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Adsorption of Some Heavy Elements on Surface of Activated Carbonized Cellulose from Aqueous Solution

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Abstract

In this study the activated carbonized cellulose in (350 ºC) by citric acid have been used to remove some heavy metals (Hg Cd, Cu, Pb) from its aqueous solution at room temperature. The adsorbed metals data applied on three adsorption isotherm models, Freundlich, Langmuir and Temkin isotherms. The adsorption results were very good fitted with isotherm models by the (R2) meaningful value. The removal metals adsorbed on surface of adsorbent from high to the less remove arranged according to its ability depending on the nature and size of metals. The free energy (ΔG) and constants of the adsorption process (Ө, n, kf, kT, b, bT) for copper, lead and cadmium were measured from isotherm curves, infra-red spectrums of the activated carbonized cellulose and cellulose itself were measured by FTIR spectrophotometer.

Keywords: adsorption, activated carbonized cellulose, heavy metals, (R2), isotherm.

1. Introduction

Adsorption is a phenomenon of binding atoms, molecules or ions on the surface of substances physically or chemically by means of hydrogen bonds, Vander Walz forces, valence dispersion forces, and bipolarization interventions [1], [2]. The adsorption process is one of the most important processes used to remove organic and inorganic pollutants of low concentrations that cannot removed by other methods. Activated charcoal distinguished by its high adsorption capacity due to the large pore size and high surface area, and it can have recovered or activated after use by heat or concentration [3]. Industrial activities are the main source of water pollution due to chemical wastes that contain heavy elements that affect health and the environment such as mercury, copper, lead and cadmium [4]. To increase the adsorption capacity of some materials, they activated with basic or acid solutions such as citric acid [5].

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The relationship between the amount of adsorbent on the material surface and the equilibrium pressure or concentration at a given temperature called the adsorption isotherm. Such as Freundlich, Langmuir and Temkin isotherms [6]. Suppose Freundlich Most solid surfaces are not homogeneous, and the change in potential energy is not uniform due to a difference in Adsorption sites for their energy levels [7]. The Freundlich equation expressed by the following relationship:

$$\ln qe = \ln kf + 1/n \ln ce$$

Where (n, kf) Freundlich constants and (qe) the amount of adsorbent at equilibrium in unit (mg /g) and (ce) the amount of concentration at equilibrium in (mg / l). The curve (ln qe) against (ln ce) gives a straight line with slope (1 / n) which represents a measure of the adsorption intensity and with a section (ln k) which represents a function of adsorption capacity. In low concentrations, but in high concentrations a slight curvature of the straight line occurs, especially at high temperatures [8],[9].

The Langmuir equation expressed by the following relationship by straight line with slope 1/q and section 1/aq:

$$1/qe = 1/ qo + 1/ qo\ kL\ ce$$

Where (qe) the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g) and (qo) is maximum adsorption capacity and (kL) Langmuir isotherm constant [10]. Through the Temkin isotherm equation for adsorption, the reaction between the adsorbent and the adsorbate can calculated as follows [11]:

$$qe = b \ln KT + b \ln Ce$$

Where (kT, b) are constants and (b) heat of adsorption in units of joules per mole can be calculated by the following equation:

$$bT = RT/b$$

Where (R) is General constant for gases, (T) is absolute temperature and (bT) is Temkin costant.

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2. Experimental Work

2.1 Reagents and chemicals

Xylenol organic indicator	EDTA	H_2SO_4	Hexamine
$Cd(CH_3COO)_2.2H_2O$	HCl	H_2S solution	$Pb(CH_3COO)_2.3H_2O$
$HgCl_2$	$Pb(NO_3)_2$	HNO_3	$Na_2S_2O_3$
$CuSO_4.5H_2O$	KI	starch	

All reagent and chemicals prepared by the BDH company accept hydrogen sulfide solution prepared in the laboratory and the standard solution prepared as in Quantitative In organic Analysis [12].

