

ADSORPTION ISOTHERM OF LEAD ON CALCIUM CARBONATE

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ABSTRACT

This study investigate the effect of concentration of lead ions (Pb^{2+}) at 0,1, 2, 3, 4, 5, 10,20,30, 40,50 and 100 mg L⁻¹, concentrations of the quantity of the adsorbed Pb on surface of calcium carbonate at a temperature of 298° Kelvin with all other variables remained constant, was carried out and this experiment was conducted in a single batch and using lead nitrate solution . The results showed that quantity of the adsorbed lead increased from 2.6 to 1924 mg kg⁻¹ Calcium carbonate, and when single and two surface Langmuir, Freundlich, Temkin, Dubinin and Polani equations were applied, they were able to describe lead adsorption on the surface of calcium carbonate at the used concentrations. The two surface Langmuir equation was most efficient in used mathematical description of lead adsorption, and the bonding energy (K) with the first and second surfaces were 4.02 and 1613.42 L mg⁻¹ respectively. The adsorption capacity (X_m) values with the first and second surfaces were 0.25 and 0.89 mg kg⁻¹ respectively , and this clearly indicated to high capacity of the second surface (carbonate surface) to adsorb lead.

Key words: two surface, bonding energy, adsorption capacity.

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الإمتزاز المتمائل حراريا للرصاص على كربونات الكالسيوم

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المستخلص

تضمنت هذه الدراسة اختبار تأثير أيون الرصاص (Pb^{2+}) بتركيزات (0, 1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 100 ملغم لتر⁻¹) على كمية المادة الممتزة على سطح كربونات الكالسيوم عند درجة حرارة 298° كلفن مع بقاء جميع المتغيرات الأخرى ثابتة ، وقد أجريت هذه الدراسة بطريقة الدفعة الواحدة وباستعمال محلول نترات الرصاص. أظهرت النتائج ان كمية الرصاص الممتزة ازدادت من 2.6 - 1924 ملغم كغم⁻¹ كربونات كالسيوم ، وبينت نتائج الدراسة عند استخدام معادلات لانكماير ذات السطح الواحد والسطحين وفروندلخ ودوبين وتمكن وبولاني في وصف إمتزاز الرصاص على سطح كربونات الكالسيوم عند التراكيز المستخدمة، ان معادلة لانكماير ذات السطحين تعد الاكفأ في الوصف الرياضي لإمتزاز الرصاص، ويطاقة ربط (K) 4.02 و 1613.42 لتر ملغم⁻¹ مع السطحين الاول والثاني على التوالي، اما سعة الامتزاز (X_m) فقد بلغت 0.25 و 0.89 ملغم كغم⁻¹ مع السطحين الاول والثاني على التوالي. مما يشير بوضوح الى القدرة العالية للسطح الثاني (سطح الكربونات) على إمتزاز الرصاص.

الكلمات المفتاحية: السطحين، طاقة الربط، سعة الامتزاز.

INTRODUCTION

Calcium carbonate is a major component of rock and biodegradable mineral components and can have a profound effect on the dynamics of mineral and rare metals. Calcium carbonate is one of the cheap sources in the landfill of heavy metals in the world (8). Calcification is an active biogenic process in the central and southern regions of Iraq. It recycles calcium carbonate in the soil body and carbon complexes have different forms and depths, depending on the nature of the prevailing environmental conditions. The nature of the carbon clusters is either primary Origin (inherited from origin) or secondary origin, accumulated in the soil body by precipitation of irrigation water, rain, and carbonate-rich groundwater (14). It was mentioned by (15) that chemisorption may be important in reducing the movement of heavy metals, including lead in calcareous soils. It was concluded by (1) that reduction of movement of the heavy element in the soils of dry areas, where carbonate minerals are available, is by adsorption by the surfaces of those minerals or by regulating the pH number in those soils. The importance of carbonate minerals in reducing the harmful impact of lead ions and environmental reform had been confirmed by (1). Calcareous soils are sink highly efficient in the retention of lead compared to non-calcareous soils and carbonate minerals are important material for the disposal of heavy metal waste.

MATERIALS AND METHODS

The adsorption of lead ion adsorption was measured using a stable equilibrium method (Batch equilibrium). The adsorption process involved thermodynamic equilibrium at a constant temperature (298° kelvin) of pure calcium carbonate (material adsorbed) as compared to different levels of lead in the form of nitrate solution. Two gram of air dried samples of pure carbonate were taken and then they were put in 120 ml capacity plastic tubes following concentrations 0,1, 2, 3, 4, 5, 10,20,30, 40,50, 100 mg L⁻¹ of lead nitrate (1 calcium carbonate : 20 solution) were added to the tubes, then they were quenched for half an hour and left for 24 hours for equilibrium. The stabilizer was then separated by centrifugation for the purpose of estimating lead

concentration using the GBC 933plus Atomic Absorption device 405.8 nm wave length.

