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EGG SHELL AS NATURAL SORBENT TO REMOVE CADMIUM IONS FROM SIMULATED WASTEWATER

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Abstract: This search offers the ability of use a natural waste as a biosorbent such as egg shells and their efficiency on heavy metals adsorption, like cadmium. Maximum removal was observed at pH 6.0. The efficiency of egg shells for the removal of cadmium was 89.7% at 5g adsorbent dose. Effect of temperature change has been calculated; and parameters of thermodynamic indicated that the sorption of cadmium is favored at high temperatures and endothermic. FTIR was recorded before and after adsorption to show the number and position of the functional groups available for cadmium binding on to the studied adsorbent. It was found that Freundlich isotherm fitted well to the data; Pseudo-second order model explains the cadmium kinetics more effectively. The results appeared that cadmium is considerably adsorbed on egg shells and it could be and economic method for the removal of cadmium from aqueous solutions.

Keywords: *cadmium ions; egg-shells; kinetic and isotherm models; thermodynamic; FTIR.*

قشر البيض كوسط طبيعي ماز لإزالة أيونات الكادميوم من مياه المخلفات المُحاكاة

الخلاصة: هذا البحث يبين القابلية لإمكانية إستعمال المُخلفات الطبيعية لتكون وسطاً مازاً مثل قشور البيض وإختباركفاءتها في امتزاز المعادن الثقيلة، كالكادميوم. وقد وجد أن موديل فريندلج هو الأنسب حسب النتائج وأكبر نسبة إزالة كانت 89.7 % عندما قيمة الدالة الحامضية 6 بإستعمال5 غم من الوسط الماز. كما تم تقييم تأثير تغير درجة الحرارة ومعاملات الثرموداينميك ووقد وجد أنه تزداد نسبة الأزالة بزيادة درجة الحرارة حيث التفاعل ماص للحرارة. وتم اجراء فحص التحليل الكيفي باستخدام جهاز الأشعة تحت الحمراء قبل وبعد الأمتزاز لغرض بيان عدد وموقع المجموعات الفعالة المتواجدة. وتم اختبار البيانات الحركية من الدرجة الاولى و الثانية , تبين انها ملائمة مع الدرجة الثانية. واظهرت النتائج بإمكانية امتزاز الكادميوم بقشور البيض الذي يعتبر غير مُكلف اقتصادياً.

1. Introduction

The designation of heavy metal indicates that each chemical element is relatively high in density and has a toxic effect when its concentration is low. For examples of these heavy metals include: mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb). Heavy metals are natural elements of the Earth's crust. They are not able to degraded or broken. Rather they come in our bodies

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through food, drinking and air. Some heavy metals (such as: copper, selenium, zinc) are important to keep the metabolism of the human body.

But, when concentrations are higher they cause toxicity. Their toxicity may result, for example, when drinking contaminated water (e.g. lead pipes), high concentrations of ambient air near the sources of emission, or intake by the food chain [1, 2]. Because of the fact that heavy-metals possible to bioaccumulation; therefore they are dangerous. Bioaccumulation refers to an increase in the concentration of a chemical in a biological organism over the years, compared with the chemical's concentration in the environment. Any time Component accumulate in living-things are taken up and stored-quicker than they are broken-down (metabolized) or exuded. Heavy-metals can come in a water-transfer by industrial and consumer waste, or possibly from acidic-rain which breaks soils and releases these metals to streams, lakes, rivers, and groundwater [3].

Negative effects of cadmium on the environment: is easy accumulation in living systems [4]; also is a confirmed carcinogen and can be a reason for lung tumors, maybe poisonous when ingested, having an influence on the kidneys and respiratory system, or exposure to cadmium in high concentrations may bring Pneumonia and cause death [5]. The sorption system is widely utilized by various researchers to get rid of heavy metals from simulated wastewater. Activated carbon has been mostly utilized as sorbent; although of its wide use in water and wastewater treatment industries it remained expensive material [6]. Currently, the need for safe and economic techniques to get rid of heavy metals from wastewater cause to use numerous agricultural-waste by-products as a new sorbent in elimination ions of heavy metals, such as: Chitosan, sawdust, citrus-peels, eggshells, etc [3]. At a recent time the world has a high population of chicken. Eggs are one of the largest food products; utilize of eggs which show that there are big amount of eggshells waste in landfills in world [5]. Moreover, if it possible to use these eggshells as a substitute for activated carbon to remove the cadmium-ion in the wastewater, there is possibility to enhance the quality of the wastewater in improving countries with reasonable device of filtration (the eggshell). This work shares in examine the use of eggshells to remove or reduce the concentration of cadmium-ion in contaminated-water.

