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Adsorptive Removal of Cd(II) from Aqueous Solution onto Beans Peel Powder as Low Cost Adsorbent.

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ABSTRACT

In this study, a local cheap substrate beans peel was used as an adsorbent for removing Cd(II) ion from aqueous solution. The quantity of adsorbed metal was estimated by using flame atomic absorption spectrophotometer. The effects of initial metal ions concentration, pH, salt and temperature have been studied. The adsorption isotherms are of L-curve type according to Giles classification and the experimental data were best fitted to Langmuir and Freundlich isotherm models. Thermodynamic functions have been calculated and indicated that the adsorption processes is spontaneous.

Keywords: Cd(II), adsorption isotherm, thermodynamics, kinetics

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INTRODUCTION

One of the most important pollutants of environment is pollution due to have metal ions. Heavy metals are one of the materials (about 40 elements) forming the earth's crust and have a high density. The main problem with these metals is that they cannot be metabolized in body [1,2]. Heavy metals accumulate in tissues and can't be exerted from the body [3]. Furthermore, they can be replaced necessary minerals for body. In most of the third world and developing countries, there is no appropriate control on waste entering to environment. It would be resulted in acute environmental pollution in plants, animals and human. Generally, heavy metals enter to water ecosystem by natural erosion of soil , volcanic eruptions , metal smelting , electroplating of metals, plastic manufacturing, production and consumption of substances containing metals , paper , dyeing and metallurgical process [4].

Cadmium is found in many domestic products like tobacco, phosphate fertilizers, polyvinyl chloride, rechargeable cells, petrol, commercial oils and is believed to cause pulmonary emphysema and bone diseases like osteomalacia and osteoporosis [5].

Cadmium is produced mainly as a by-product from mining, smelting, and refining of zinc, lead and copper and the estimated total world production about 20000t in 1997 while the total release is estimated at about 380 - 3,800[6]. It have been demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of metals such as cadmium [7]. Different methods such adsorption on goethite [8] and cellulose/chitin beads[9]have been used for mineralization of heavy metals from aqueous solution .Also, there are many of processes and techniques have been applied to mineralization of heavy metals and other pollutants.

Because of high performance and ease of use , adsorption is introduced as more popular applied method for water treatment [10,11]. In this method heavy metals are adsorbed in the pore surface of adsorbent which is insoluble in water. One of the most common adsorbent for heavy metals is activated carbon, which because of its high cost of activating processes is very expensive. In recent years cheap adsorbents have been attractive to many of researchers. Cheap adsorbents are widely and easily in reach and their preparation cost is low. These adsorbents are mainly a waste result of industrial and agricultural activity and have cellulose base.

In adsorption technology, no need for complex reforming processes, efficient and selective for heavy metals.

MATERIALS AND METHODS

Hydrochloric acid, sodium chloride and sodium hydroxide were supplied by Fluka , cadmium nitrate was supplied by Sigma .

Grinding beans peel in the form of powder was washed with excessive amounts of distilled water; several washings were performed to remove dust and impurities. The powder was then dried under sunlight for 5 hours and then in an oven at 120°C for a period of 1.5 hour and kept in airtight containers, then the powder was sieving and particle size of 150µm was obtained.

The qualitative analysis of adsorbent powder reveal the existence of saponions,alkaloids,flavones and terpenes.No resins,coumarins,and steroids had been detected. Also, The adsorbent powder was examined by elemental analyzer (EA3000A,Euroea). FT-IR analysis of powder was examined using Infrared spectrophotometer, 8000, shimadzu.

Adsorption isotherm

Solutions of metal ions (10 mL) of known concentrations (50-500 ppm) were added to flasks containing 0.2 g of powder . The flasks were shaken in a thermostatically controlled water bath (Shaker water bath, CL002, K&K Scientific) at a speed of 150 rpm till equilibrium is attained (45 min). This time is sufficient for the adsorption process to reach equilibrium in each case. After the equilibrium time elapsed, the suspensions were centrifuged at 3000 rpm for 10 min by using CL008, JANETZI – T5 centrifuge, . The clear supernatants

were assayed for metal, after appropriate dilution, spectrophotometrically by using atomic absorption spectrophotometer AA-6300, Shimadzu) and equilibrium concentrations were obtained by comparing the experimental data with the calibration curve.