2.2 Procedure

A quantity of cellulose pelleted and made as compressed balls by hand and placed in the Furnace at temperature (350ºC) for ten minutes to get carbonized cellulose (100) gm. of this cellulose took and soaked in 0.6 M citric acid for half an hour at room temperature (25°C) and dried at temperature (40°C) to the next day. It washed several times until PH (6.5 - 7) obtained, dried and left inside the desiccator until the next day. The functional groups of cellulose and activated carbonized cellulose were diagnosed using an American-made FTIR Spectrophotometer [13]. The solutions of the studied elements (Hg, Cd, Pb, Cu) were prepared at concentration of (20, 30, 40, 50, 100) ppm from the standard solutions of these elements at concentration 1000 ppm. Thermal adsorption experiment was carried out in the form of a one-time experiment for the heavy elements under study, (1.5g) of adsorbent material was taken from activated carbonized cellulose and put in sealed glass containers with a capacity of (100) ml, solutions of elemental ions (Cd, Pb, Cu, Hg) were added. At the indicated concentrations and final volume 50 ml to glass containers and closed tightly and the vessels were shaken at a temperature of (25°C) for a period of time (2, 4, 8) hours. The solutions filtrated and filtrates collected, and the concentrations of heavy elements evaluated by the volumetric methods [12].

The adsorption (removed elements) percentage (%Ɵ) was calculated from the following law:

$$\%\Theta = [(C_i - C_f) / C_i] \text{ X } 100$$

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Where C_i is an initial concentration of the elements (mg/L), C_f is the final concentration of the elements (mg/L) the adsorbed amount of the element calculated from the following formula [14]:

$$q_e = V_{sol}(C_o - C_e) / m$$

Where;

q_e = the amount of adsorbent per unit (mg / g.)

V_{sol} = total solution volume of adsorbent in unit (L.)

C_0 = the initial concentration of the solution in (mg / L.)

C_e = concentration at equilibrium in (mg / L.)

m = weight of the adsorbent in units (g)

3. Results and Discussion

The infrared spectrum (FTIR) showed on the surface of the adsorbent (activated carbonized cellulose) absorption beams for the free (OH) group and the (COO) group in (3782) cm^{-1} and (2347) cm^{-1} respectively in figure (2) which contains a pair of electrons, leads to the binding of heavy elements on the adsorbent surface through polar and basic or acidic groups [15]. The non-activated cellulose does not contain these beams, as shown in Figure (1).

