated with heavy metals. Heavy metals are not biodegradable into the aquatic environment, where they are absorbed by living organisms and accumulate in living organisms [1]. Lead and cadmium are among the most toxic environmental pollutants that cause health risks and are deposited in the skin, brain, liver, pancreas and heart muscles and cause serious toxicity [2]. Therefore, wastewater contaminated with minerals must be treated before being discharged to the environment.

Heavy metals are removed from water using traditional methods of removal in several ways, such as ion exchange, chemical precipitation, membrane filtration, electrochemical treatment, and co-sedimentation, which are characterized by being costly and ineffective if the concentration of the minerals present is a small concentration, ranging from 1-100 mg/L [3, 4]. Therefore, chemisorption using activated carbon is more effective for metal removal and organics [5]. However, activated carbon is a very expensive method in wastewater treatment. In such cases bio sorption is an alternative method compared to conventional methods [6].

The advantage of bio sorption include its cost-effectiveness [7], high efficiency, reduced sludge production, bio sorption material regeneration, and mineral recoverability. Bio sorbents are prepared from biomass from naturally occurring waste. They contain different types of functional groups on their surface, including hydroxyl, amine, amide, carboxylate, and phosphate, which are found to be responsible for the absorption of minerals [8].

Many researchers have used bio sorbent materials [9, 10, 13] such as tea leaves, fruit purees, apricot kernels, and orange peels. The latter is considered waste and is widely consumed material in the world. The modified bio sorbent was characterized using spectroscopic. Adsorption behaviours including effect of pH [10], isotherms and adsorption kinetics were studied for the adsorption of lead(II) and copper(II) from their aqueous solution. Many other variables are influencing the adsorption technique like adsorbent dosage, initial concentration of adsorbents, contact time, mixing speed, and temperature.

The aim of this research is to apply fresh orange peel (FOP) as bio adsorbent to remove Ni and Cd ions from a sample of wastewater to evaluate the removal percentage at various FOP dosages, Ni and Cd initial conditions, pH, contact time, and temperature.

## 2. Experimental Procedure

### 2.1. FOP Preparation

The raw material used in this research is orange peels, which is a good adsorbent material in terms of cost and environmentally friendly to remove heavy ions from water, where peels were collected and cut into small pieces of 1-2 mm and washed several times with tap water and then with hot water at a temperature of about 60 °C to remove the colour from it. The washed peels then dried in a thermal oven at a temperature of 70 °C for a period of 4 hours. Afterward, the dried peels left for a whole day at room temperature to be ready for later experiments.



**Figure (1).** Raw material preparation of orange peel.

### 2.2. Simulated Wastewater Preparation

Simulated wastewater was prepared in the laboratory by preparing a stock solution for each of the ions nickel and cadmium with an initial concentration of 1000 ppm for each of them, separately. A solution (1000) ppm of cadmium was prepared by weighing 1 g of cadmium and dissolving it in a dilute solution of nitric acid with

heating until all the quantity of the substance was dissolved and the resulting solution was transferred to 1L volumetric flask and completed with deionized water with acidification of the standard solution by 1% of nitric acid to keep the solution as long as possible. The preparation of stock solution (1000) ppm of nickel was done by weighing 4.478 g of aqueous nickel sulfate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ) with distilled water and heating until all the precipitate was dissolved and completing the volume to 1 L using a volumetric bottle of 1 L with acidifying the harmful solution using  $\text{HNO}_3$  diluted to 3%. Then, the diluted solutions were prepared from diluting the original prepared solution and used as standard solutions according to the concentrations to be used for conducting the experiments.

### 2.3. FOP Dose

5 weights of FOP were added, which are (0.5, 0.75, 1, 1.5, and 3) g into 5 solutions of nickel with a concentration of 50ppm and a volume of 50ml and were placed in a shaker for 4 hours at a speed of 250 rpm. The solution then filtered and the filtrate was taken for the purpose of examining the nickel and cadmium ions using a flame atomic spectrometer type 210VGP.

### 2.4. Ni and Cd Initial Concentrations

An experiment was conducted to measure the concentrations of nickel and cadmium in simulated wastewater by using 1 g of fresh orange peels, where the weight of fresh peels used as an adsorbent was fixed to different concentrations for each of the solutions prepared from the ions nickel and cadmium at concentrations (10, 20, 30, 40, and 50) ppm for each sample. Then the sample was filtered and the concentration of each of the two ions in the filtered form was examined using a flame atomic spectrometer.