Calculation of the amount of ionic adsorbent type: The amount of adsorption lead ion was calculated by estimating the difference between lead concentrations before and after equilibrium according to the following equation:

$$M^{2+} - ad. = \frac{V(C_{in} - C_{fin})}{W} \dots (1)$$

Whereas : M^{2+} = concentration of the adsorbed in units (mg kg⁻¹), C_{in} = ion concentration of lead before equilibrium (mg L⁻¹), C_{fin} = concentration of lead ion after equilibrium (mg L⁻¹), V = volume of added solution (ml), and w = weight of calcium carbonate (g).

Mathematical Description of Adsorption:

The results of adsorption were described above (18). Agencies:

Langmuir equation (I) (11)

$$C/X=1/K X_m + C/X_m \dots\dots (2)$$

Whereas : X = quantity of adsorbed lead (mg kg⁻¹), C = concentration of lead in equilibrium solution (mg L⁻¹), K = constant represents the bond energy (L mg⁻¹), X_m = constant expresses the maximum adsorption (mg kg⁻¹).

Langmuir equation (II) (11)

Whereas : X = amount of adsorbed lead (mg kg⁻¹), C = concentration of lead in equilibrium solution (mg L⁻¹), K_1 and K_2 = constant represents the bond energy (L mg⁻¹), b_1 and b_2 = constant.

Freundlich equation (5)

$$X=K_1 b_1 C / (1+K_1 C) + K_2 b_2 C / (1+K_2 C) \dots (3)$$

Log X=b Log C+Log K ... (4)

Whereas : X = the amount of adsorbed lead (mg kg⁻¹) and, C = concentration of lead in equilibrium solution (mg L⁻¹), K and b = constants.

Temkin equation (22)

$$X=\alpha+\beta Lnc \dots (5)$$

$$C_e/q=1/Kb+1/bC_e \dots\dots(6)$$

Whereas : X = the amount of adsorbed lead (mg kg⁻¹), C = concentration of lead in equilibrium solution (mg L⁻¹) and β, α = constants.

Dubin-Radushkevich equation (3)

$$\text{Log } q=\text{log } K_f +n \text{ Log } C_e \dots (7)$$

Whereas : C_e = concentration of ionic type (lead) in equilibrium solution, q = quantity of ionic adsorbent type (lead), b = maximum adsorption, K = binding power factor (mg L⁻¹)

, K_f = distribution coefficient, and n = constant. Analysis of correlation coefficient by Excel (2010). Because the adsorption equation (Langmuir and Freundlich) don't give an idea of the adsorption mechanism, the use of the Dubinin equation is used to describe adsorption on one type of surface. This type of adsorption is analogous (D-R) and more general than Langmuir because it does not require surface homogeneous and fixed surface. Adsorption was obtained from the following equation :

$$\ln q = \ln q_m - K \epsilon^2 \dots\dots (8)$$

$$\epsilon = [RT \ln (1 + 1/C_e)] \dots (9)$$

ϵ = polani-potential, q = amount of lead adsorbed on the surface of calcium carbonate in units (mol g⁻¹), K = the adsorption power constant expressed in (mole² Kg⁻²), and q_m = adsorption capacity. The rate of adsorption capacity (ϵ) can be calculated from the constant value (K) according to the following equation : The significance of calculation of ϵ is to detect the type of adsorption process, with a value of 8-16 KJ m⁻¹, the adsorption process is interpreted as an ion exchange (9).

$$\epsilon = (-2K)^{-0.5} \dots\dots (10)$$

$$\ln q = \ln q_m - K \epsilon^2 \dots\dots\dots(11)$$

$$\epsilon = [RT \ln (1 + 1/C_e)] \dots\dots\dots(12)$$

The adsorption criteria (adsorption capacity and bonding energy) were determined using the linear formula of the equations mentioned above.

RESULTS AND DISCUSSION

The results of table 1 show that the measured lead ion shows a constant tendency to adsorption on the surfaces of calcium carbonate . The amount of absorbent material increases with the increase of the primary concentration of lead. The extracted quantity (removed from the solution) increased from 2.6 to 1924 mg kg⁻¹ calcium carbonate. The amount of adsorption that expresses the ability of carbonate metal to chemically remediation increased by increasing the concentration, as it can be seen from the shape of the carbonate's ability to hold the heavy metals. The increase in the ionic concentration of the added solution may be due to the chemical treatment of heavy metals removal several mechanisms includes coagulation, co-precipitation, entrapment (4,16) . Sweep co-precipitation by thrombotic one of the main mechanisms to be used in reclamation process (13,19,17).