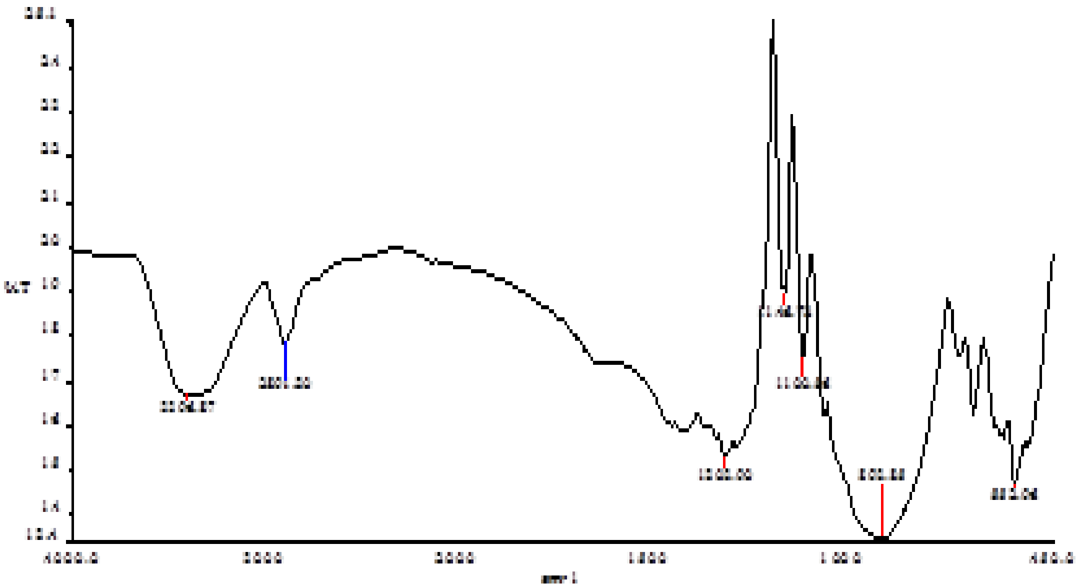

Fig. (1): FTIR Spectrum for Cellulose

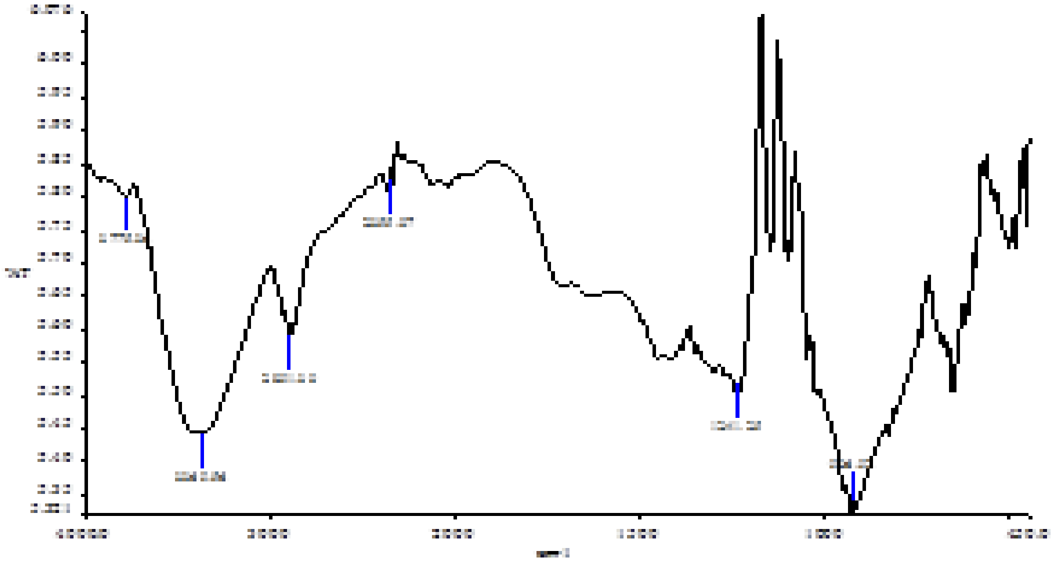

Fig. (2): FTIR Spectrum of the Activated Carbonized Cellulose

Table (1) and Figures (3) and (4) show the percentage of adsorption (% Ө) and the amount of elements that were removed from the aqueous solution in (2, 4, 8) hr. at concentration (100) ppm. The amount of adsorbed elements on the surface of adsorbents depends on the equilibrium among the adsorption competitions of the size of the ions, the stability of the bonds of element ions on adsorbents, the nature of the adsorbents and to the distribution of the active groups on the surface of adsorbents. Despite of the high size of lead, but mercury was more absorbable, followed by cadmium, and lead then copper depending on molar mass of the elements is more important at adsorption process [2].and to the strength of the bond with transition metals that receive pair of electrons from the surface of the adsorbent material.

Table (1) The percentage of adsorbed elements on the surface of activated carbonized cellulose (%Ө) at concentration (100 ppm) in different time

Hg	Cu	Pb	Cd	hr.
75.2	28	47.37	50	2
79.2	35	54.39	58.33	4
84	45	64.29	75	8

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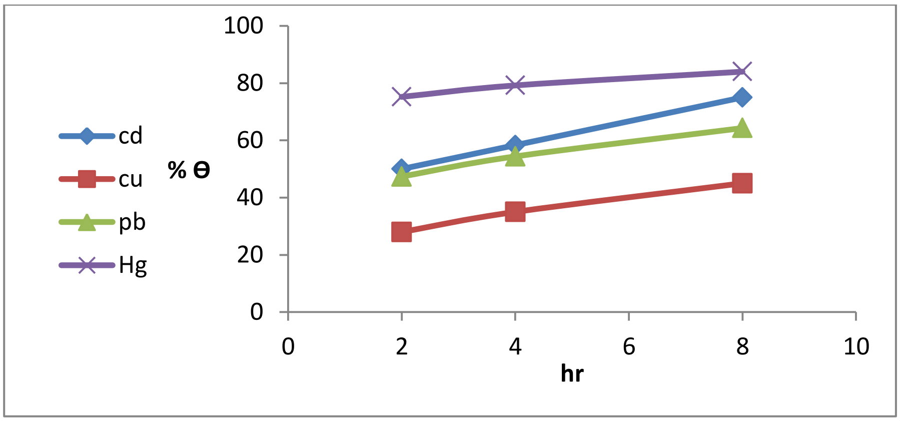

