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# Adsorption Study of Lead Ions Pb2+ by Using Ion – Exchange Resin and Some Natural Clays

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## Abstract

The adsorption capacity of three types of Iraqi clays (kaoline, porceline and bentonite) and three types of ion – exchange resin and imported zeolite are investigated. The adsorption data are presented using adsorption isotherm curves and are best fitted using the Langmuir adsorption equation that yields the maximum adsorption capacity of adsorbents (ion – exchange or clays). Iraqi clays show high adsorption capacity reached to 99.7% and sometimes similar to the adsorption capacity of ion – exchange. The effect of initial concentration of lead ions solutions on the amount of adsorption are studied also.

Langmuir constants equations have been calculated for the seven different adsorbate at 25°C. The percentage of lead removal at equilibrium increases with increasing initial lead ions concentrations. The results obtained could be useful for the application of Iraqi clays for the $Pb^{2+}$ removal from industrial waste water.

## Introduction

Lead is one of the most common toxic metals found at hazardous waste and superfund sites [1]. Sorption technology based on ion–exchange processes and physical and chemical sorption has found increasing application in various fields during the past years [2]. The use of sorption processes for the removal of heavy metals from waste water is especially promising. Inorganic sorbents are interesting because they are in many cases cheaper than polymeric chelate ion exchangers. However, sorption of heavy metals on inorganic sorbents depends strongly on the pH value and ion – exchange properties of the clay minerals [3-9]. The adsorption of $Pb^{2}$ by calcareous soil is poorly understood in contrast with adsorption by noncalcareous soils [10]. Most Iraqi studies related to Geological studies involved soil elements analyses and any mechanism adsorption study involving kinetics study about the objective of the present study is not found in featrecher .

The adsorption reactions affects on mobility and availability of trace elements, including Pb. Adsorption isotherms most frequently used are Freundlich and Langmuir ( i.e., equation (1) and (2), respectively )

$$Q = K_F.C_e^{1/n} \quad \text{..........................................(1)}$$

$$Q = (K_L.b)/(1+K_L.C_e) \quad \text{..........................................(2)}$$

Where; $K_F$ and n are Freundlich coefficients; $C_e$ is concentration of $Pb^{2+}$ in equilibrium solution, mg $L^{-1}$; $K_L$ is Langmuir coefficient related to binding energy of Pb to soil solids; and b is Langmuir adsorption maximum, i.e., the maximum amount of Pb adsorbed on soil solids as monolayer, mg/g; $Q_e$ is the amount of Pb adsorbed (mg/g) which calculated using the equation below:-

$$Q = \frac{(Co - Ce).V}{m} \quad \text{..........................................(3)}$$

Where; $C_o$ is the concentration of contaminant in the solution before mixing with adsorbent (mg/L); $C_e$ is the equilibrium concentration of Pb left in the solution after the experiment (mg/L); V is volume of test solution (ml); and m is the mass of adsorbent.

The Langmuir Eq.2 can be rearranged into a linear form as shown in Eq.4 by plotting $C_e/Q_e$ as a function of $C_e$. Parameters $K_L$ and b can determined from the linear graph.

$$\frac{Ce}{Q_e} = \frac{1}{b} + K_L.Ce \quad \text{..........................................(4)}$$

The Langmuir model assumes that:

(a) Adsorption energy is constant and independent of surface coverage;
(b) Adsorption occurs at localized sites with no interaction between various ions in the solution;
(c) Maximum adsorption occurs when the clay surface is covered by monolayer of cations.

## Materials and Methods

The composition of Iraqi clays and Zeolite used in this study is given in Table 1, and the composition of the three standards ionic – exchanger is given in Table 2. (0.5 g ) of clay sample or ionic – exchanger was placed with a solution was prepared by a suitable dilution of the standard lead acetate solution (concentration 1000 mg $L^{-1}$) with distilled water and all experiments were carried out in round bottom 250 ml flasks at a constant temperature of 25°C using a rotary shaker (100 rpm) . A solution volume (100 ml) with deferent initial lead concentration and pH values was mixed with a definite amount of adsorbent.