The quantity of metal adsorbed was calculated according to the following equation [12] :

$$Q_e \text{ or } \frac{x}{m} = \frac{V(C_o - C_e)}{m} \quad (1)$$

Where Q_e is the sorption capacity (mg/g) ,x is the the quantity adsorbed (mg), m is the weight of adsorbent (g), C_o initial concentration (mg/L), C_e is the equilibrium concentration (mg/ L) and V is the volume of solution (L).

Desorption isotherm

The elution extent of the adsorbate was determined using distilled water as elution media. Solutions of different concentrations of each adsorbate (10 mL) were added to flasks containing 0.2 g of powder. The flasks were placed in time 45 min a constant temperature bath at 20°C. After equilibrium, the suspensions were centrifuged, and the supernate was decanted carefully and set aside for assay. A 10 ml portion of distilled water was added; after shaking for 30 min , the suspensions were centrifuged. The clear supernate was again decanted and the adsorbate content was determined [13] .

The amount of desorbed metal was calculated according to the following equation:

$$\text{The amount desorbed (mg/g)} = \frac{C_{ed} \times V}{m} \quad (2)$$

Where C_{ed} is the concentration of desorbed at equilibrium (mg/L),V is the volume of eluent (L) and m is the weight of adsorbent (g).

[

Effect of temperature

Adsorption experiment was repeated in the same manner at different temperatures (20,30, 40 and 50°C) to estimate the basic thermodynamic functions of the process.

Effect of pH

Adsorption experiment was carried out as mentioned previously as a function of pH using a fixed concentration of metals ions. Hydrochloric acid and sodium hydroxide were used to adjust the pH vale in the range from 1 to 6.8 . The pH of the suspensions was measured as well as at the end of experiment using pH-meter.

Effect of ionic strength

The effect of the addition 0.01-0.3g of sodium chloride to solutions containing fixed concentration of metal ions equilibrated with 0.2g of beans peel were investigated under the same experimental conditions described before.

RESULTS AND DISCUSSION

Analysis of Surface

CHNS Analysis of Surface

The CHNS ration analysis of adsorbent particles is shown in Table 1.It indicated the existence of a rise in carbon and higher values component of hydrogen, nitrogen, and this is attributed to the plant origin of the

components of the powder which provides a retaining effective aggregates feature, they are responsible for the high properties of the adsorption material adsorbent.

Table 1: Surface CHNS analysis

Element	Percentage
Carbon C	52.878
Hydrogen H	4.264
Nitrogen N	7.219
Sulfur S	0.000

FTIR analysis of Surface

FTIR spectrum of powder peel beans illustrates the effective groups as Figure 1 shows. As the emergence of a broad absorption peak when wave number 3100-3500 cm^{-1} indicates the presence of interference overlapping between the peak -OH and - NH , and the peak that appears when the extent of 2800-2950 cm^{-1} represents vibration stretch of alkyl groups $-CH_2$ and $-CH_3$ .Wave number 1600-1760 cm^{-1} gives an indication of the existence of the bonds C = O groups of carboxyl and amide . Some peaks when the term 800-1550 cm^{-1} can be attributed to OH and C- N bending .