Fig. (3): The percentage of adsorbed elements on the surface of activated carbonized cellulose (%Ө) in different time at (100) ppm

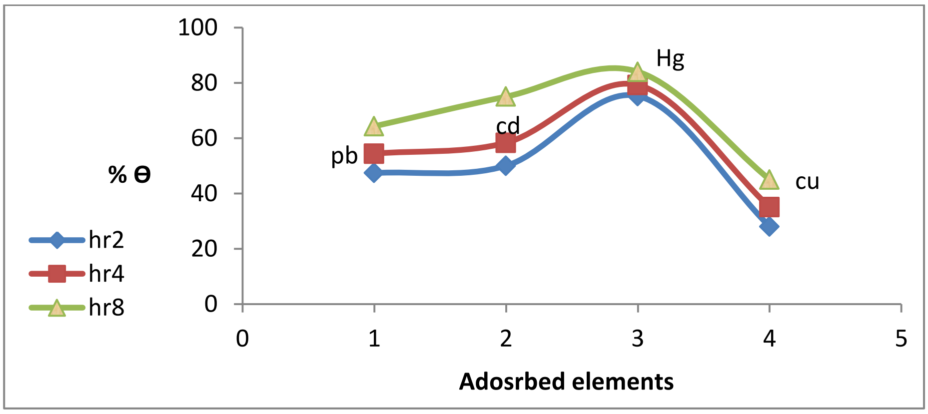

Fig. (4) The percentage of adsorbed elements (%Ө) on the surface of activated carbonized cellulose at (100) ppm

Adsorption isotherms are signals of the distribution of adsorbates on the adsorbents. Which is an important step to choose the appropriate form to describe the study data and the most applied models in this study were Freundlich, Langmuir and Temkin isotherms, and the studied elements (Cd, Pb, Cu) results were shown on the isotherm curves through the R^2 value as it's obvious at Figures (5-13) and Tables (2-4)

Table (2) Free energy and adsorption data for cadmium

∆G kj/mole	ln ce	ln qe	1/qe	1/Ce	Ce	qe	Co
10.438	2.83	-2.3	10	0.058	17	0.1	20
	3.21	-1.79	6	0.04	25	0.166	30
	3.4	-1.09	3.03	0.033	30	0.333	40
	3.68	-1.09	3.03	0.025	40	0.333	50

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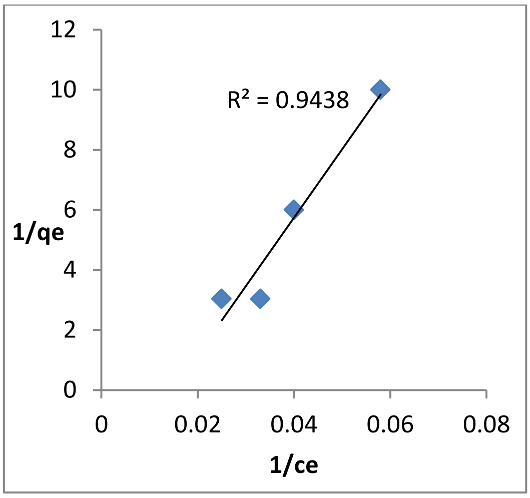

Fig. (5): Langmuir's absorption isotherm for (Cd) on the surface of activated carbonized cellulose

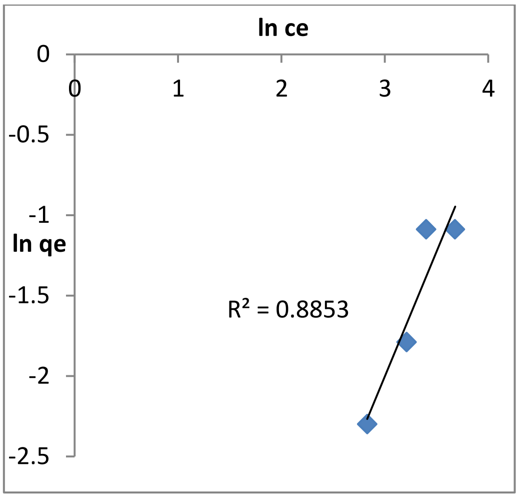

Fig. (6): Freundlich's absorption isotherm for (Cd) on the surface of activated carbonized cellulose