After that the samples were shaken for (5, 10, 15, 20 and 30) min., the suspension was then filtered and the lead concentration in the filtrate was determined using atomic absorption spectroscopy (AAS) type GBC 993 plus (England) and the lead concentration (ppm) was determined.

The particle size of Iraqi clays were in the range of (50–5) μm while for Zeolite was 300 μm and for ionic-exchange range of (40 – 50) μm. The difference between the Pb concentration of initial solution and the filtered supernatant was taken as the Pb retained by the adsorbent surface.

Freundlich and Langmuir equation (1 and 4) were used to interpret the equilibrium adsorption data and respective adsorption coefficients were calculated. Stepwise regression procedure was used to study the relationship between the coefficients and the adsorbent properties.

## Results and Discussions

The adsorption data show a highly significant fit to the Langmuir adsorption isotherm (Table 3). Adsorption isotherms were plotted between the amounts of lead ions adsorbed per gram of the clay sample (mg/g) as a function of the equilibrium free ion concentration in the solution (mg/L), Figures (1 – 7) show the amount of Pb adsorption by various clays, and Figures (8-14) show a linear relations of eq.4 .The sequence of the variation of the maximum adsorption capacity (b) for the seven adsorbet at 10 mg/l lead ions was as:

$Z_2$ < Bentonite < Zeolite < Porceline < $Z_1$ < Kaoline < $Z_3$

At 20 mg/l lead ions the sequence was as:

$Z_2$ < Bentonite < $Z_3$ < $Z_1$ < Zeolite < Kaoline < Porceline

At 30 mg/l lead ions the sequence was as:

$Z_2$ < Bentonite < $Z_3$ < $Z_1$ < Kaoline < Zeolite < Porceline

At 40 mg/l lead ions the sequence was as:

$Z_2$ < Bentonite < $Z_1$ < $Z_3$ < Zeolite < Kaoline < Porceline

At 50 mg/l lead ions the sequence was as:

$Z_2$ < $Z_1$ < Zeolite < Bentonit < $Z_3$ < Kaoline < Porceline

In general porceline shows a highest maximum adsorption capacity (b), bentonite and kaoline show good maximum adsorption capacity reach to the ionic exchanger maximum capacity values as shown in Table 3. The amount of adsorption of lead ions on the seven adsorbates surfaces increase with initial concentration of lead ions solution increase, because of the high adsorption capacity which calculated from Langmuir equation constant eq. (2). The Langmuir constant ($K_L$) which related to binding energy [11] of lead ions to clay surface were calculated also and the sequence of variation of ($K_L$) for various clay at 10 mg/L lead concentration was as:

$Z_2$ < Bentonite < Zeolite < Porceline < $Z_1$ < Kaoline < $Z_3$

At 20 mg/l concentration the sequence was as:

$Z_2$ < Bentonite < $Z_3$ < $Z_1$ ≡ Zeolite < Kaoline < Porceline

At 30 mg/l concentration the sequence was as:

$Z_2$ < Bentonite < $Z_1$ < $Z_3$ < Zeolite < Kaoline < Porceline

At 40 mg/l concentration the sequence was as:

$Z_2$ < $Z_1$ < Bentonite < $Z_3$ < Zeolite < Kaoline < Porceline

And at 50 mg/l concentration the sequence was as:

$Z_2$ < $Z_1$ < Zeolite < Bentonite < $Z_3$ < Knoline < Porceline

This results indicate to the existence of an active sites on Iraqi adsorbate (porceline, kaoline and bentonite), this active sites related with lead ions like ionic exchanger active sites ($Z_3$, Z1) and zeolite.