Table 1. Change in quantity change Absorption material and percentage of adsorption with primary concentration at (298°) Kelvin for lead ion solutions.

Primary concentration added (mg L ⁻¹)	Absorption quantity (mg kg ⁻¹)	Percentage of adsorption %
0	-65.40	-
1	-50.80	- 254.00
2	-21.00	-52.50
3	2.60	4.33
4	7.40	9.25
5	22.80	22.80
10	120.80	60.40
20	320.20	80.05
30	520.20	86.70
40	720.20	90.03
50	914.40	91.44
100	1924.00	96.20

The use of coagulants, such as iron, aluminum and calcium salts, converts the soluble water ions to form insoluble deposits or to form sediment precipitates, including the ammeshment of floc particles (24, 6 ,20, 10) , or the mixing of heavy metal ions with the

crystalline layers of other precipitated solid phases, as well as coagulation processes (2,23). It was by(12) noted that the use of calcium carbonate or lime as a clot was more economical than iron and aluminum salts. The main mechanism for calcium carbonate and

lime is the formation of insoluble deposits separated from water or the formation of a sweep precipitation for heavy metals by cadence(enmeshment of calcium minutes Ca-

floc particles) (12). If the mass of heavy ion is expressed, Figure 1 shows the high preference for lead. The obtained results agreed with findings of (20,19, 12) .

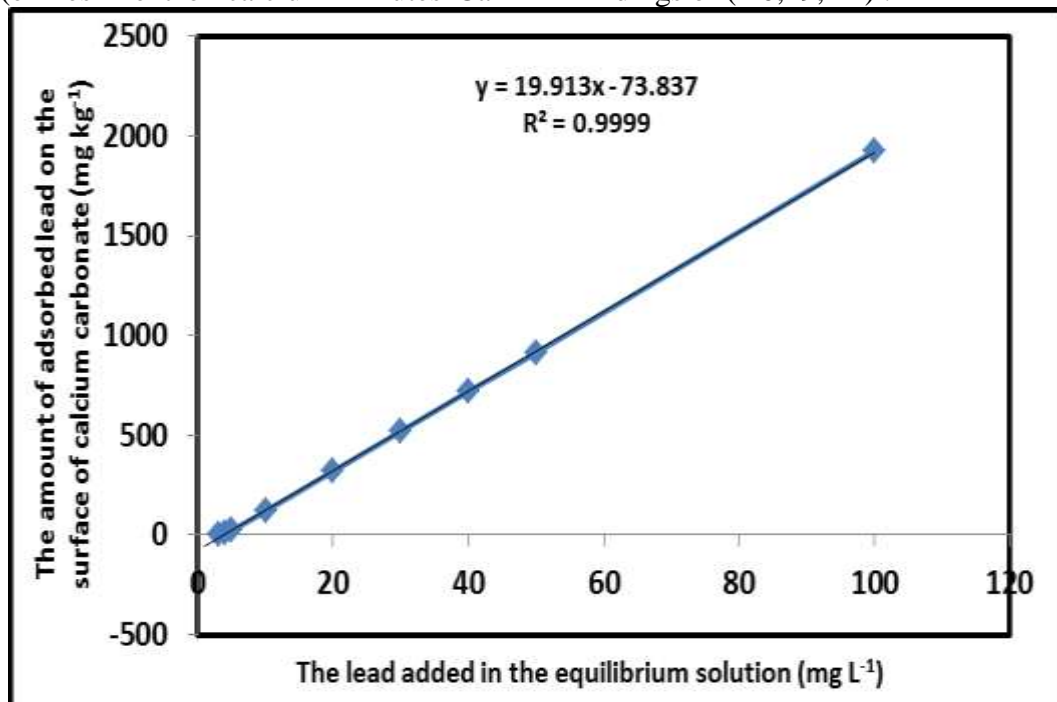


Fig. 1. Correlation between adsorbed on the surface of carbonate and the ionic type of lead in the added solution.

Mathematical description of adsorption equations : Table 2 shows the values of the determination factor (R^2) and the standard error (SE) for adsorption equations obtained by applying the single-surface and two-sided Langmuir, Freundlich, Temkin, Dubinin and Polani were significant for all equations, which give a clear indication of the possibility of using any of these six equations, but the

equation of the two-sided Langmuir is the most efficient in the description of mathematical for adsorption of lead. Moreover, this equation showed a very large match for the values of actual adsorption and calculated values of this equation and to have less SE which earns them advantage in the mathematical description of the rest of the equations.