Table (3) Free energy and adsorption data for lead

ΔG k j/mole	lnce	ln qe	1/qe	1/Ce	Ce	qe	Co
8.940	2.98	-4.61	100	0.05	19.7	0.01	20
	3.33	-2.81	16.67	0.035	28	0.06	30
	3.58	-1.95	7	0.028	35.7	0.143	40
	3.67	-0.92	2.5	0.026	38	0.4	50

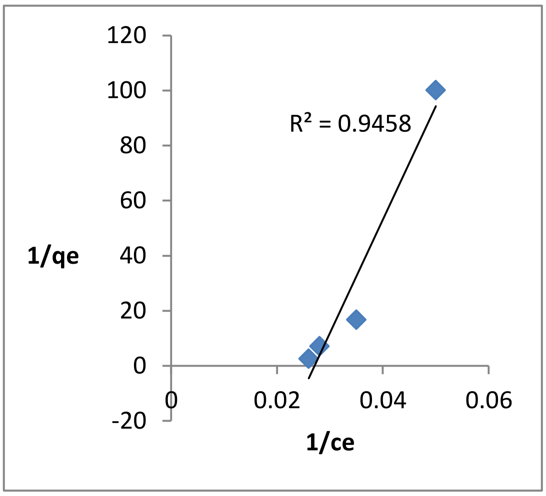

Fig. (7): Langmuir's absorption isotherm for (Pb) on the surface of activated carbonized cellulose

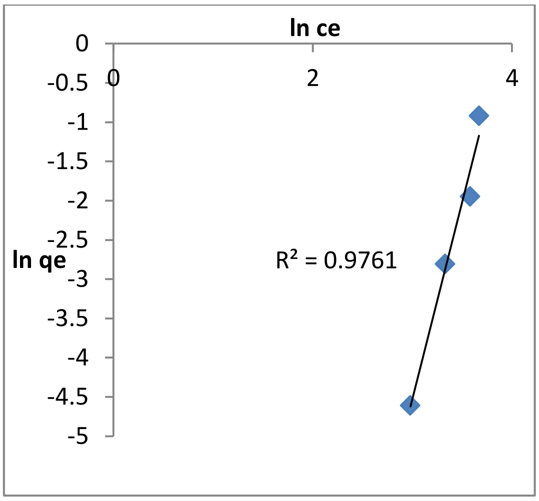

Fig. (8): Freundlich's absorption isotherm for (Pb) on the surface of activated carbonized cellulose

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Table (4) Free energy and adsorption data for copper

ΔG k j/mole	lnce	ln qe	1/qe	1/Ce	Ce	qe	Co
6.395	1.54	-0.67	1.95	0.21	4.66	0.511	20
	1.74	-0.21	1.23	0.175	5.71	0.81	30
	2.2	0.0295	0.97	0.109	9.1	1.03	40
	2.88	0.0676	0.93	0.056	17.8	1.07	50

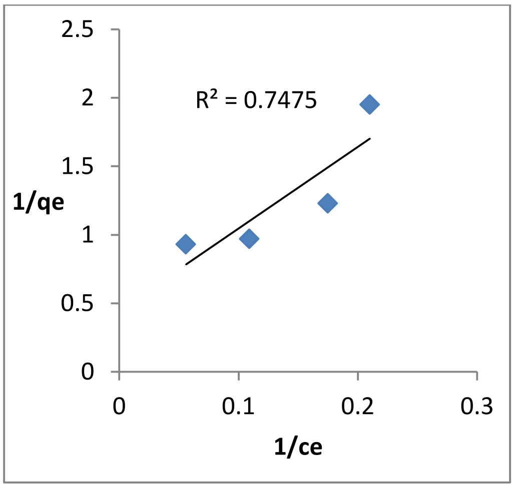

Fig. (9): Langmuir's absorption isotherm for (Cu) on the surface of activated carbonized cellulose