### 2.5. Contact Time Effect

In this experiment, the time factor was changed, as two solutions were prepared for each of the two ions – nickel and cadmium, with a capacity of 500 ml, separately, at a concentration of (50) ppm for each Ni and Cd individually, and by adding 10 g of fresh orange peels prepared as an adsorbent to remove heavy ions from the water and placed in a device shaker at a speed of 250 rpm. The samples were measured at different time periods were withdrawn, then the samples were filtered, and the concentrations of the ions nickel and cadmium were measured using the flame atomic spectrometer.

### 2.6. pH Effect

In this experiment, the Ni and Cd solutions pH was changed. Three samples of two solutions were prepared for each of the two ions, nickel and cadmium at pH (3.5, 5, and 6), respectively, at constant volume of 100 ml, initial concentration of 50 ppm, FOP dosage of 1 g and contact time of 4 hours after shaking at speed 250 rpm, filtration of sample to separate FOP and analysis of the filtrate for detection Ni and Cd using absorption atomic spectrometer.

### 2.7. Temperature Effect

In this experiment, the Ni and Cd solutions temperature factor was changed, three samples of two solutions were prepared for each of the two ions, nickel and cadmium at temperatures (28 ,35, and 45) °C, respectively, with a capacity of 100 ml, separately, at a concentration of (50)ppm for each Ni and Cd individually, and by adding 1 g of fresh orange peels prepared as an adsorbent to remove heavy ions from the water and placed in a device shaker at a speed of 250 rpm. The samples were measured after 4 hours period, then the samples were filtered, and the concentrations of the ions nickel and cadmium were measured using the flame atomic spectrometer.

In all previous experiments, the equation for measuring the removal percentage and adsorption uptake were adopted [6], as shown below:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

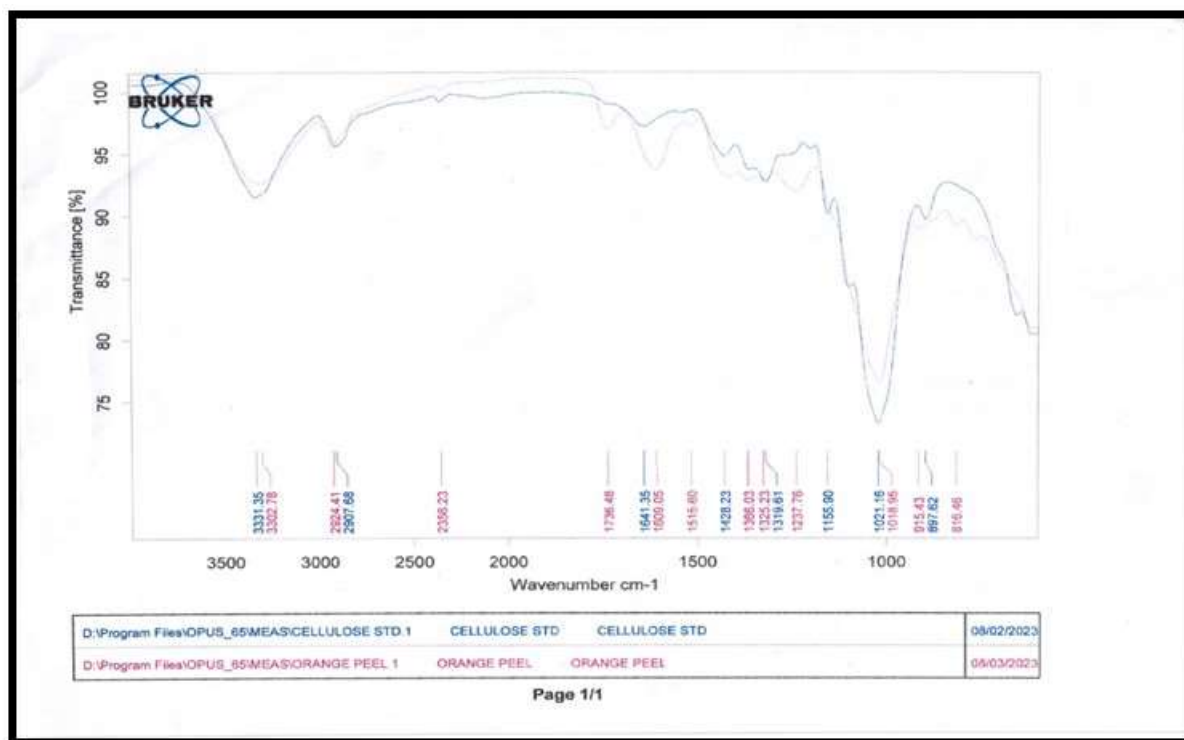
$$\text{Adsorption uptake (qe)} = (C_0 - C_e) \times V/M$$

