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Research Article

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Removal of pb (II), cd (II) Ions onto dried *Conocarpus erectus* leaves using batch adsorption and study the adsorption thermodynamics

Ihab. A. Al-tameemi[1], Tarikak. Nasser[2] and Thuraya. M. A[1]

[1]Department of Chemistry, College of Education, University of Basrah, Iraq
[2]Department of Marine Chemistry, Basra Marine Center, Basra University, Iraq

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ABSTRACT

Wastes of the Iraqi date dried Conocarpus erectus leaves was used to study removal of heavy metal cations (Cd+2& pb+2) from simulated artificial waste water using batch adsorption process. The dried parts of the date Conocarpus erectus leaves, were grinded to ≤150 micro mater in size and used directly in different adsorbent / metal ion ratios, starting with metal ion concentration of (100ppm). The adsorption efficiencies were found to be pH dependent, increasing by increasing the pH in the range from(3-9). Date Conocarpus erectus leaves succeeded to achieve 89.9% removal for Cd+2 ions & 95.1% for pb+2 ions within (60 min) contact time, at room temperature. 25Co and pH value of (9).The removal order was found to be Pb (II) >Cd (II).This study is one of the first reports of removal of the highly toxic Cd2+ and Pb2+ in mixed systems based on the adsorption by natural materials. The thermodynamic parameters were given and showed that ΔH° was endothermic-positive value, ΔG° was found (a spontaneous process-negative value) and ΔS° was found positive value- increase of disorder of the process. fuctional groups (C-O and C-N) identification were given using FTIR spectrophotoscopy.

Key words: Adsorption, lead and cadmum, Lerngmuir and Temkin model, *Conocarpus erectus* leaves, adsorption thermodynamic

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INTRODUCTION

The Pollution is addition of unwanted and undesirable foreign matter to environment as a result of enormous industrial development and modernization[1]. The heavy metals are of special concern because they are non-degradable and therefore persistent. Commonly encountered metals of concern include Pb2+, Cu2+, Zn2+, Co2+, Ni2+ *etc*. These metals are toxic both in their chemically combined forms and in the elemental form, Some in-place treatment technologies available for the removal of heavy metal ions from aqueous solutions are chemical precipitation [2], flotation [3], biosorption [4–6], electrolytic recovery, membrane separation [7], removal by adsorption on minerals [8,9] and activated carbon adsorption [10,11].despite these wide methods, they have disadvantages, which include incomplete metal removal requirements and expensive equipment . Recently many researchers in the world wide investigated low-cost adsorbents with high metal binding capacities. Agricultural by-products have been widely used for treatment of water containing heavy metal. These agricultural materials include; peat, wood, pine bark, banana pith, soybean , cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, wool, orange peal, compost and leaves [12]. The present work is attempted to investigate the possibility of the utilization of one kind of tree leaves: *Conocarpus erectus* for removal of pb(II), cd(II) from waste water. Optimization variables include; contact time, pH ,temperature, particle size, and initial ion concentration. The Freundlich, Langmuir and Temkin adsorption isotherms were used to investigate the adsorption process. Kinetic study was also carried out to evaluate the order of adsorption[13].

EXPERIMENTAL SECTION

Adsorption experiments

For the adsorption experiment, the effect of adsorbent weight on the adsorption of the ions was investigated (0.5 - 2g) of the adsorbent was weight respectively into conical flasks. 20 ml of 100 mg/L solution of each of the metal ions solution was added and the mixture shaken at 185 rpm for 60 min. After the biosorption experiment, the biosorbent was separated from the solution by filtering through a Whatman (0.45 μm) filter paper and the filtrate was analyzed for the pbII), cd(II) ions concentration. The pb (II), cd(II) ions concentrations before and after the biosorption were determined by using Flame Atomic Absorption Spectrophotometer (Shimadzu 6000). The equilibrium pb(II), cd(II) ions sorptioncapacity could be calculated as equation bellow;