The $Z_2$ ionic exchanger show lowest efficiency reached to 53% only and show lowest adsorption capacity and $K_L$ values which related to the variation of functional group as show in Table 2. Iraqi bentonite adsorbate removed 99.7% of lead ions which reach to the efficiency of $Z_3$ and $Z_1$ while Porceline and Kaoline removed (97 - 98) % of lead ions from the solution, table 4 shows the amount of adsorption and efficiency percentage of the seven adsorbet surfaces.

These preliminary results suggest that Iraqi clays seem to be important to the fixation of heavy metals, (i) the clays surface chemistry which determines properties like to the cation exchange capacity. (ii) The adsorption capacity of clays increase with initial concentration lead ions solution increased. Therefore, the knowledge of heavy metals retention by Iraqi clays are required.

## Conclusion

The removal of lead ions from synthetic solution was demonstrated successfully on a laboratory scale with a selective ion – exchange process. The following conclusion can be drawn from this study:

The data obtained from this study applied to Langmuir and Freundlich isotherms.

The Langmuir isotherm gives an adequate correlation coefficient value ($K_L$, b). $K_L$: indicate to the binding energy of lead ions to adsorbet surface; b: indicate to the maximum amount of lead ions adsorbed on clay surface as monolayer.

Iraqi clays show high ($K_L$, b) values and adsorption efficiency reach to 99.7% (by using bentonite). The amount of adsorption of lead ions on the seven adsorbate surfaces increase with initial concentration of lead ions increase. The mechanism of remove lead ions is ion – exchange with adsorbate active sites and physical adsorption and in the case of using bentonite. absorption processes was associated with adsorption processes, which resulted from the comparison between the maximum adsorption capacity of bentonite and the highest adsorption efficiencies 99.7% of lead ions adsorption.

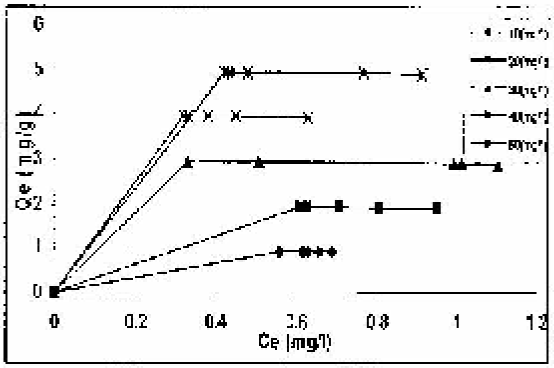

Fig 1: adsorption isotherms for (Z1).

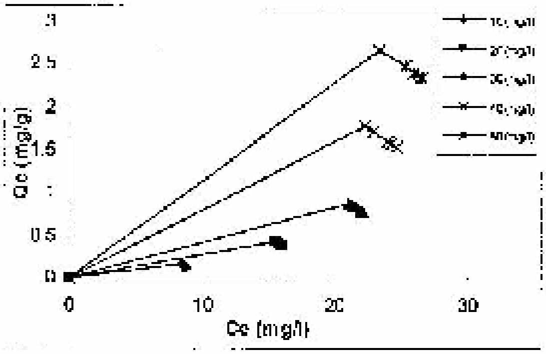

Fig 2: adsorption isotherms for (Z2).

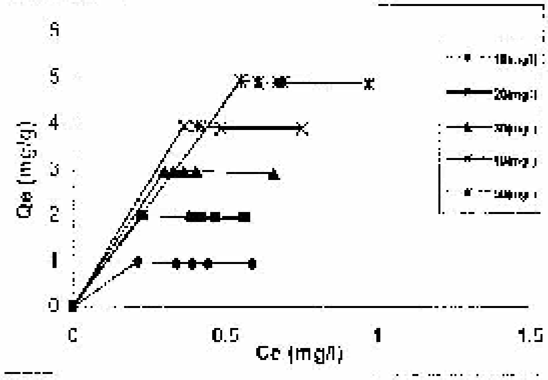

Fig 3: adsorption isotherms for (Z3).