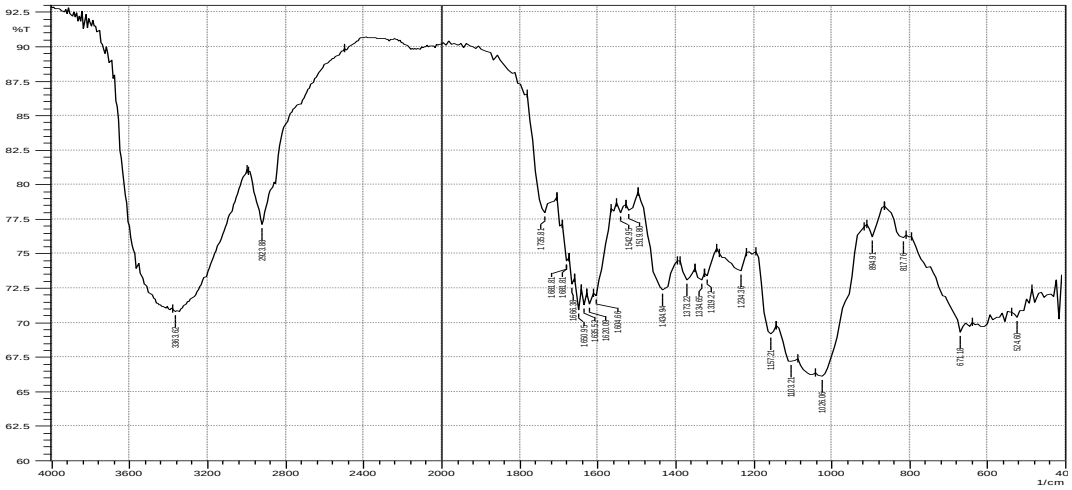

Figure 1: FTIR spectrum of powder peel beans.

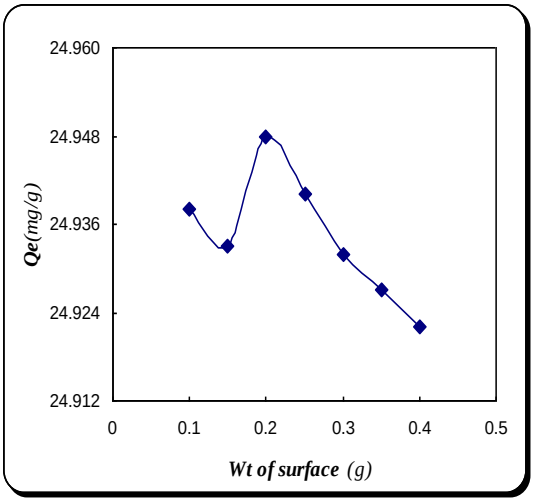

Figure 2: Effect of adsorbent dose

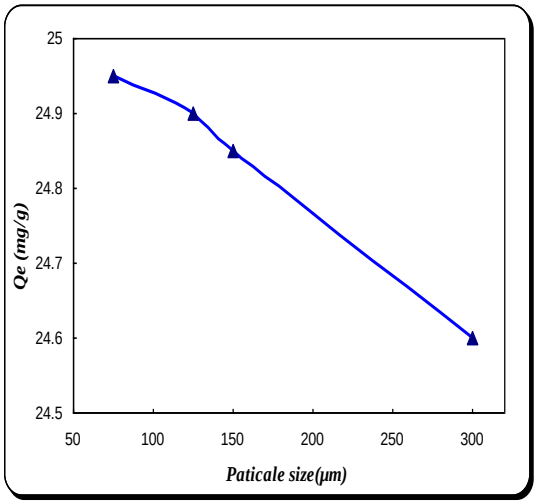

Figure 3: Effect of particle size

Effect of adsorbent dose

The removal study of Cd (II) ions using peel beans powder at a constant concentration 500 mg / L and different weights of the surface at temperature 20 ^{o}C is shown in Figure 2.

According to the results shown in the Figure 2 the amount of the adsorbent for the removal of Cd(II) ions increases as the weight of adsorbent increases. The increased weight of adsorbent means increasing the number of active sites formatted for the adsorption of ions on surface . The effectiveness of any surface, thereby correlates with increasing the amount of adsorbed ions from the solution until it reaches a specific value represents the amount of adsorbent material in the saturation stage, are not affected by increasing the weight of powder peel beans.

Effect of particle size

The importance of the particle size of adsorbent material has been studied as Figure 3 shows. That increase in particle size decreased the percent removal. At a fixed adsorbent dosage, the decrease in particle size increases the Cd(II) ion uptake. The increase in adsorption smaller particles is attribute to the greater accessibility of pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent[14] .

The time required to reach equilibrium concentration in adsorption metal ions on the surface of beans peel in different times was 0-120 min . when the temperature 20°C and constant concentration of ion (500 mg /L) and using that particle size of 150µm . Results of the study showed that the time required to reach equilibrium concentration is 30 for Cd(II) .

The plot amount of adsorbent versus equilibrium concentration to give the general shape of isotherm adsorption and desorption as shown in Figures 4 and 5 respectively.