$$Q_e = V(C^{\circ} - C_e)/m \ldots (1) [14]$$

Where ; Q_e is the equilibrium pb(II), cd(II)) ions sorption capacity (mg/g), V is the suspension volume (l), m is the mass of durian material (g),*Co* = Initial concentration of solution, *Ce*= Concentration of the solution after adsorption. To determine the effect of concentration on the adsorption of the metal ions, 2g of the adsorbent, being the optimum adsorbent weight in the previous experiment was added to 50 ml each of varying concentrations (between 5 - 100 mg/L) of the metal ion solutions. The mixtures were shaken and the concentration of the metal ions adsorbed was determined. The effect of contact time was also investigated by adding 2g of the adsorbent to 20 ml of 50 mg/L of pb(II), cd(II) ions being their respective optimum adsorption concentrations; and shaking using varying contact times (30 –180 min) and the percentage of adsorbed ions determined. The effect of pH on adsorption of the metals was investigated using 0.5g of the adsorbent and 20 ml of 100 mg/L of pb (II), cd(II) ions. The mixture was shaken for 60 min for pb (II), cd(II) and the amount of ion adsorbed was determined.

Preparation of adsorbent

Conocarpus erectus leaves were collected from gardens of AL-basrah University, basrah, Iraq. The leaves were extensively washed with deionize water to remove dirt ,dried in an oven at 90Cº for a period of 1.5 hr,then ground and screened to obtain the average particle size 150µm.the powder was preserved in glass bottles for use as adsorbent, The some physical properties of the chosen adsorbent are listed in Table 1.

Table 1. Characteristics of the Adsorbent

Properties	Value
Porosity(%)	76.9 ± 5.321
Langmuir surface area(m2 /gm)	1.3822

RESULTS AND DISCUSSION

FT.IR Characterization of Conocarpus erectus

FT-IR apparatus type shimadzu (4000-400 cm^{-1}) was carried out in order to identify the functional groups in the *Conocarpus erectus* leaf powder that might be involved in the adsorption process. FT-IR analysis was carried out in order to identify the functional groups in the *Conocarpus erectus* leaf powder that might be involved in the adsorption process. The FTIR spectrum in the range of 400-4000cm is shown in Fig.1.as shown in figure, the spectrum displays a number of adsorption peak, which indicates the complex natural of the material examined stretching, which is consistent with the peak at 1101.28 and 1319.22 cm assigned to alcoholic C-O and C-N stretching vibration. The absorption band wave numbers of 2920.03-2852.52 cm can be assigned to CH and $-CH_2$ stretching, respectively [15].The absorption band wave number of ketone group is about 1652.88cm.thatresult of binding of this group with the cations of metal.

Effect of pH

The pH is one of the most important parameters of biosorption of heavy metals[16]. The biosorption of pb(II),cd(II) by *Conocarpus erectus* leaf powder at different pH values(3-10) is presented in Fig2. The optimal pH for removal of pb(II), cd(II) was(9-10) respectively. The removal percentages of pb(II), cd(II) ion on *Conocarpus erectus* powder at an initial concentration of 100 ppm and at an initial pH=(9-10) respectively ,using 0.5g of the adsorbent with 100mLof pb(II),cd(II) ions solution (95.1%,89.9%.) respectively .At pH higher than 9 both metals were precipitated due to the formation of hydroxides and removal due to sorption was very low .The minimal adsorption at low pH may be due to the higher concentration and high mobility of the H+, which are preferentially adsorbed rather than the metal ions [17,18]. At higher pH values, the lower number of H+ and greater number of ligands with negatives charges results in greater pb(II), cd(II) adsorption. For example, carboxylic groups (–COOH) are important groups for metal uptake by biological materials [19,20]. At pH higher than 3-4, carboxylic groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced [21].