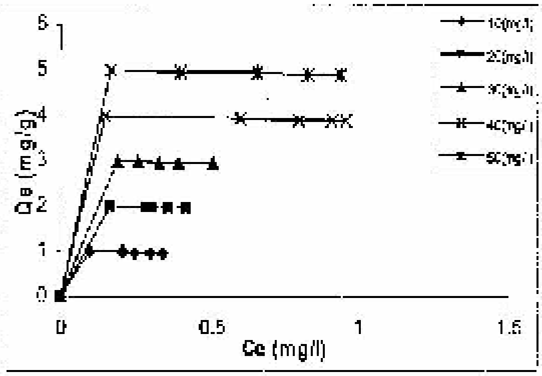

Fig 4: adsorption isotherms for Kaoline.

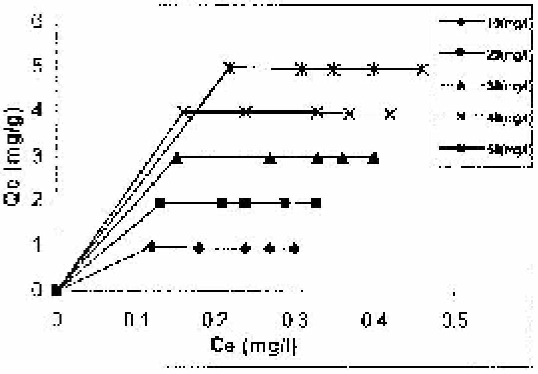

Fig 5: adsorption isotherms for Porceline.

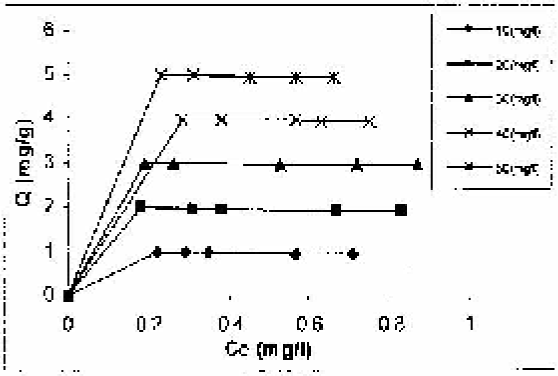

Fig 6: adsorption isotherms for Zeolite.

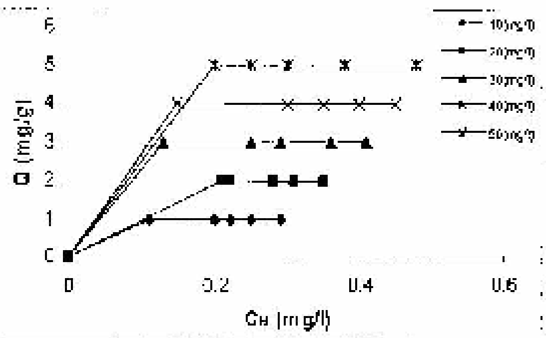

Fig 7: adsorption isotherms for Bentonite.