When comparing the adsorption isotherm shown above ,it has been find that they follow product L according to classification Giles, as well less energy adsorption increase the covered part of the surface and adsorption increases with increasing concentration of material adsorbent [15,16] .

These properties mean that the curve follows the equation (Langmuir adsorption) for the adsorption [17,18]:

(3)

$$\frac{Ce}{Qe} = \frac{1}{q_m.k_L} + \frac{1}{q_m}.Ce$$

Figure (6) shows the linear relationship of C_e / Q_e versus C_e according to Langmuir isotherm . The values of Langmuir constants as well as the correlation coefficient are presented in Table 1. Although drawing $\log Q_e$ versus $\log C_e$ (Figure 7) illustrates the adsorption of Cd (II) on the surface of the adsorbent material according to Freundlich isotherm[19,20] . The drawing Q_e versus $\ln C_e$ (Figure 8) explains adsorption of Cd (II) on the surface of the adsorbent material according to Timken Isotherm[21] . The results of three isotherms are summarized in Table 2.

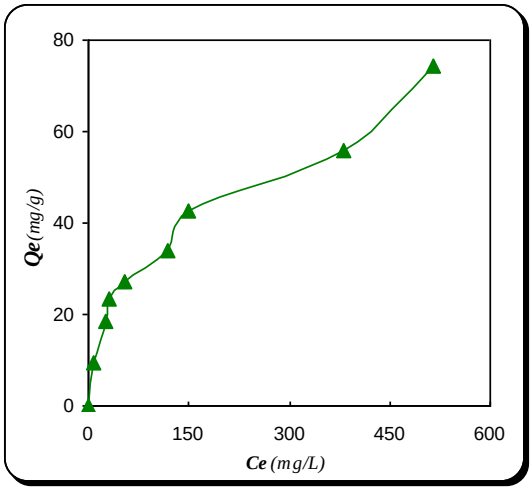

Figure 4: Effect of initial concentration

Table 2: Constants for Langmuir, Freundlich and Timken t

Langmuir equation			*Freundlich equation*			*Timken equation*		
K_L	*a*	r^2	K_F	*N*	r^2	K_T	*B*	r^2
0.833	**0.013**	**0.995**	**1.810**	**2.145**	**0.980**	**2.281**	**35.028**	**0.910**