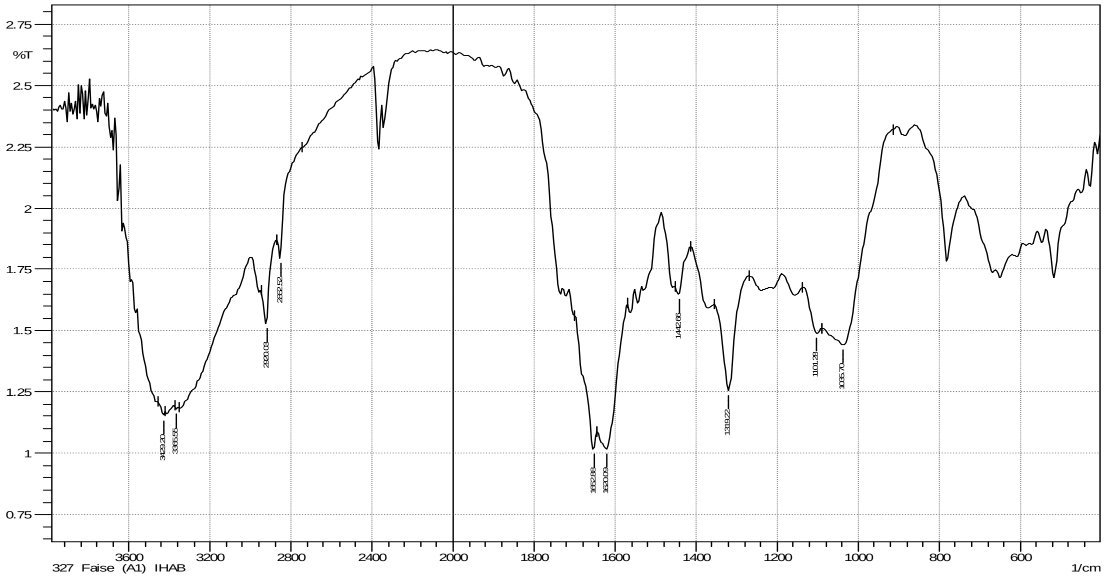


Fig (1)FT- IR of *Conocarpus erectus* leaf powder

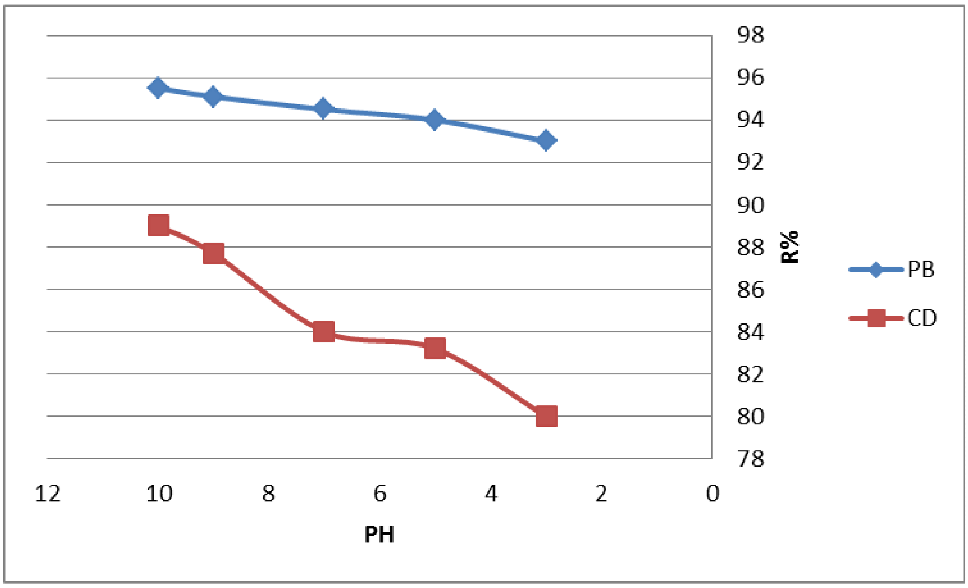


Fig (2) Effect of pH on adsorption of pb ,cd

Effect of adsorbent weight

One of the parameters that strongly affect the sorption capacity is weight of the adsorbents. With the fixed metal concentration it can easily be inferred that the percent removal of metal ions increases with increasing weight of the adsorbents as shown from Fig. 3This is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent[22] . the removal percentages of pb(II), cd(II) ion *Conocarpus erectus* powder at an initial concentration of 100 ppm and at an initial pH=(9) ,using at different weight of the adsorbents (0.5_3g) with 50mLof pb(II), cd(II) ions solutions(97.9%-94%) respectively.