Where:  $C_0$ : Initial calculation of Ni or Cd ppm,  $C_e$ : equilibrium concentration of Ni or Cd ppm, V: sample volume (L), and M: FOP mass (g)

### 3. Results and Discussion

#### 3.1. FTIR Analysis

Figure (2) show FTIR analysis for cellulose (blue curve) and FOP (red curve) which shows functional group and fingerprint peak patterns.

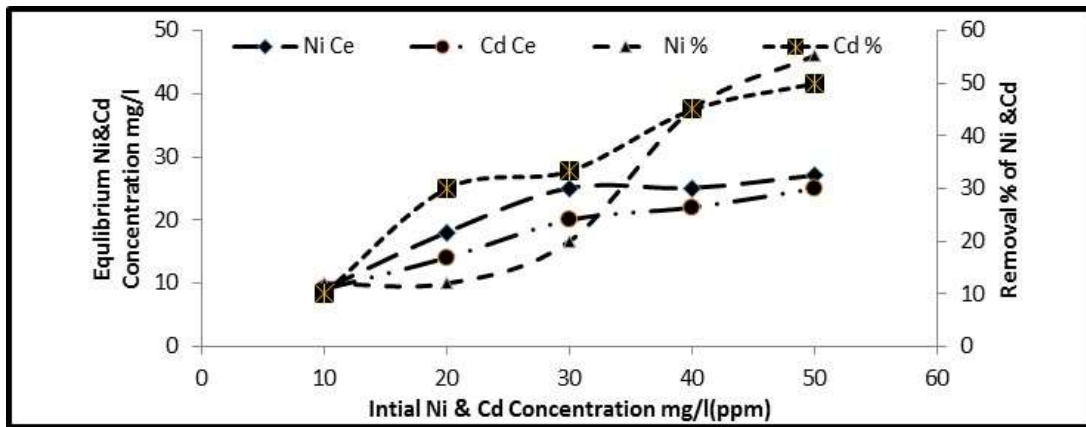


**Figure (2).** FTIR peaks for FOP with standard FTIR of cellulose standard curve.

Peaks in the above figure show 3331 and 3332  $\text{cm}^{-1}$  which refer to OH group which contains functional group and humidity in cellulose material [11], whereas the peaks at 2907 and 292  $\text{cm}^{-1}$  are assigned to CH bond of chemical structure of hydrocarbons where 2358  $\text{cm}^{-1}$  refers to C=C as an organic material with carbon double bond and 1609-1641  $\text{cm}^{-1}$  refers to C=O of carboxylic acid that is usually presents in fiber materials containing pectin and several peaks ranging from 1325 to 1155  $\text{cm}^{-1}$  refer to C-O bonding of phenols. Comparing with a previous study that used orange peels, the results agree with the current study in terms of the peaks that appeared for the purpose of cadmium adsorption [12].

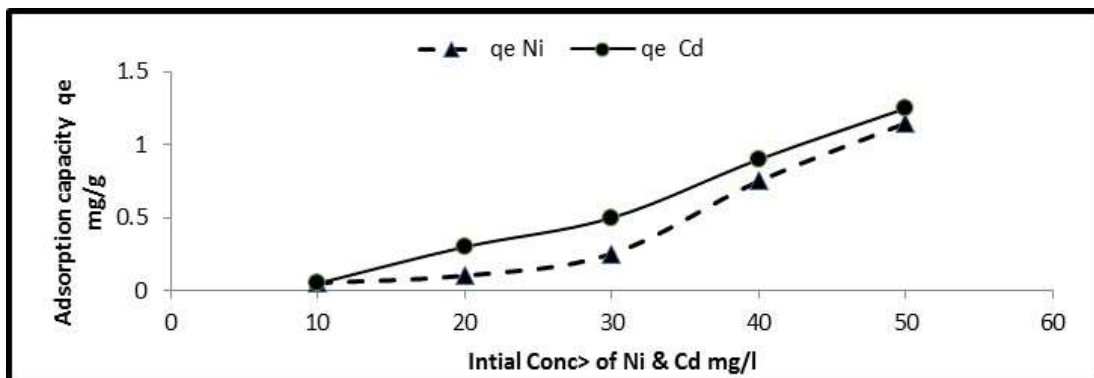
#### 3.2. Initial Ni and Cd Concentration

At different initial concentrations of Ni and Cd (10, 20, 30, 40 and 50) mg/l of volume 50 ml with constant dosage of FOP 1 g under room temperature with speed of shaking (250 rpm), the obtained result of equilibrium concentration and % removal after 4 hours contact time are shown at Figure (3).