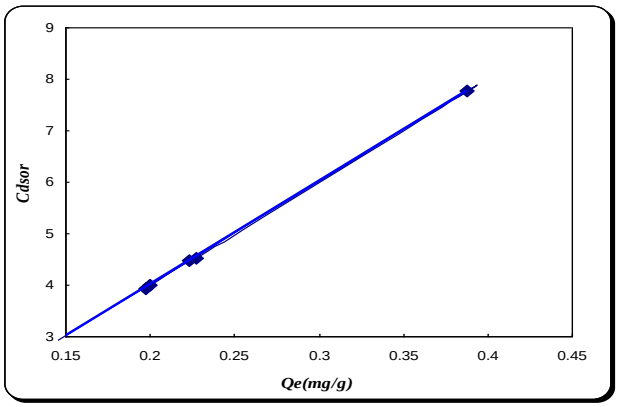

Figure 5: Desorption isotherm

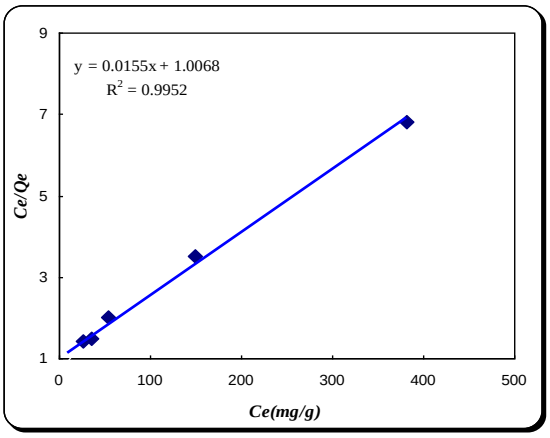

Figure 6: Langmuir adsorption isotherm

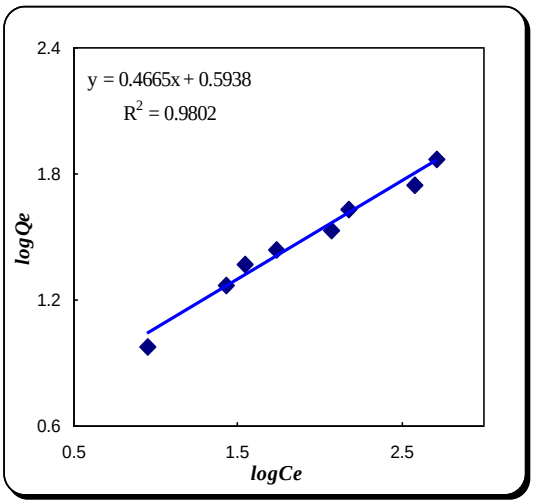

Figure 7 : Freundlich adsorption.

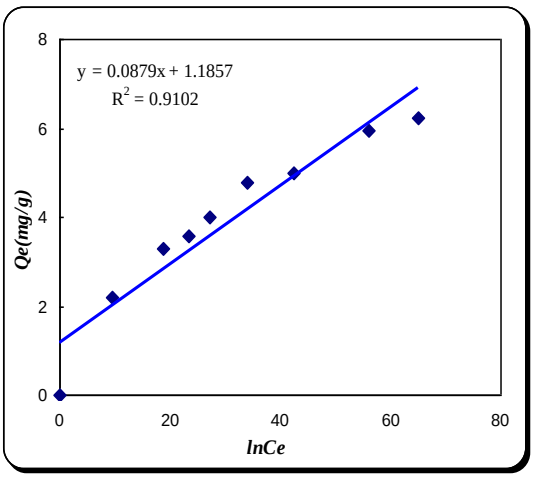

Figure 8: Temkin adsorption isotherm

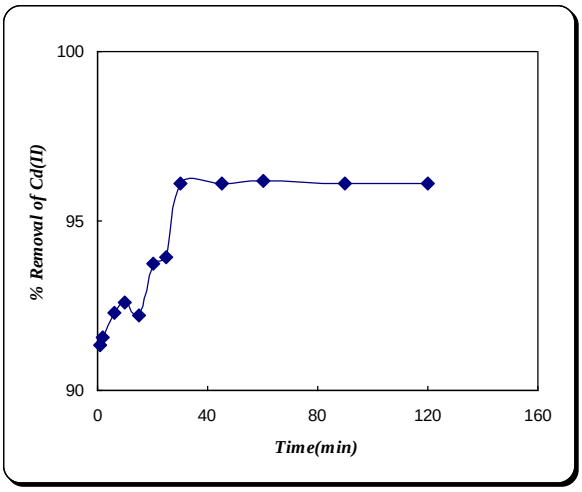

Figure 9: Effect of contact time

Effect of contact time

The percentage of substance adsorbed on the surface of the beans peel used different times 0-120 min was studied and recorded the amount of material removed of water aqueous as shown in Figures 9.

The results showed that the percentage of metal ions removed from aqueous solution increases with time to end this surface saturation ions used .

Effect of temperature

The effect of temperature on the metal ion adsorption on the surface of the beans peel in different temperatures (20, 30, 40 and 50°C) was investigated . It is through the use of equation 1 to calculate the amount of adsorbent .

The plot of Q_e versus C_e for the purpose of obtaining adsorption isotherm as a function of temperature as shown in Figure 10, which indicates that the Q_e increase with increasing temperature.

Thermodynamic parameters, such as Gibbs free energy change (ΔG^o), enthalpy change (ΔH^o) and entropy change (ΔS^o), were calculated using Gibbs free energy and Vant Hoff,s equations:

$$\Delta G^o = -RT\ln K \quad (4)$$

$$\log K = (\Delta S^o / 2.303R) - (\Delta H^o / 2.303RT) \quad (5)$$

where *K* is the equilibrium partition constant calculated as the ratio between sorption capacity (Qe) and equilibrium concentration (Ce), *R* is the gas constant (8.314 J/mol/K) and *T* is the temperature(Kelvin).The results are showed in Table 3 , which illustrate that the adsorption process is endothermic process, as the temperature increases leading to increase the kinetic energy of the adsorbed molecules on the surface leading to disengagement metal ion surface[22,23] . The results showed that the adsorption of the chemical type where value of ΔH adsorption is high .