Effect of Initial Concentration of pb(II),cd(II)ions

To study the effect of initial concentration of metal on the adsorption, the operating conditions were set as follows: Volumes of solutions used were 20ml, concentration of metal ranging between 5 and 100 mg / l ,were gently shaken with 0.5 g of *Conocarpus erectus* leaf powder (size 150µm) for 90 min for pb (II), cd (II) ions with initial pH of the solution of pb(II), cd(II)ions was(9). Fig. 4 shows the effect of metal concentration to removal of pb(II), cd(II) ions *Conocarpus erectus* leaf powder. The heavy metals are adsorbed by specific sites provided by the acidic functional groups on the biocarbon, while with increasing metal concentrations the specific sites are saturated and the exchange sites due to excessive surface area of the biocarbon are filled[23]. It is clear that with increasing initial concentrations, the metal removal decreases. The removal percentages of pb(II), cd(II)ion on *Conocarpus erectus* powder at an initial concentration from(5-100) ppm and at an initial pH=(9) ,using(0.5g of adsorbent)with 20mL of pb(II), cd(II) ions solutions (95.1 %,89%.) respectively .

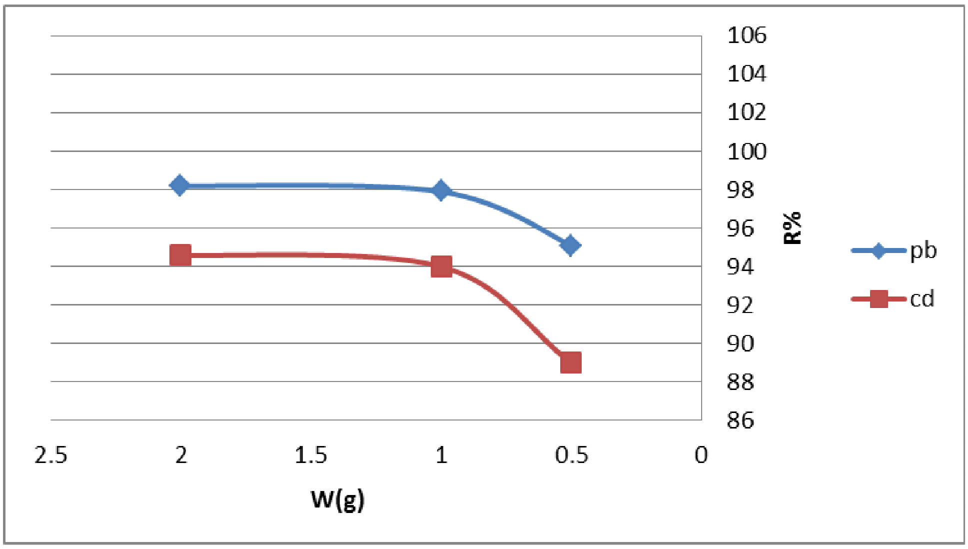