Table 2. Standard error (SE) and determination factor (R^2) vales for lead adsorption

Equations	SE	R^2
Langmuir Single-faced	0.033	0.94
Langmuir biplane	First surface	0.015
	Second surface	0.000
Freundlich	0.69	0.59
Dubinin	0.69	0.59
Temkin	631.37	0.11
Polani	1.65	0.56

The superiority of the two-sided Langmuir equation in the mathematical description of the process of adsorption of lead ion on calcium

carbonate may lead to conclude clearly that there were two types of adsorbed surfaces in this material, as shown in fig 2 .

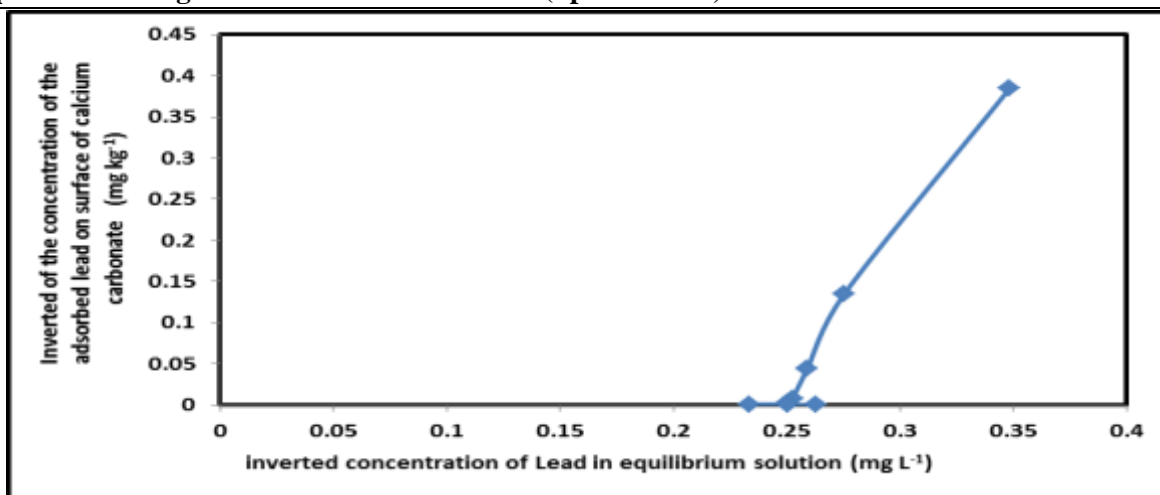


Fig.2. Relationship between the inverted concentration of lead in the equilibrium solution as a function of inverted concentration of adsorbed lead on surface of calcium carbonate

Maximum adsorption capacity and bonding energy

Table 3 shows the adsorption parameters of the two-sided Langmuir equation, which show that the bonding energy value of lead reaction with the first surface was 4.02 L mg^{-1} while the lead bonding value at the second surface $1613.42 \text{ L mg}^{-1}$ Which indicates that the value of lead bonding energy at the surface of the second reaction and its superiority over the bonding energy of the first surface increased by 401 times. The adsorption capacity at the first surface was less than the adsorption capacity at the second surface. The first adsorption capacity was 0.25 mg Kg^{-1} while the adsorption capacity at the second surface 0.89 mg Kg^{-1} , which indicates the increase in lead adsorption capacity at the surface of the second reaction and exceeds the adsorption capacity of the first surface by 4 times. Which clearly indicates the high capacity of the second surface (carbonate surface) on lead adsorption. This can be explained to one or more of the following mechanisms:

1. Deposition of ionic type in the form of carbonate
2. Replacement of the added ion

type replacing calcium in the carbonate compound 3. Ion adsorption on carbonate surface. This agrees with findings of (12,7,1). The ability of calcium carbonate in adsorption of ionic positive matter to heavy metals can be explained by the presence of electrical charge on carbon metal surfaces. In this regard, two theories explain the source of charges on carbonate surfaces. The first theory: proved by (21) explained that the source of the shipments was the result of the fracture of the edges of the metal calcite and in this theory it was assumed that the positive and relatively small calcium ions were carried out inside the crystal and the large charge negative carbonate ions rush outwards and result in the emergence of a negative charge on the surface of crystalline or minute calcium carbonate . The second theory refers to the amphoteric behavior of carbonate minerals. The type of surface charge depends on the degree of soil reaction and the zero point of the charge falls within the degree of reaction 8 - 9.5 . Thus the carbonate charge was positive when the reaction was less than 8 with a negative charge when the reaction was more than 9.5.

Table 3. Shows the values of the two-walled Langmuir equation for lead adsorption

X_{m2} mg kg^{-1}	K_2 L mg^{-1}	X_{m1} mg kg^{-1}	K_1 L mg^{-1}
0.89	1613.43	0.25	4.02

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