Table 3: Values of thermodynamic parameters

kJ.mol^{-1}) (ΔH^o	ΔG^o (kJ.mol^{-1})	ΔS^o (J.mol^{-1}.k^{-1})	K
3767.406	**-3264.810**	**24.000**	**3.8199**

Effect of pH

Several different acidic functions (1.0-6.8) were used to study the effect of pH on adsorption of metal ions on the surface of the beans peel at 20°C and concentration (500 mg/L) . Through the use of equation 1 values of Q_e was extracted ande drawn against the acidic function as shown in Figure 11.

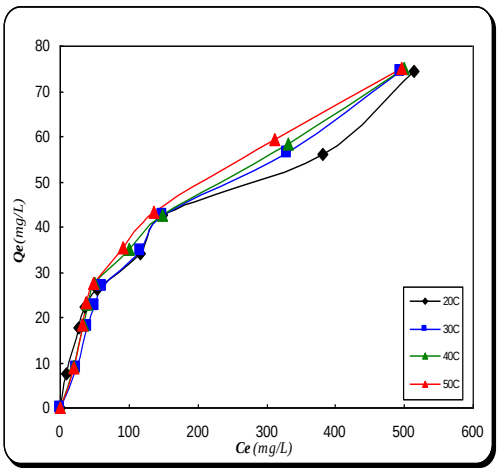

Figure 10: Effect of temperature

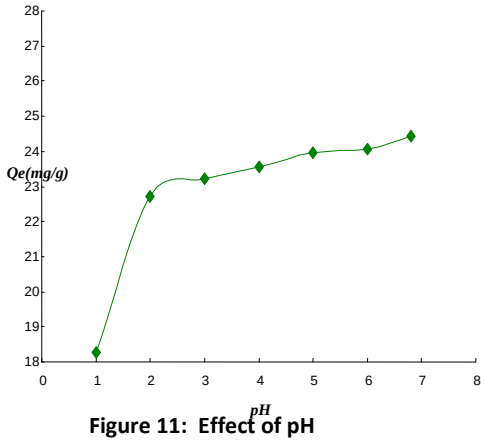

Figure 11: Effect of pH

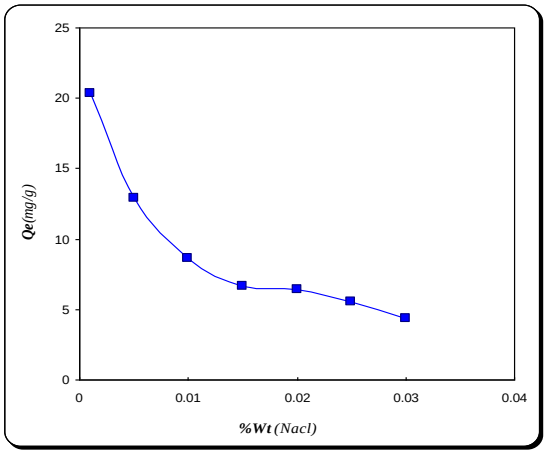

Figure 12: Effect of salt concentration

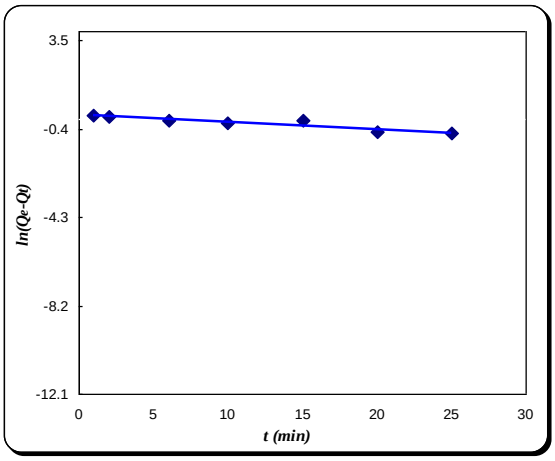

Figure 13: Pseudo-first order kinetic model

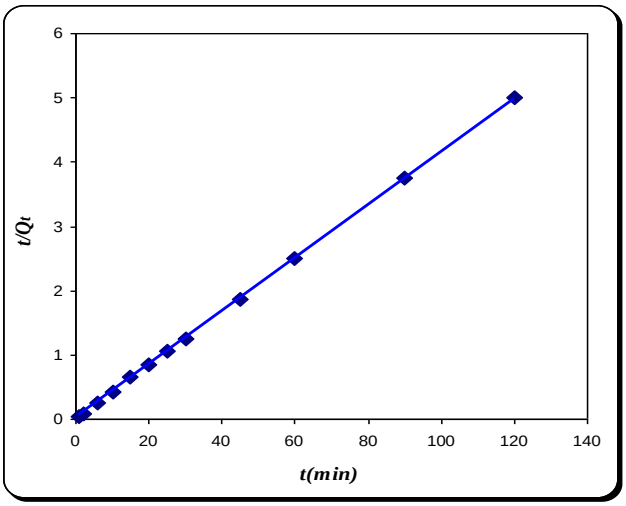

Figure 14: Pseudo-second order kinetic model

This can be explained by noting that the amount of adsorbent increases with increasing pH vale .Above value of 6.8 ions begin degradation , leading to the formation of insoluble hydroxide $Cd(OH)_2$[24,25].

In very low pH media the adsorbent surface was highly protonated and protons are strongly competing with metal ions , which was not favorable for metal ion uptake[26] . At higher pH values(below 7), the adsorbent surface began acquiring a net negative charge making the situation electrostatically favorable for a higher uptake of metal ion [27] .

Effect of salt

Several different concentrations of pure sodium chloride salt (0.01, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 mol/L) were used to study the effect of strength ionic adsorption of metal ions on the surface of the beans peel at 20°C.The results are shown in Figure 12.

This can be clarified by a competition between the sodium ions and metal ions in the adsorption on the surface of the beans peel including sodium ions characterized by a smaller size of metal ions. The transition ion in solution faster to the adsorption of sodium ions faster than the adsorption of metal ions[28].

Adsorption Kinetic

Both kinetic models ,pseudo first and pseudo second order using equations 6 and 7 respectively have been applied [29,30] .

(6) $$\log(Q_e - Q_t) = \log Q_e - k_1.t$$