Fig (3) Effect of adsorbent weight on adsorption of pb , cd

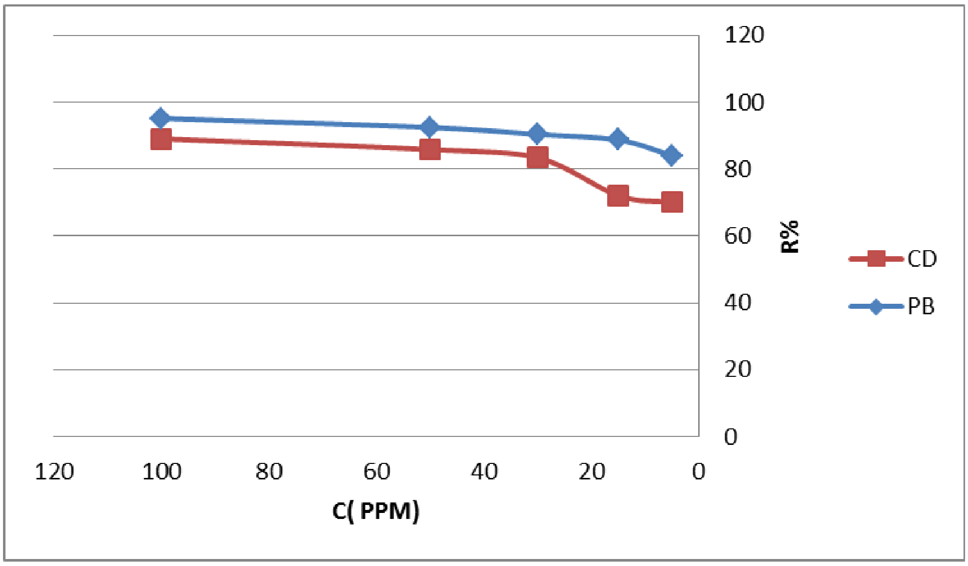
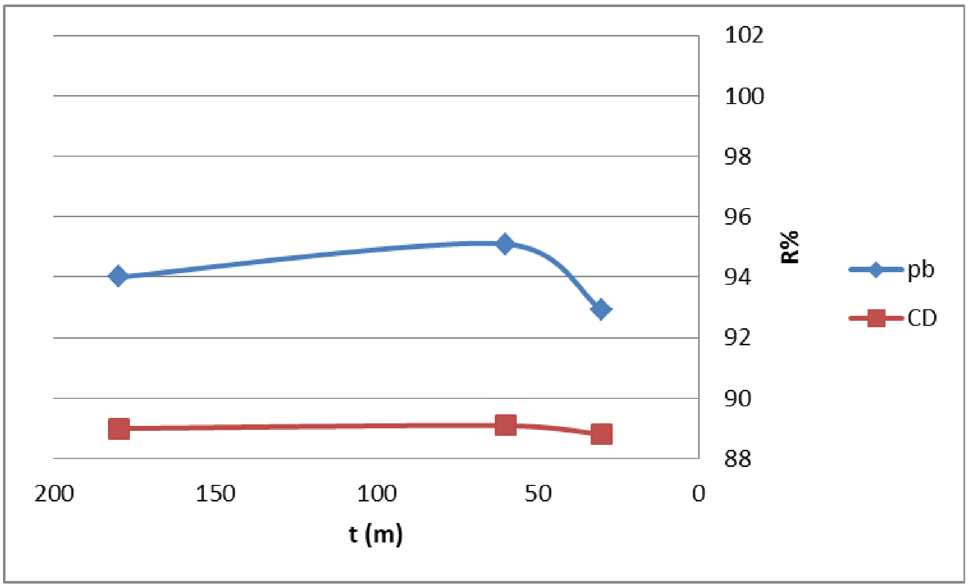


Fig (4) Effect of concentration on adsorption of pb,cd

Effect of contact time

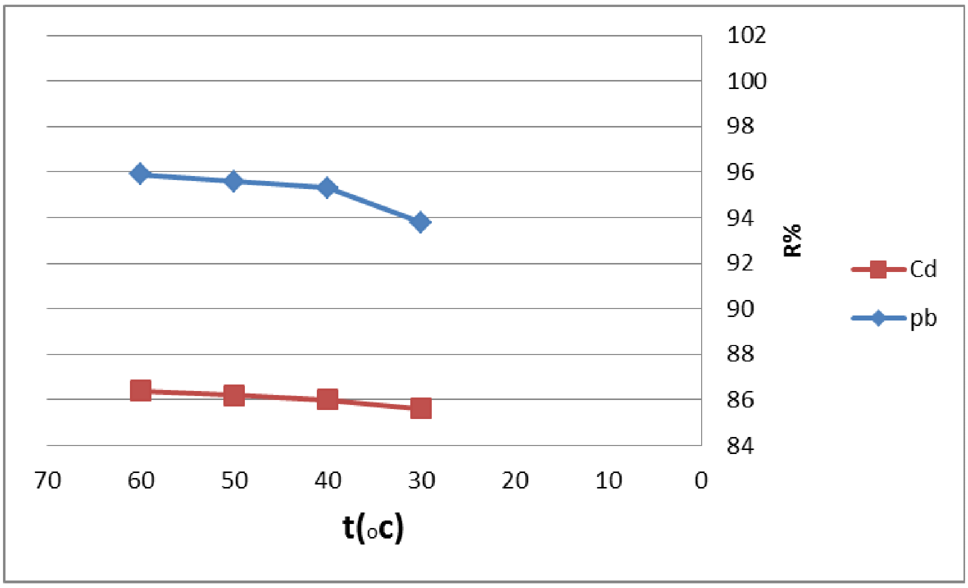
Fig5 shows the removal percentages of pb(II), cd(II)ions on *Conocarpus erectus* leaves powder at an initial concentration of 100 ppm and at an initial pH(9),using 0.5g of the adsorbent with 20mL of pb(II), cd(II)ions solutions (95.1%,89.1%)respectively. From this figure, it is clear that the metal removal percentages increased with an increase in contact time before attaining equilibrium. The rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metal [24]. A very fast increase in the biosorption rate of pb(II), cd(II)ions on *Conocarpus erectus* leaf powder may be observed in the first 30 minutes for all pH-values studies, followed by a less rapid increase and a practically constant plateau after 60 min, in all cases. .Equilibrium time was attained at 60min,for pb(II), cd(II)ions on *Conocarpus erectus* leaves powder. To ensure enough time to reach equilibrium; 60 min of contact was used throughout the batch experiments.