**Figure (3).** Equilibrium conc. and removal of Ni and Cd at different initial conc.

The results show increasing removal % of both metals with increasing initial concentration due to effect of the different concentrations between liquid phase and solid phase, which plays as driving force to transfer the ions from liquid phase towards adsorption site at FOP surface until equilibrium state, where Figure (4) shows Ni and Cd uptake as adsorption capacity which increases with increasing of initial concentration which depends on the amount of adsorbed adsorbate (Ni and Cd) per one gram of adsorbent (FOP).



**Figure (4).** Effect of Initial conc. Of Ni and Cd on adsorption capacity.

### 3.3. Effect of FOP Dosage

To investigate the effect of FOP dosage on the uptake of Ni and Cd ions from their solutions at constant initial concentration of 50 ppm and volume of 50 ml with pH 3.5 at room conditions and shaking speed of 250 rpm, Figure (5 & 6) show the residual concentration and % removal of Ni and Cd, where applied FOP dosage (0.5, 0.75, 1, and 1.5) g shows removal for Ni ions (14, 26, 42, and 64)%, while for Cd (22, 36, 52, and 78)%, which refers to increasing adsorbent dosage lead to increasing uptake due to available of surface area [13] that related to the increasing of FOP mass, while adsorption capacity shows increasing at dosage less than 1 g and constant value more than that due to weakness of mass transfer of metals ions to transfer from liquid phase to FOP surface.

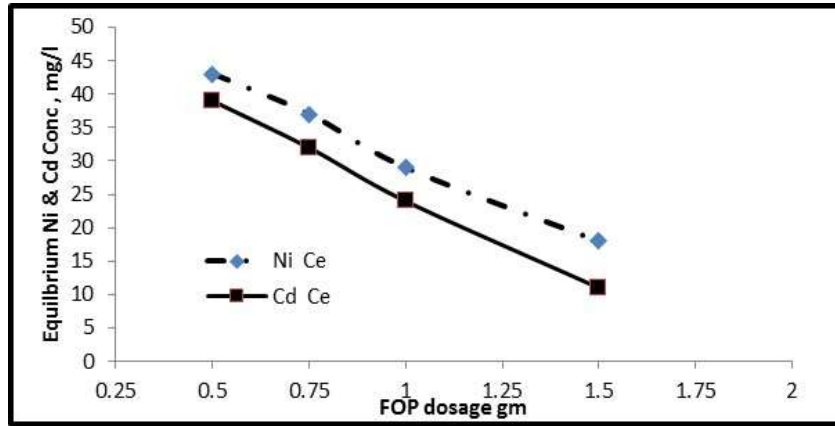


Figure (5). Residual Ni and Cd at equilibrium at different FOP dosage.

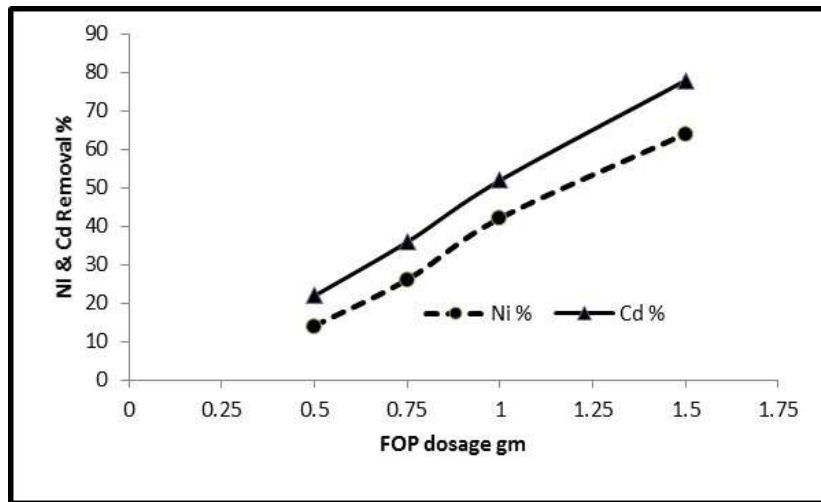


Figure (6). Removal % of Ni and Cd at equilibrium at different FOP dosage.