where Q_e and Q_t are the adsorption capacity (mg/g) at equilibrium and at time t respectively, and k_1(min^{-1}) is the pseudo-first order rate constant of the adsorption. By plotting of log(Q_e-Q_t) versus t a straight line can be obtained as Figure 13 shows and k_1 and correlation coefficient can be determined.

$$\frac{t}{Q_t} = \frac{1}{h} + \left(\frac{1}{Q_e}\right)t \quad (7)$$

$$h = k_2 Q_e^{\,2}$$

hence h(mg g^{-1}min^{-1}) can be regarded as the initial adsorption rate and k_2 is the rate constant for pseudo-second-order adsorption (g mg^{-1}min^{-1}) . Plotting of t/Q_t versus t gives a straight line as Figure 14 illustrates. k_2 and correlation coefficient can be determined .

The kinetic constants and correlation coefficients for both models pseudo first order and pseudo second order account in the Table 4. The correlation coefficients values of pseudo second order model a relatively high , and that the amount of the adsorbent calculated by this model close to the value that has been determined through experiments. While the value of the correlation coefficient for the pseudo first order model of adsorption unconvincing in. Therefore, the second model - pseudo be more appropriate to describe the kinetics of adsorption of metal ions on the surface of the peel beans.It is clear that the adsorption of Cd(II) ion follows pseudo second order kinetic .

CONCLUSIONS

On the basis of the experimental results of this investigation , the following conclusions can be pointed out :

- The results of atomic spectroscopy show that the increase in the amount of adsorbent increase the equilibrium time.
- The beans peel as adsorbent can be used for the removal of heavy metals ions from aqueous solution.
- Langmuir and Freundlich isotherm model adequately described the adsorption of metal ions onto beans peel.
- Thermodynamic studies confirmed that adsorption process of metal onto beans peel was endothermic process . The thermodynamic value of ΔG^o is negative for system , indicating spontaneous process . As that type adsorption is chemical from where value of adsorption is ΔH high (20 kJ.mol^{-1}).
- The percentage removal of metal ions was dependent on pH solution and NaCl concentration .

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