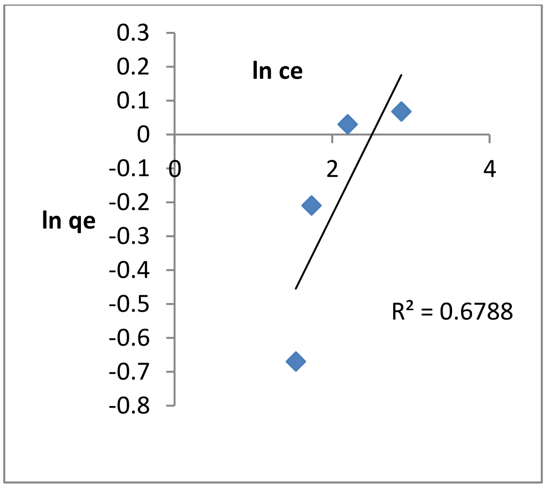

Fig. (10): Freundlich's absorption isotherm for (Cu) on the surface of activated carbonized cellulose

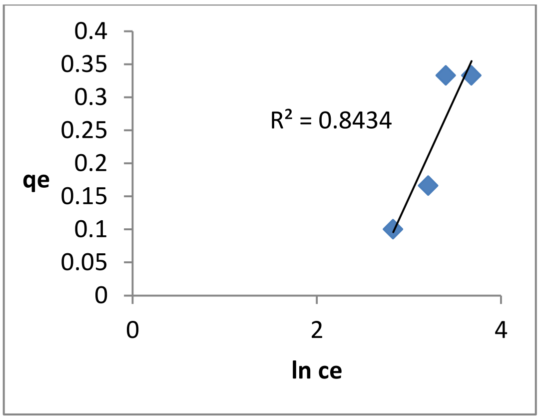

Fig. (11): Temkin's absorption isotherm for (Cd) on the surface of activated carbonized cellulose

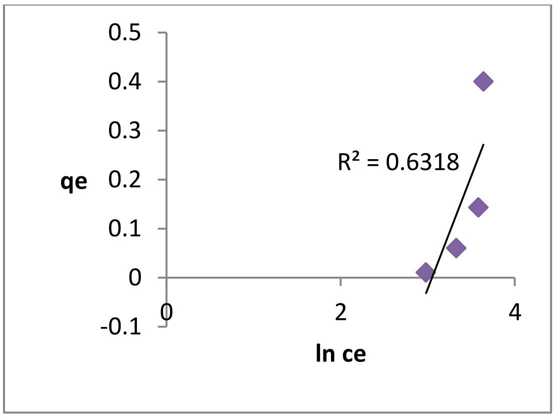

Fig. (12): Temkin's absorption isotherm for (Pb) on the surface of activated carbonized cellulose

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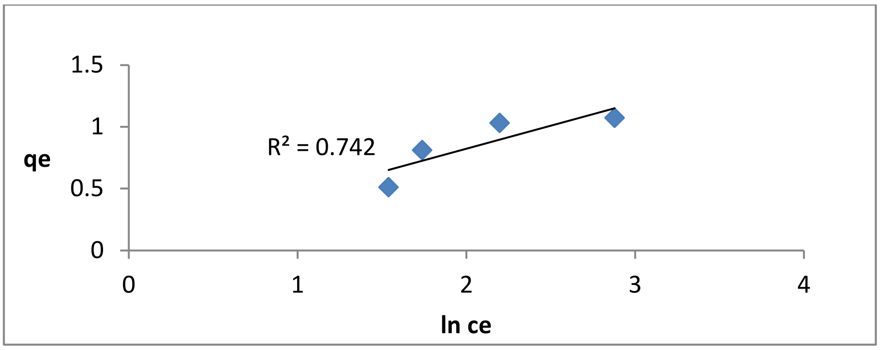

Fig. (13): Temkin's absorption isotherm for (Cu) on the surface of activated carbonized cellulose