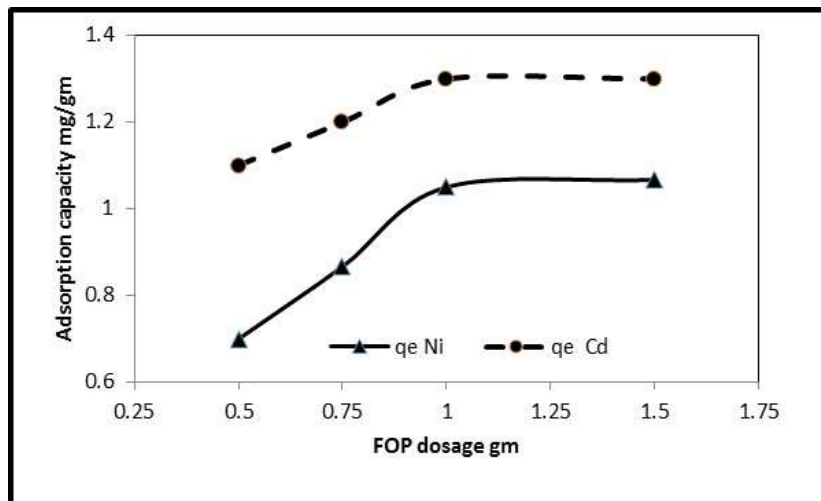
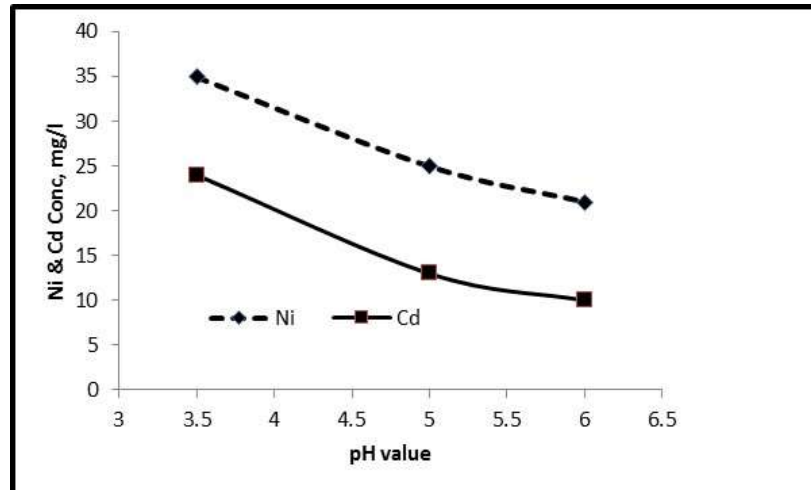


Figure (7). Relationship curve of adsorption uptake at different FOP Dosage.

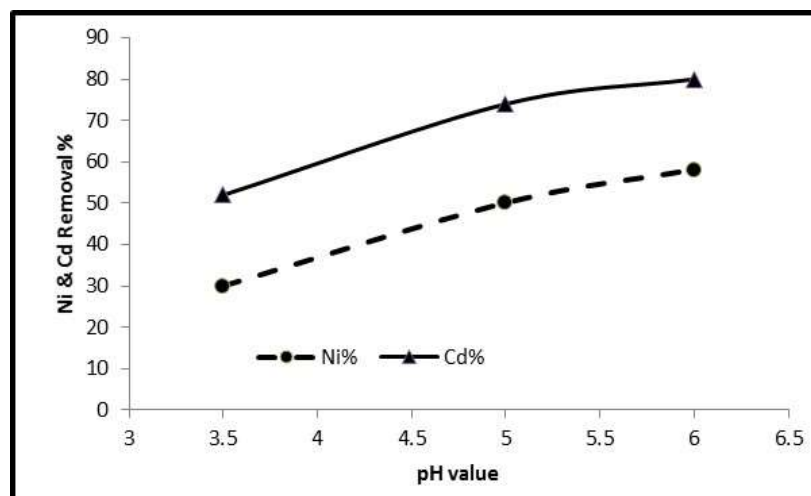
### 3.4. Effect of pH Value of Ni and Cd Solutions

pH variable effect was estimated at values (3.5, 5, and 6) for Ni and Cd removal individually at conditions of 100ml of 50 ppm initial concentration and 1 g. FOP dosage during room conditions and shaking speed 250 rpm,