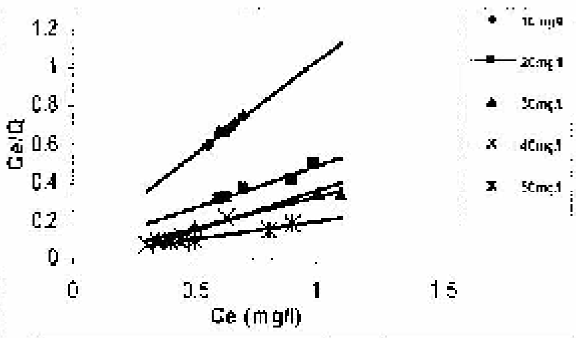

Fig 8: Linearised Langmuir isotherm for Z1

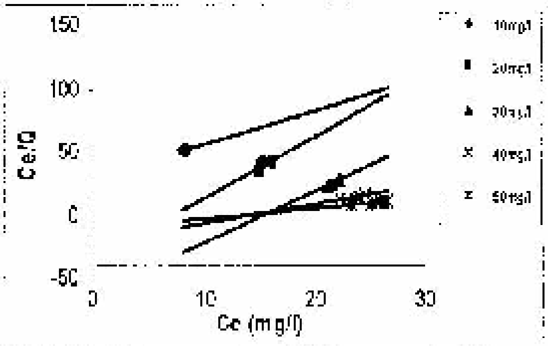

Fig 9: Linearised Langmuir isotherm for Z2

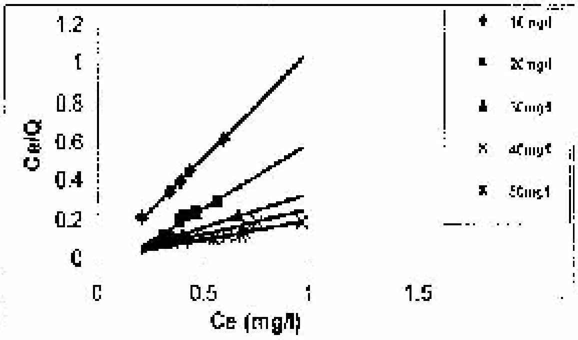

Fig 10: Linearised Langmuir isotherm for Z3

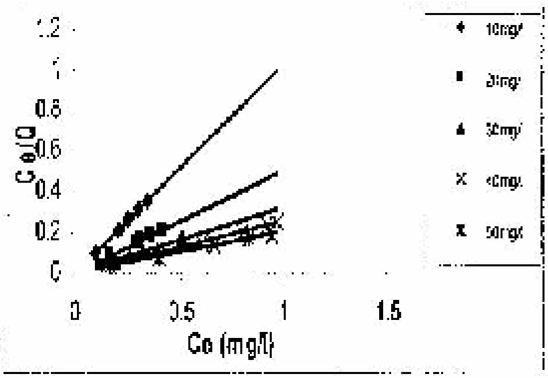

Fig 11: Linearised Langmuir isotherm for Kaoline

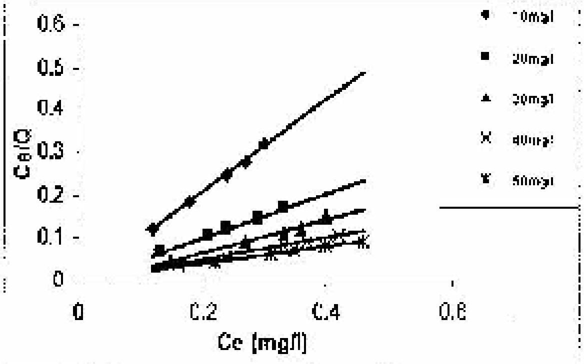

Fig 12: Linearised Langmuir isotherm for Porceline

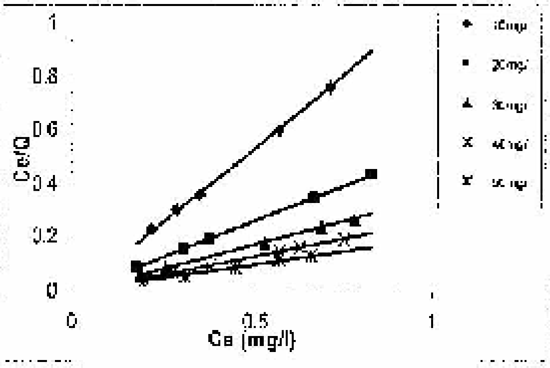

Fig 13: Linearised Langmuir isotherm for Zeolite

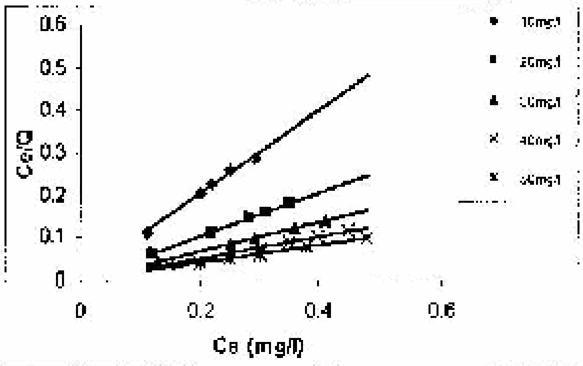

Fig 14: Linearised Langmuir isotherm for Bentonite

Table (1): chemical analyses of Iraqi clays (supplied geological scanning company)