2.Materials and Methods

2.1 Synthetic Wastewater Preparation and Adsorbent (Eggshells)

The synthetic solution of cadmium ion prepared by dissolving the $Cd(NO_3)_2.4H_2O$ with distilled water; to obtain the desired initial concentration was according to Eq.1 [7]:

$$W = V \times C_i \times \frac{M.wt}{At.wt} \qquad (1)$$

Where: W: Weight of heavy metal salt (mg); V: Volume of solution (1liter)

C_i: Initial concentration of metal ions in solution (mg/l); M.wt: Molecular weight of metal salt (g/mole); At.wt: Atomic weight of metal ion (g/mole).

pH of solution was adjusted to a required value by adding (0.1M) HNO_3 or (0.1M) NaOH as required. The concentration of nickel was measured by Atomic Absorption spectrophotometer (AAS) (GBC 933 plus, Australia).

The chicken-eggshells samples were collected from house-waste; washed with distilled water many times to remove dirt. The eggshells were then dried in oven at 40^{o}C (because at high temperature > 40^{o}C protein component in eggshell can denature) [1]; and ground into small particles; sieved to fine powder of a sizes $\leq$ 0.6mm and stored in air tight container for use.

1.2 Adsorption Procedure and Measurement

All adsorption tests carried out on the batch type. A 100ml wastewater solution of desired concentration (50mg/l) was taken with the required amount of eggshells (0.5g-6g) in 250ml Erlenmeyer flasks, and then shaken with different agitation speed (100-250rpm) at a room temperature (approximately 25±5°C) for a contact time of 180min. The pH of solution was adjusted to the required value (2-8); by adding either 0.01M HCl or 0.01M NaOH. The supernatant was separated by filtration. The supernatant was separated by filtration (filter-paper Whatman 70mm). Initial and final concentration of cadmium ion was specified by the Atomic Absorption Spectrometer (AAS). The equation (2) used to calculate the amount of cadmium sorbed by the eggshells was as follows [7]:

$$R\% = \frac{C_i - C_f}{C_i} \times 100 \qquad (2)$$

Where: C_i = initial concentration of the metal (mg/l); C_f = final concentration of the metal (mg/l).

3. Results and Discussion

The following results deals with the use of eggshells as sorbent to remove Cd (II) ion from simulated wastewater. "Fig. 1" shows a brief summary of the experimental work for removal process.

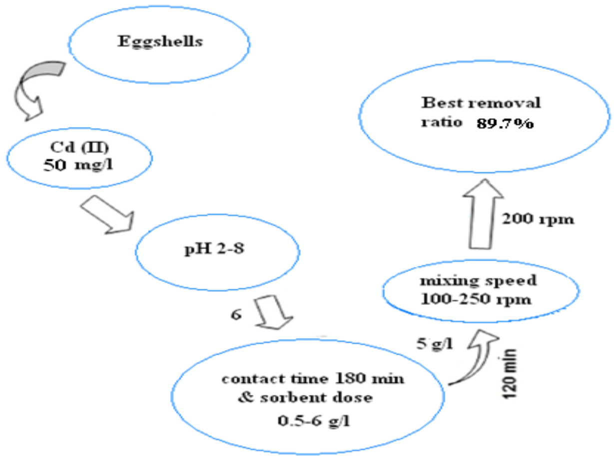

Figure 1. summary of the experimental work.

3.1 Effect of pH

The pH of the solution plays a very important role in the metal uptake. Both adsorbent surface metal binding sites as well as metal chemistry in solution are influenced by solution pH. At low pH values, metal cations and protons compete for binding sites on adsorbent surface which results in lower uptake of metal. It has been suggested that at highly acidic condition, adsorbent surface ligands would be closely associated with H_3O^+ that restricts access to ligands by metal ions as a result of repulsive forces [8, 9]. It is to be expected that with increase in pH values, more and more ligands having negative charge would be exposed which result in increase in attraction of positively charged metal ions. In addition at higher pH the lower binding is attributed to reduced solubility of the metal and its precipitation [8, 9]. Range of pH that tested in this search was (2-8); the percentage adsorption of Cd(II) ion increased with an increase in pH value "Fig.2". The maximum adsorption took place around pH 6; this result agrees with that obtained by Ziad et. al., 2016 [10].