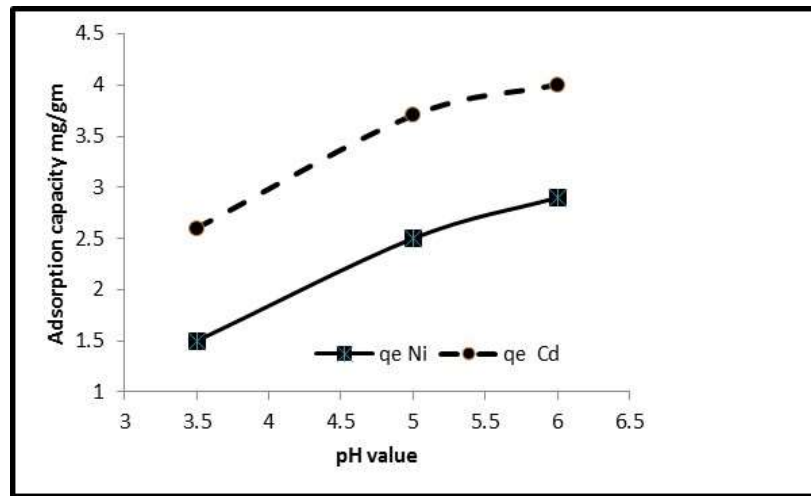
for assessment of FOP surface charges which represented as cellulose tissue that have OH negative groups as chemical formula. Figures (8 & 9) show decreasing of residual Ni and Cd ions at equilibrium and increasing removal % at increasing pH from 3.5 to 6 due to for high acidity condition [12]. There are increasing of proton  $H^+$  which plays role as competitor with cationic ions of Ni and Cd to adsorb towards negative sites at FOP surface, removal % were increased for Ni and Cd ions from 30% to 58% and 50 % to 80 % at increasing pH from 3.5 to 6, respectively. For adsorption uptake there are increasing at increasing pH were recorded (1.5 to 2.9) mg/g for Ni and (2.6 to 4) mg/g for Cd as shown in Figure (10). Increasing of pH more than 6 may cause chemical precipitation of heavy metal so it is preferred to treatment heavy metals pollution by chemical precipitation for high content concentration of metals ions and followed by adsorption techniques And that these results were consistent with a previous study on the removal of cadmium at (pH=5 ) with a better removal of 45% [12] .



**Figure (8).** Residual Ni and Cd at equilibrium at different pH values.



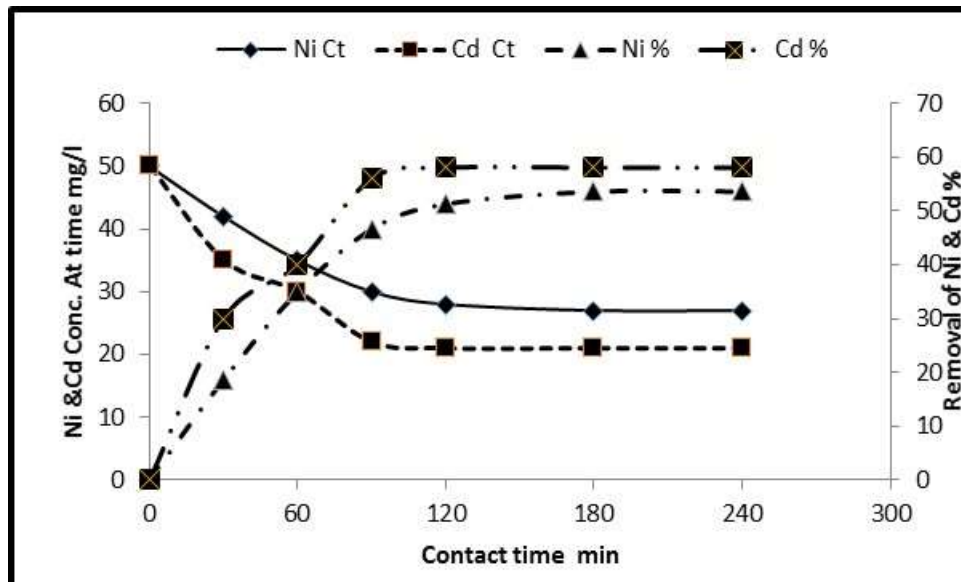
**Figure (9).** Effect of pH on Removal % of Ni and Cd ions.