Fig(5) Effect of contact time on adsorption of pb,cd

Effect of temperature on the adsorption rate

Increase of temperature from 20 to 60 ◦C increased the sorption of pb(II),cd(II) ions indicating the process to be endothermic. The increases in uptake of pb(II),cd(II) ions with temperature may be due to the desolvation of the adsorbing species, the changes in the size of pores, and the enhanced rate of intraparticle diffusion of adsorbate, as diffusion is an endothermic process.. The biosorption was found to decrease with increase in temperature and the sorption capacity (Q) was also found to decrease. The interactions are found to be exothermic in nature [25],[26] for which the evaluation of thermodynamic.This show in Figuer(6). The removal percentages of pb(II), cd(II)ions on *Conocarpus erectus* powder at different temperature from(30-60) and at an initial pH=9 ,using(0.5g) of adsorbent with 20mL of pb(II) cd(II)ions solutions (95.9 %,86.4%.) respectively.



Fig(6) temperature on adsorption of pb,cd

RESULTS AND DISCUSSION

Isotherms

Biosorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich andTempkin models are commonly used to fit experimental data when solute uptake occurs by a monolayer biosorption [28]-[29]. Langmuir isotherms assume monolayer biosorption, and are described by equation (2):

$Q_e = (Q_{max}bC_e)/(1+bC_e)$……………..(2)

The Freundlich isotherm is described by equation (3):

$Q_e = K_F\, C_e$………………(3)

Where Q_e and $Q_{max}$are the equilibrium and maximum sorption capacities (mg/g biosorbent),C_e is equilibrium concentration (mg/l solution), b is the equilibrium constant, K_F and n are Freudlich constants characteristic of the system.

While, Tempkin model Heat of adsorption and the adsorbate–adsorbate interaction on adsorption isotherms were studied by Tempkin and Pyzhev [30], who suggested that because of these interactions the energy of adsorption of all the molecules decreases linearly with coverage.

Temkin isotherm is represented by following equation

$Q_e = B_1 \ln K_t + B_1 \ln C_e$………(4)

Where:

$B_1 = RT/b$……………..(5)

The adsorption data can be analyzed according to equation (4). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants $K_T$andB_1. $K_T$is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption..The investigation of adsorption shows in fig (7,8,). The experimental data was better described by the Freudlich isotherm than Langmuir and Temkin isotherm. The regression coefficient (R2) was (0.984%,0.962%,) respectively for pb(II), cd(II)ionsfor the Freudlich isotherm. In contrast, the Temkin and Langmuir isothem model were less precise, with a lower R2 value .