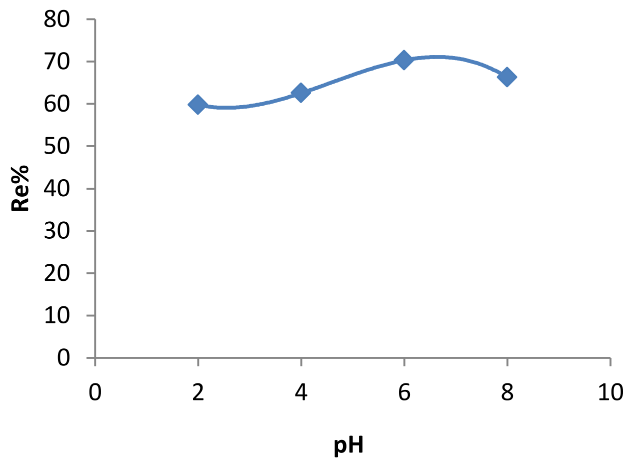

Figure 2. Effect of pH

3.2 Effect of amount of Eggshells

The studying of sorbent dose on the removal of cadmium ions was reported in "Fig. 3". weight of 0.5-6 g eggshells by shaking 200 rpm with 50 mg/L of Cd concentration for 1 hr, at room temp.(approximately 25±5◦C), and pH 6. It is shown that the removal efficiency of Cd increases as the mass of the biosorbent increases; such a trend is mostly attributed to an increase in the sorptive surface area and the availability of more active adsorption sites [11].

After more increase in weights of sorbent than 5g we notice that no effect on the removal rate because of the adsorbent was sufficient to adsorb [10]. So the suitable weight which utilized for the next tests was 5g.

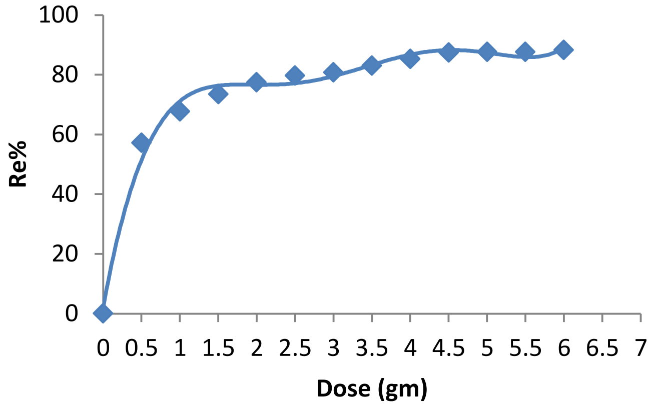

Figure 3. Effect of amount of Eggshells.

3.3 Effect of Contact Time

The effect of contact time on the batch adsorption of Cd ion concentration of 50 mg/l using the optimum pH6 and sorbent dose 5g, respectively is shown in "Fig.4". The removal increases with time and attains saturation in about 120 min. The metal showed a fast rate of adsorption during the first 60 min of the adsorption and the rate of percent removal becomes almost insignificant due to a quick exhaustion of the adsorption sites. Within 120 min of operation about 89.7 % of Cd ion was removed from the solution [12].

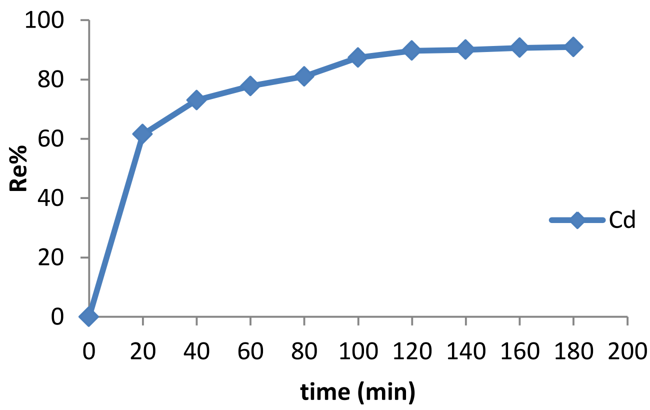

Figure 4. Effect of contact time

3.4 Effect of Agitation speed

The study on the effect of Agitation speed was conducted by varying speeds of 100 to 250 rpm (Fig.5), at optimum pH of 6 with adsorbent dose of 5g and contact time of 60 minutes at room temperature(25±5^{o}C). Cd removal increases with the increase in the speed of agitation due to that at higher speeds better contact between the adsorbent and adsorbate is possible [11]. So the optimum was 200rpm because no more effect on the removal if the speed above this range.