| Bentonite<br>pH=7.63 | | Kaoline<br>pH=7.66 | | Porceline<br>pH=7.12 | | Zeolite<br>pH=3.23 | |
|---|---|---|---|---|---|---|---|
| Constituent | $W_t$% | Constituent | $W_t$% | Constituent | $W_t$% | Constituent | $W_t$% |
| $SiO_2$ | 56.77 | $SiO_2$ | 48.57 | $SiO_2$ | 62.6 | $SiO_2$ | 32.52 |
| $Al_2O_3$ | 15.67 | $Al_2O_3$ | 35.05 | $Al_2O_3$ | 3.4 | $Al_2O_3$ | 27.64 |
| CaO | 4.48 | CaO | 0.6 | CaO | 8.1 | CaO | 11.38 |
| MgO | 3.42 | MgO | 0.77 | MgO | 6.3 | $Na_2O$ | 4.20 |
| $K_2O$ | 0.60 | $Na_2O$ | 0.08 | $Na_2O$ | 0.15 | L.O.I. | 24.25 |
| $Na_2O$ | 1.11 | $Fe_2O_3$ | 1.34 | $Fe_2O_3$ | 1.2 | _ | |
| $Fe_2O_3$ | 5.12 | $TiO_2$ | 1.19 | $P_2O_5$ | 1.09 | | _ |
| L.O.I. | 12.49 | L.O.I. | 12 | L.O.I. | 14.1 | _ | _ |

Table (2): Properties of ($Z_1$, $Z_2$ and $Z_3$)

| $Z_1$ | | | $Z_2$ | | | $Z_3$ | | |
|---|---|---|---|---|---|---|---|---|
| Functional group | Water regain | Mesh | Functional group | Water regain | Mesh | Functional group | Water regain | Mesh |
| $R\text{-}SO_3\text{-}H^+$ | 0.3 - 0.45 | 52<br>100 | $R\text{-}CO_2\text{-}H^+$ | 0.8 – 1.0 | 14 52 | $R\text{-}SO_3\text{-}H^+$ | 0.46- 0.7 | 52 – 100 |

Table (3): Langmuir constant for adsorption $Pb^{+2}$ on the seven surfaces.

| Types of clays and resins | b | | | | | K | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 10 | 20 | 30 | 40 | 50 | 10 | 20 | 30 | 40 | 50 |
| $Z_1$ | 13.1869 | 7.8719 | 6.0714 | 6.6448 | 2.2453 | 13.755 | 18.18 | 18.867 | 15.576 | 11.11 |
| $Z_2$ | 0.1343 | 0.079 | 0.0648 | 0.0709 | 0.0814 | 0.003 | 0.0068 | 0.0157 | 0.0469 | 0.1029 |
| $Z_3$ | 68.2829 | 8.438 | 13.78 | 14.2819 | 8.5944 | 62.893 | 12.5156 | 40 | 55.55 | 14.66 |
| Kaoline | 25.4828 | 25.745 | 16.4 | 19.7692 | 20.46 | 24.3902 | 50 | 54 | 76.923 | 100 |
| Porceline | 9.9376 | 42.6079 | 38.06 | 42.1142 | 33.815 | 9.1743 | 83.3 | 100 | 166.66 | 166.66 |
| Zeolite | 5.4236 | 9.7536 | 17.21 | 17.0982 | 3.7882 | 4.9261 | 18.5185 | 50 | 66.66 | 19.607 |
| Bentonite | 1.8991 | 3.9376 | 4.8457 | 5.074 | 4.056 | 1.923 | 7.6923 | 14.285 | 20 | 20 |