**Figure (10).** Effect of pH on adsorption uptake of Ni and Cd ions.

### 3.5. Effect of Contact Time

Bach experiment of contact time effect at condition 500 ml of Ni and Cd 50 ppm individually with FOP dosage 10 gm. with stirring speed 250 rpm at room temperature where recorded results as shown in Fig.(11) for Ni and Cd concentration and removal % at sampling interval times which show decreasing in residual concentration and increasing in removal at increasing of contact time until reach equilibrium state [2] at time 120 min due to stop mass transfer of adsorbents toward adsorbing sites of FOP surface may be referred to saturation state and inability of adsorbent to accept more Ni and Cd ions.



**Figure (11).** Effect of pH on adsorption uptake of Ni and Cd ions.

Figure (12) show uptake approach of Ni and Cd as amount of adsorbed ions per one gram of FOP which show sharp state of adsorption for contact time less than 120 min then keep constant for longer time which fit with the invalidity of contact time more than 2 hours to increase the adsorption capacity of adsorbent's surface to accept more heavy metals ions. And that these results were consistent with a previous study on the removal of cadmium, which showed the best removal was at 120 minutes.



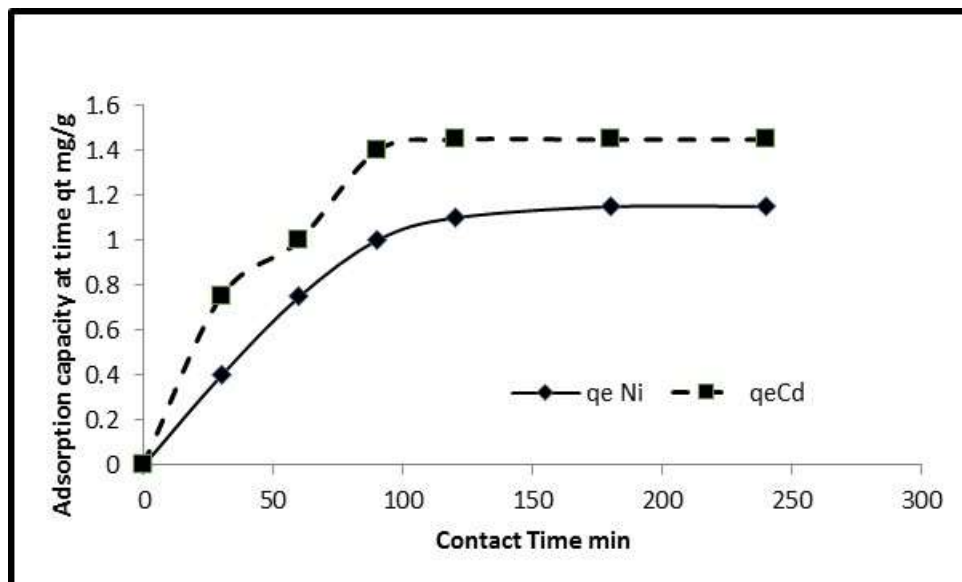


Figure (12). Effect of pH on adsorption uptake of Ni and Cd ions.

### 3.6. Effect of Temperature

Figure (13) shows positive effect of temperature on the adsorption of Ni and Cd by fresh orange peel. The removal percentage was increased at temperature increasing where found the highest Ni and Cd ions uptake was achieved at 45 °C with (66 and 84) % respectively. The rise of solution temperature increased the adsorption competence of ions on FOP indicating that the process was endothermic. Increase in temperature increased the rate of the progression of the Ni and Cd ions from the solution onto the unoccupied sites of FOP which fitted with obtained results of previous work [12] that explained by the weakened the thickness of the surface layer of FOP, thereby enhancing the dispersion resistance of adsorbents to adsorbents.