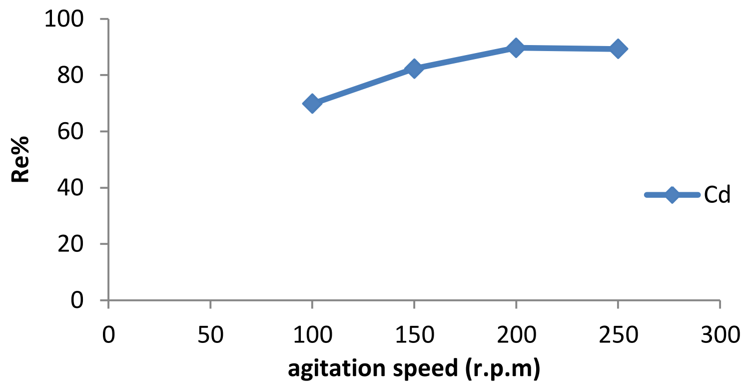

Figure 5. Effect of agitation speed.

3.5 Isotherm Models

Equilibrium adsorption studies were carried out varying the adsorbent doses (0.5–6g), and the temperature (25±5ºC). Adsorption isotherms are the equilibrium relationships between the concentrations of the adsorbed cadmium and cadmium ion in the solution. Langmuir and Freundlich isotherm models were used to investigate the adsorption equilibrium between the cadmium solution and the eggshells phase. The Langmuir adsorption isotherm equation, expressed as follows, requires for its applicability a mono- layered coverage on the surface of adsorbent [13]:

$$q_e = \frac{q_m b C_e}{(1+bC_e)} \qquad (3)$$

Where: q_e is the sorbed metal ions on the biomass (mg/g), q_m is the highest ability of sorption for monolayer coverage (mg/g), b is the constant associated with attraction of binding site (L/mg), and C_e is metal ions concentration in the solution at balance (mg /L). And Freundlich model is [14]:

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad \text{(Linear form)} \qquad (4)$$

Where: K = constant indicative of the proportional adsorption ability of the adsorbent (mg/g), 1/n = constant expressive of the strength of the adsorption (both K and n are being expressive of the range of adsorption and the grade of non-linearity between solution and concentration, respectively). The results of both models are presented in Table 1.

Table 1. Parameters of Isotherm forms.

Langmuir coefficients	Cd (II)	Freundlich coefficients	Cd (II)
R^2	0.884	R^2	0.981
q_m	-4.0323	n	0.6730
b	0.0258	K	0.0536

In comparison with the experiential isotherms with the theoretical isotherm models appeared that equation Freundlich are suitable of the experiential data for eggshells.

3.6 Kinetic Models

Adsorption mechanism of dye is explained by the adsorption kinetics models, which these are pseudo-first-order and pseudo-second-order. Studies of these models explain the adsorption behavior of dye on egg shells. The pseudo-first-order and pseudo-second-order models, respectively, [15]:

$$\ln(q_{eq} - q_t) = \ln q_e - k_1 t \qquad (5)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right) \qquad (6)$$

Where q_{eq} and q_t (both in mg g^{-1}) are the amount of dye adsorbed at equilibrium and at time correspondingly. K_1 (min^{-1}) and K_2 (g mg^{-1} min^{-1}) are the kinetics rate constants for the pseudo first- and second order models, correspondingly. Table 2 showed the results below:

Table 2. Parameters of Kinetic Models.

Cd II	$q_{e\ experimental}$	Pseudo-first-order			Pseudo-second-order		
		$k_1$1/min	$q_{e\ calculated}$	R^2	k_2	$q_{e\ calculated}$	R^2
	0.910	-0.033	0.850	0.974	0.120	0.948	0.995

From Table 2 it found that the theoretic values of q_e (cal) accepted well with the experiential uptake values, q_e (exp) in the case of pseudo-second-order model. Further, the relation coefficient (R^2) was 0.995, suggesting that this sorption procedure can be described as well by using pseudo-second-order process.