Table (5) Freundlich ,Langmuir and Temkin constants

Elements	**kf**	**b (j/mole)**	**kT**	**bT**	**n**	**R_L**
Cd	1.9	8117.86	12.39	0.3052	0.64	0.409
Pb	2.97	5393.06	21.08	0.4594	0.2	0.397
Cu	0.16	6672.69	1.24	0.3713	2.1	0.187

As a Langmuir isotherm curve (plot $1/q_e$ vs $1/c_e$) the R^2 value for the elements (Cd, pb, Cu) were (0.9438, 0.9458, 0.7475) respectively. This indicates a single layer adsorption and an equilibrium distribution of transition element ions on the surface of the activated carbonized cellulose except the copper results were not compatible with the Langmuir equation [16]. The term equilibrium parameter (separation factor) ($RL_)$) is a basic form of the Langmuir isotherm can have computed from Langmuir constant (k_L) as:

$$R_L = 1/\ 1+ (1 + k_L\ C_o)$$

Where the R_L value is more than (1) the nature of adsorption is unfavorable and leaner if $R_L = 1$, irreversible if $R_L = 0$ and favorable when $0 < R_L < 1$. From table (5) the calculated R_L values for studied elements were (0.409, 0.397, and 0.187) for the elements (Cd, Pb, Cu) respectively, so the R_L values indicated that the adsorption data favorable as Langmuir isotherm model [17].

As a Freundlich isotherm curve (plot $\ln q_e$ vs. $\ln c_e$) the R^2 value for the elements (Cd, pb, Cu) were (0.8853, 0.9761, 0.6788) respectively and the Freundlich equation as:

$$\ln qe = \ln kf + 1/n \ln ce$$

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Where (K_f) is an indicator of adsorption capacity and (n) is strength of adsorption of elements on the surface of adsorbent if (n) = 1 then the adsorption process is independent on concentration ,at normal adsorption (favorable adsorption) (n) will be above (1) and if (n) is below of (1) the adsorption be cooperative adsorption [18] . (n) is the heterogeneity factor of the adsorbent surface and its high value indicates high surface heterogeneity the calculated ($K_{)}$ and (n) values for (Cd, Pb, Cu) were (1.9,2.97,0.16), (0.64,0.2,2.1) respectively. As Figures (6, 8, 10) and Table (5) the value of (n, K_f) and R^2 indicates that the adsorption of lead and cadmium on the surface of the activated carbonized cellulose have more adsorption capacity and is more consistent with the Freundlich equation than copper and that copper is more strongly adsorbed on the surface of the activated carbonized cellulose.

As Temkin isotherms curve (plot qe vs ln C_e) the R^2 values for the elements (Cd, Pb, and Cu) were (0.8434, 0.6318, and 0.742) respectively and the Temikn equation as:

$$q_e = b \ln K_T + b \ln Ce \quad \text{and} \quad b= R_T / b_T$$

table (5) show's Temkin constants (b, k_T , b_T) for (Cd,pb,Cu) the data as this isotherm show the heat of sorption and adsorption without depending on the value of concentration[18]. The results in tables (2-4) for free energy (ΔG) of adsorption on the surface of the activated carbonized cellulose ranged between (6.395 – 10.438) k j /mole, which indicates the physical adsorption process [19].

Table (6) Effect of concentration to adsorption percentage (% ϴ) on activated carbonized cellulose

Elements	20 ppm	30 ppm	40 ppm	50 ppm	100 ppm
Hg	100	100	100	100	84
Pb	80.3	72	64.3	62	64.29
Cd	83	75	70	60	75
Cu	95.34	94.29	90.9	82.2	45

The results in Table (6) indicate that the adsorption decreases with increasing concentration due to the saturation of the pores available on the surface of the activated carbonized cellulose and Mercury has been reduced at low concentrations of less than (100ppm) from the solution for adsorption all mercury material on the surface of activated carbonized cellulose.

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4. Conclusion

In this research some heavy elements (Hg, Cd, Cu, Pb) have been removed from aqueous solution at room temperature using activated carbonized cellulose and the results were fitted on three of adsorption isotherm models Freundlich, Langmuir and Temkin isotherms. As all mercury removed at a concentration below (100ppm), so it can have considered as a standard method for removing mercury from its aqueous solutions.

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