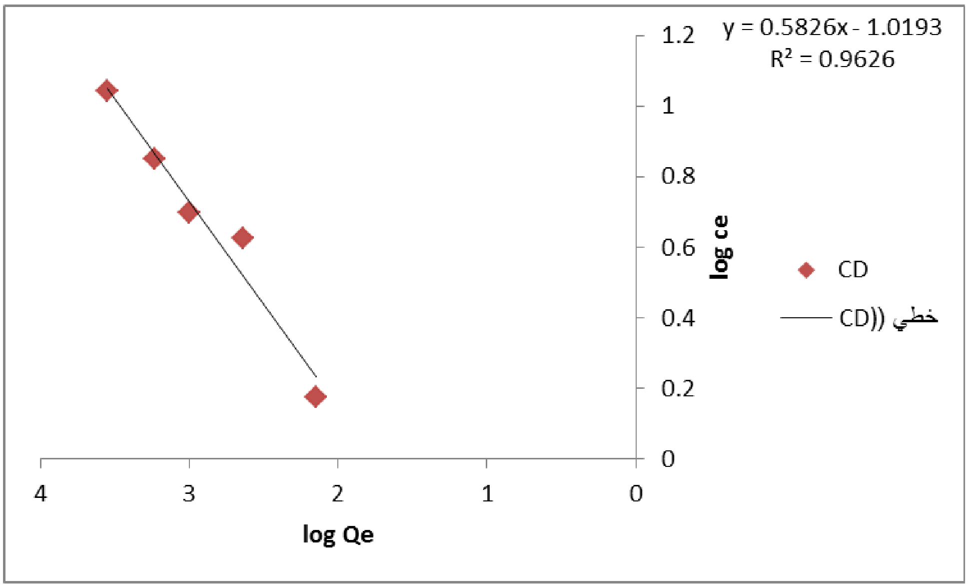


Fig (7) Freundlich isotherm for the adsorption of cd (II) ion on *Conocarpus erectus* leaf powder at25c°under optimum conditions

Thermodynamic Studies:
Adsorption process was found useful to calculate thermodynamic parameters such as change in free energy ΔG°, enthalpy ΔH° and entropy ΔS°.Using the following equations ;

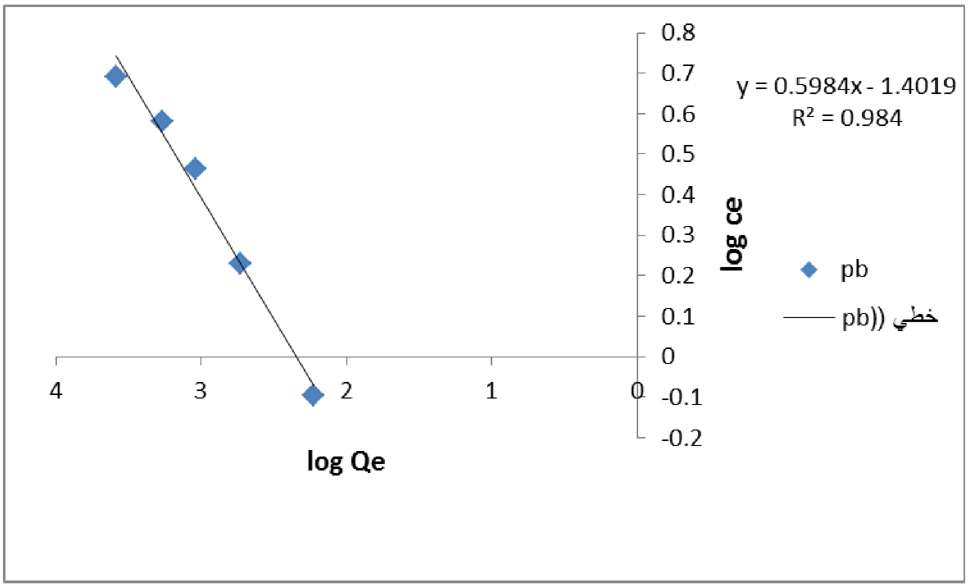
$\Delta G° = -RT \ln K$ ………….(1)

$\mathrm{Log}\, K = (\Delta S°/2.303R) - (\Delta H°/2.303\, RT)$ ………… (2)

$\Delta G° = \Delta H° - T\Delta S°$ …………. (3)

As K is the equilibrium constant ,T is the absolute temperature (K°) and R is the gas constant (33).