3.7 Effect of Temperature and Thermodynamic Parameters

It is well known that thermodynamic parameters can evaluate the orientation and feasibility of the physicochemical adsorptive reaction. The three thermodynamic parameters considered were standard enthalpy ($\Delta H°$), standard free energy ($\Delta G°$), and standard entropy ($\Delta S°$). The value of $\Delta H°$ and $\Delta S°$ was obtained from the following equation [14, 15]:

$$lnK_d = \left(\frac{\Delta S^{\circ}}{R}\right) - \left(\frac{\Delta H^{\circ}}{RT}\right) \quad (7)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - \Delta S^{\circ} T \quad (8)$$

Where K_d is the distribution coefficient; ΔH, ΔS, and T the enthalpy, entropy, and temperature in Kelvin, respectively; R is the gas constant (8.314 J/mol K) and Gibbs free energy change ΔG^0. Influence of temperature change at 298, 308, 318, and 328K (25, 35,45, and 55C^o) "Fig.6", the values of distribution coefficient and thermodynamic parameters are presented in Tables 3 and 4, respectively.

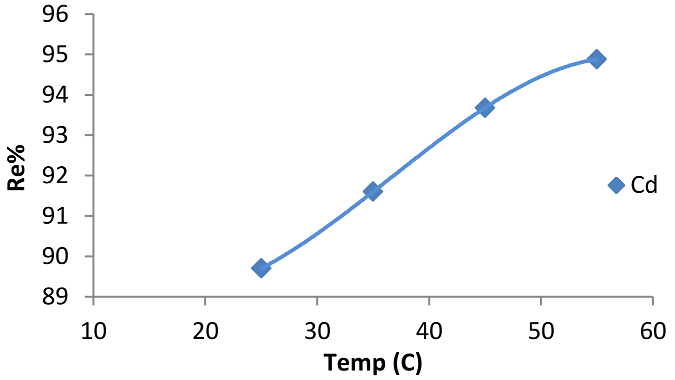

Figure 6. Influence of temperature change

By increasing the temperature percentage removal of heavy metals increased, which means that adsorption process was endothermic in nature.

Table 3: The distribution coefficients at various temperatures.

Metal	k_d				R^2
	298 k	308 k	318 k	328 k	
Cd (II)	8.7088	10.905	14.823	18.531	0.995

Table 4: The thermal parameters of cadmium adsorption on the eggshells.

Metal	ΔH(J/mol)	ΔS(J/mol K)	ΔG (kJ/mol)			
			298 k	308 k	318 k	328 k
Cd (II)	20.885	-87.962	-217.912	-225.246	-232.559	-239.872

From results it may be watched that the removal rate of cadmium on eggshells increases with increasing the temperature. The enhancement of the adsorption capacity when temperature is increased is due to increased mobility and diffusion of the ionic species. The adsorption experiment could be regarded as a heterogeneous and reversible process at equilibrium [10, 16]. This indicates that the sorption of cadmium is favored at high temperatures and endothermic, so the adsorption extent increased with rising temperature. Similar result was reported by [10].

4. FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) analysis has been used for the examination of functional groups on the surface of eggshells; shown in Fig.7; and all the band assignments are listed in Table5. By the observations in the FTIR spectra, the chemical composition of resulting eggshell particle is strongly associated with the presence of carbonate minerals within the eggshell matrix. In contrast to the resulting eggshell membrane particle, the presences of amines and amides would be expected to contain positively charged functional groups such as $–NH^+_3$ and $–CO–N^+H_2–$, depending on the pH of the aqueous solution [17].