Table (4) data of Ce, % and $Q_e$ for adsorption lead ions on the seven surfaces.

| Types of resins and clays | $C_e$ (mg/l) | | | | | | | % of adsorption | | | | | | | Q (mg/g) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 10 | 20 | 30 | 40 | 50 | 200 | 500 | 10 | 20 | 30 | 40 | 50 | 200 | 500 | 10 | 20 | 30 | 40 | 50 | 200 | 500 |
| $Z_1$ | 0.56 | 0.61 | 0.33 | 0.32 | 0.42 | 1.5 | 1.50 | 94.40 | 96.95 | 98.9 | 99.2 | 99.16 | 99.25 | 99.7 | 0.944 | 1.939 | 2.967 | 3.968 | 4.958 | 19.85 | 49.85 |
| $Z_2$ | 8.38 | 15.6 | 21.02 | 22.2 | 32.2 | | | 16.20 | 21.92 | 29.93 | 44.5 | 53.6 | – | – | 0.162 | 0.439 | 0.890 | 1.780 | 2.68 | | |
| $Z_3$ | 0.21 | 0.23 | 0.30 | 0.36 | 0.55 | 1.4 | 1.70 | 97.90 | 98.85 | 99.00 | 99.1 | 98.90 | 99.30 | 99.6 | 0.979 | 1.977 | 2.970 | 3.964 | 4.945 | 19.86 | 49.83 |
| Kaoline | 0.10 | 0.17 | 0.19 | 0.15 | 0.17 | 40 | 135 | 99.00 | 99.15 | 99.35 | 99.6 | 99.65 | 80.00 | 73.0 | 0.990 | 1.983 | 2.981 | 3.985 | 4.983 | 16.00 | 36.50 |
| Porcellane | 0.12 | 0.13 | 0.15 | 0.16 | 0.22 | 20 | 130 | 98.8 | 99.35 | 99.50 | 99.6 | 99.55 | 90.00 | 74.0 | 0.988 | 1.987 | 2.985 | 3.984 | 4.978 | 18.00 | 37.00 |
| Zeolite | 0.22 | 0.18 | 0.19 | 0.28 | 0.23 | 1.6 | 2.00 | 97.90 | 99.10 | 99.36 | 99.3 | 99.54 | 99.20 | 99.6 | 0.978 | 1.982 | 2.981 | 3.972 | 4.977 | 19.84 | 49.80 |
| Bentonite | 0.11 | 0.12 | 0.13 | 0.15 | 0.20 | 1.4 | 16.0 | 98.90 | 99.40 | 99.56 | 99.6 | 99.65 | 99.30 | 96.8 | 0.989 | 1.988 | 2.987 | 3.985 | 4.980 | 19.86 | 48.40 |

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### الخلاصة

تمت دراسة سعة امتزاز ثلاثة انواع من الاطيان العراقية وهي ( الكاؤلين، والبورسلانايت، والبنتونايت) وثلاث انواع من الراتنجات والزيولايت المستورد . وتم تحليل نتائج الامتزاز من خلال ايزوثيرمات الامتزاز (متساويات درجة الحرارة) والتي تطابقت مع مستقيمات لانكماير المعروفة ومنها حصلنا على اعظم سعة امتزاز للراتنجات والاطيان العراقية والزيولايت . وظهر أن للاطيان العراقية سعة امتزاز عالية وصلت الى 99.7% وهذه النتيجة مشابهة لسعة الامتزاز على الراتنجات، كما ودرس تأثير اختلاف التركيز الابتدائي لمحاول ايونات الرصاص على كمية الامتزاز (Qe) . وتم قياس ثوابت معادلة لانكماير للسطوح المازة السبعة عند درجة حرارة الغرفة (oC25) ، ان نسبة ايونات الرصاص المزالة بالمواد المازة السبعة تزداد بزيادة التركيز الابتدائي