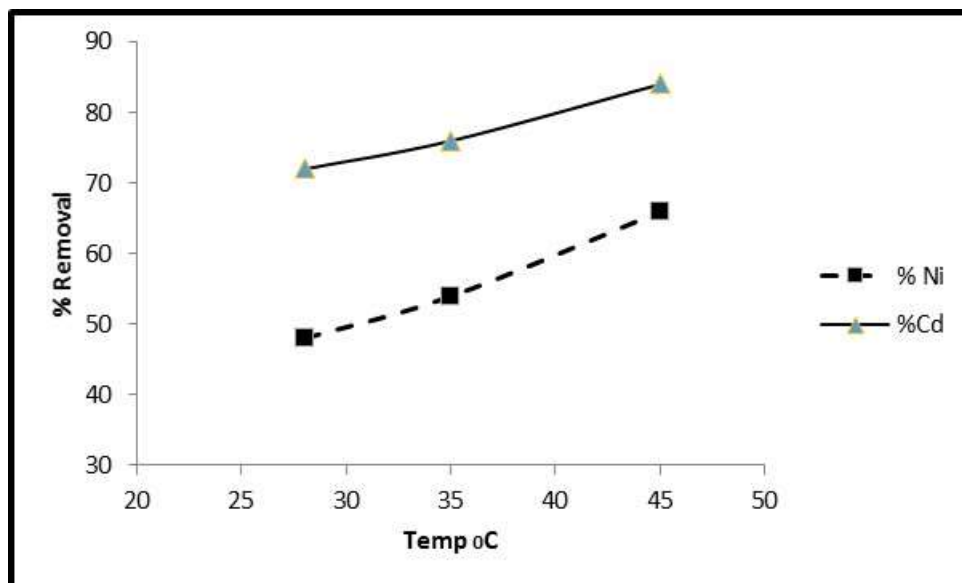


Figure (13). Effect of temperature on adsorption up take of Ni and Cd ions.

**Table (1).** Results and Conditions.

Variables parameters	Constant parameters	Removal %		Adsorption uptake mg/g	
		Ni	Cd	Ni	Cd
<b>FOP dosage gm.</b>	Volume 50 ml Co 50 mg/l pH 3.5 Time 4 hrs. Temp 28 °C				
0.5		14	22	0.7	1.1
0.75		26	36	0.867	1.2
1		42	52	1.05	1.3
1.5		64	78	1.06	1.3
<b>Initial conc. Co mg/l</b>					
10	Volume 50 ml FOP 1 gm. pH 3.5 Time 4 hrs. Temp 28 °C	10	10	0.05	0.05
20		10	33	0.1	0.3
30		16.67	33.3	0.25	0.5
40		37.5	45	0.75	0.9
50		46	50	1.15	1.25
<b>pH value</b>					
3.5	Volume 100 ml Co 50 mg/l FOP 1 gm Time 4 hrs Temp 28 °C	30	52	1.5	2.6
5		50	74	2.5	3.7
6		58	80	2.9	4
<b>Time t min</b>					
30	Volume 500 ml FOP 10 gm. Co 50 mg/l pH 3.5 Temp 28 °C	16	30	0.4	0.75
60		30	40	0.75	1
90		40	56	1	1.4
120		44	58	1.1	1.45
180		46	58	1.15	1.45
240		46	58	1.15	1.45
<b>Temp °C</b>					
28	Volume 100 ml FOP 1 gm. Co 50 mg/l pH 6 Time 4 hrs.	48	72	2.4	3.6
35		54	76	2.7	3.8
45		66	84	3.3	4.2

**Table (2).** Comparable adsorption capacities with literature and contributing factors of other adsorbents with orange peel.

Agricultural biosorbent	Adsorbent dose (g/L)	Initial adsorbate concentration (mg/L)	Adsorption capacity, (mg/g)	Reference
Orange peel	20	50 (Cd)	2.57	[14]
Pine sawdust	0.49	60 (Cd)	3.47	[14]
Orange peel	1	10 (Ni)	1.05	[15]
Orange peel	1.59	40 (Ni)	2.36	[16]

#### 4. Conclusions and Recommendations

The possibility of using low-cost adsorbents in the field of removing heavy elements instead of traditional high-cost materials and their ease of availability, such as agricultural waste. The percentage of nickel and cadmium removal with initial concentration of 50 ppm was increased when the dose and pH of 6 at best contact time of 120 min. The removal percentage and adsorption capacity increased with increasing temperature, 66% for nickel

and 84% for cadmium at a temperature of 45 degrees Celsius, evidence that adsorption is endothermic. For future works, it is possible to re-work using dried peels and activated for the purpose of removing organic and inorganic pollutants.

**Conflict of Interest:** The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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