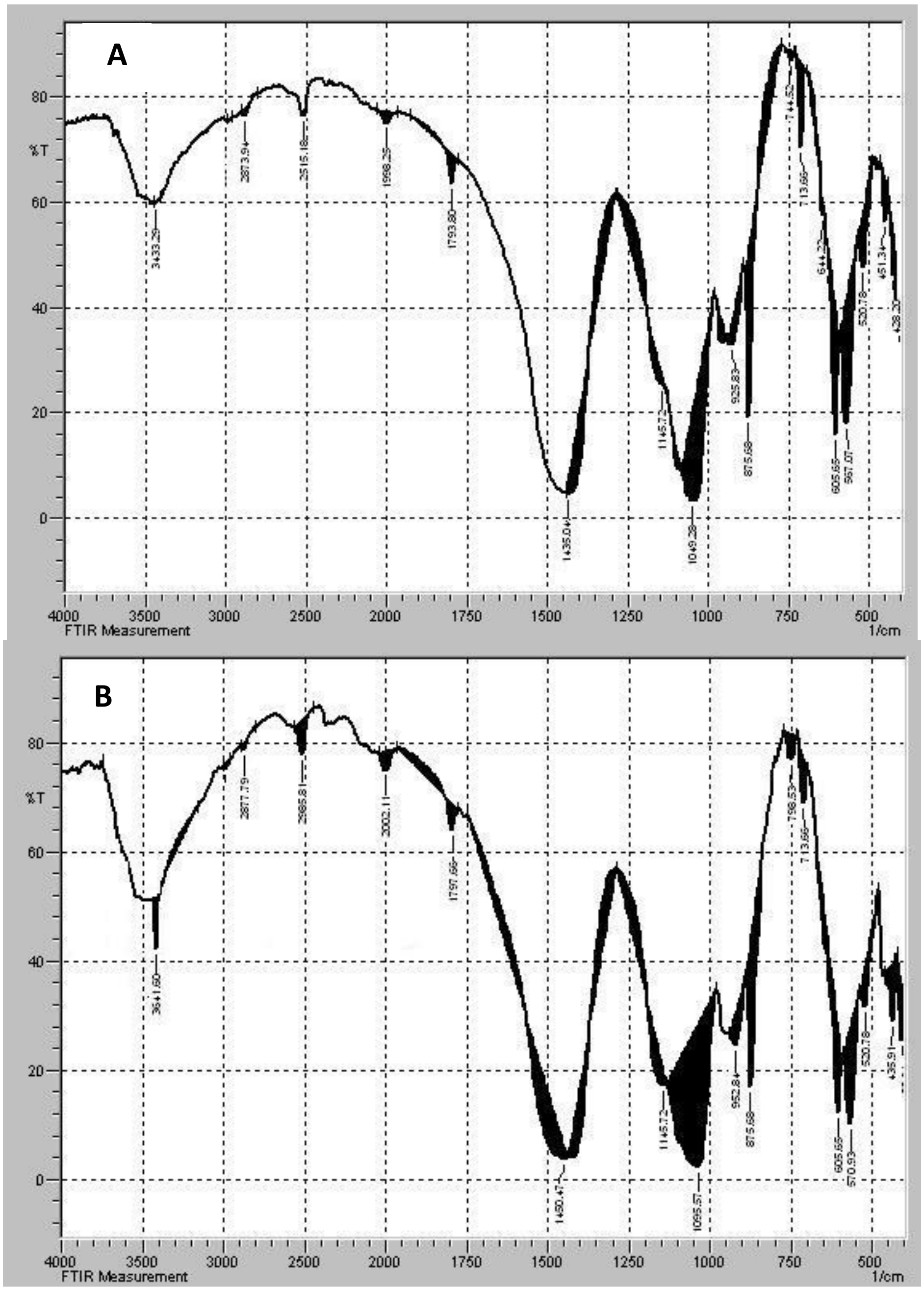

Figure 7. Analysis of Fourier Transform Infrared Spectroscopy; (A) before & (B) after adsorption of Cd(II).

Table 5. The band assignments (FTIR)

Waveform number (cm^{-1}) before adsorption of Cd(II)	Assignment Groups	Waveform number (cm^{-1}) after adsorption of Cd(II)
3433.29	Carboxylic acid, Amides, Alcohols, Amines	3641.60
2873.94	Alkanes, Carboxylic acid	2877.79
2515.18	Alkanes, Carboxylic acid	2965.81
1998.25	Alkanes, Alkenes, Carboxylic acid	2002.11
1793.80	Alkanes, Alkenes, Carboxylic acid	1797.66
1435.04	Alkanes, Alkenes, Carboxylic acid	1450.47
1145.72	Ethers, Ketones, Carboxylic acid	1145.72
1049.28	Ethers, Ketones, Carboxylic acid	1095.57
925.83	Alkenes, Anhydrides, Phosphines	952.84
744.52	Alkyl halides, Aromatic	796.53
567.07	Alkyl halides,	570.93

5. Conclusions

Of the results reached in this research; the following: the egg shells produced from domestic use were used to treat industrial water contaminated with cadmium ions. Experiments have shown that the pH has an effective effect on the treatment process, and the best removal ratio was at pH 6. The temperature change has a clear effect on the removal process, where the removal rate increased from 89.7% to 94.88% at 55C^o, so the reaction is endothermic in nature. Finally Egg shell, like most other natural absorbents can be used in the treatment process of heavy metals as cadmium ions; adding that is cheap material and thus it would be convenient to use it in industrial wastewater treatment plants.

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