Van't Hoff equation was used to estimate the values of ΔH° and ΔS° from the intercept, and slope of the plot which was ln K vs. 1/T (fig. 9).Table (2) showed the thermodynamic parameters values for the adsorption processes. From this the table, adsorption was found endothermic (ΔH° was positive), reaction was spontaneous (ΔG° was negative), and solid solution interface was random because ΔS° was increased. The change in adsorption enthalpy was measured and found -20 to 40 KJ.mol^{-1}, compared to chemisorption which was -400 and -80 KJ.mol^{-1} (34).values of ΔH° physisorption was found the dominant mechanism.



Fig(8) Freundlich isotherm for the adsorption of pb (II) ion on *Conocarpus erectus* leaf powder at25c°under optimum conditions

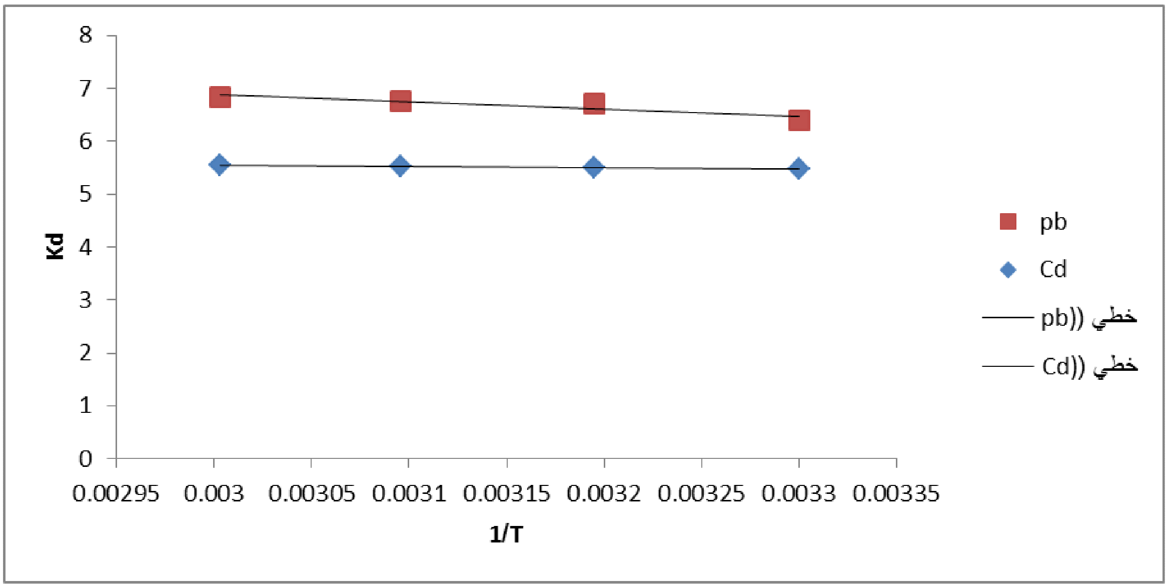


Fig (9) Plot of Van't Hoff equation for adsorption process with *Conocarpus erectus* leaves as adsorbents

Table (2) the thermodynamic parameters for adsorption process with *Conocarpus erectus* as adsorbents

heavy metal	Temperature K°	ΔG° KJ.mole^{-1}	ΔH° KJ.mole^{-1}	ΔS° J.mole^{-1}.K^{-1}
Pb	303	-16.135	6.615	57.865
	313	-17.43		
	323	-18.17		
	333	-18.939		
Cd	303	-13.782	1.519	46.159
	313	-14.322		
	323	-14.825		
	333	-15.329		

CONCLUSION

The result of batch adsorption clarifies the percentage of removal of metal ions from their wastewater solution. The initial concentration of metal ions vary from 5 ppm to 100 ppm with experimental conditions as time of contact, pH, initial concentration and the weight of loading material. The batch adsorption result showed that removal percentage was higher for dried *Conocarpus erectus* . Thermodynamic studies confirmed that the process was endothermic. The fit of the adsorption data into the Langmuir isotherm confirmed monolayer adsorption. The data thus obtained from this investigation would be useful in designing and fabricating an efficient treatment plant for Pb (II) and cd(II) rich effluents, representing of effective in cleaning environment.

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