Studying the Thermodynamic Functions of adsorption of ion , Pb (II) on a new composite surface

Isam Hussein Ali

Department of Chemistry - Collage of Science - Wasit University

Conclusion

A new type of compound was prepared in this study (AML). It was identify by infrared spectroscopy. Use the composite to remove the Pb + 2 lead ion from its Aqueous solution by adsorption at certain conditions of the temperature and weight of theadsorbent material and the acidity and contact time. The composite was found to be effective in removing the lead ion at an acid function higher than 7 and at 25 ° C and contact time (90 min. The results showed that the adsorption on the surface was followed by Freundlich for adsorption. The thermodynamic functions (ΔS°,ΔH°,ΔG°) .were calculated

Keywords: Bentonite, Binary Lead, Adsorption

Introduction

Pollution is defined as any change in the proportions of air, water or soil components that affect humans, animals and plants, and types of environmental pollution: air pollution, water pollution, soil pollution, food contamination, radiation pollution, etc. (1, 2) Pollutants are therefore defined as substances or non-material effects that change the environment's characteristics negatively and endanger the lives of organisms in general and threaten their safety, directly or indirectly, and pollutants on three types of air, water and soil.. An important characteristic of contaminants is their interaction with each other or with other substances to produce synergistic effects, making the study (environmental pollution) more complex.

That the accumulation of these pollutants affects the effect may be more severe than expected from the impact of each contaminant individually(3). The removal of organic and inorganic pollutants from the water medium is a major challenge for workers in this area, as pollution of ions in some processes, such as photosynthesis and water absorption(9).

The most important sources of pollution of rivers and streams are mainly metallurgical factories, pesticide factories, batteries, electrical and dye industries, oil refineries and automotive fuels, which contain organic lead compounds such as tetrahedra, which adsorption from pores on Surface of skin.

The lead has other effects in the soil. Hughes (13), Hounstra (12), Andersson (11) and Tyler (10) show that the increase in lead ratio in the soil may determine the enzymatic activity of the microbes and, as a result, The roots of the plants have the ability to take a very large amount of lead and the absorption speed is increased by increasing the concentration of the lead ion in the solutions. Over time, the lead collides strongly with the cell wall Which leads to an increase in the hardening of the cells of plant walls (14). The maximum allowable lead in m The drinking water after treatment specified by EPA is 0.03 mg / l.

Currently, alternative methods of wastewater treatment are being studied. Research is currently focused on the efficiency of the adsorbent in terms of interest and licenses.

Adsorption is known as the phenomenon of the binding of a substance in the form of atoms, molecules or ions, which is called adsorbate on the surface of a liquid or solid substance called adsorbent The adsorption process is automatic in heavy elements is a serious problem of the environment as a result of the factories Of their untreated water to water sources, the lack or sometimes lack of control makes water pollution a serious matter of life in general(4). Metal compounds that touch the surface of the earth can contaminate groundwater through leaking from the soil after rain and snow. One important problem is the accumulation of toxic metals in plants, which in turn leads to the harmful effects of human and animal organisms. Most metals are highly toxic and non-degradable, and the ionic presence of these metal elements in the aquatic environment is common due to industrial activities. This is a matter of concern, because many of them are highly toxic. One of the most important sources of pollution of metal element ions is the industrial activities, which include waste from metallurgy, tanning, electroplating, battery manufacturing and other activities(5) . Lead is mainly found in the oxidized state (Pb2 +) dissolved in the case of the oxidation of quaternary (Pb4 +) insoluble in natural water. Lead is a blue or silvery color, corrosion-resistant, highly dense (6), a soft, deformable metal and roads fused at (327 c °). Lead is the toxic metals accumulated within the body of the organism and plant, increasing its concentration over time (7).

Lead is transferred into the body by blood flow and then to the bone, which is the accumulation of lead, liver, kidney, and brain(8). Other reports have also indicated toxic effects of lead

The composite can be designed to have different properties such as strength and hardness (which

supports the hardness of materials) such as graphite, aramid and other materials, which are becoming an integral part of low strength materials or low hardness materials without any negative impact on density , and resistance to pressure and use under high temperature conditions. The basic materials overlap to produce a composite with superior properties on each of the constituent materials alone, ie, the only way to look at the composite is to look at the unique and characteristic properties of the basic elements of the components The fiberglass structures are thinner For acrylics of the oldest species on the hybrid structures of ceramics / plastic (18)

The attapulgite consist of two layers of $SiO3^{-2}$, such as amphibole 6 N-n (Si_4O_{11}) that are parallel to the chain axis .The attapulgite are connected to each other by common oxygen atoms. The spaces between the chains are filled with water molecules(19) .

composite was prepared (AMU) for the removal of lead ion. The effect of some factors on the adsorption efficiency was investigated. The thermodynamic functions of the adsorption process ΔS° ΔH° ΔG°

experimental part

Instruments and tools used and tools used

1. Infrared Spectrometer Type:

conjunction with the lack of degrees of freedom of the adsorbed substance, thermodynamically, (ΔS°) (15). The change in entropy (ΔS°) can be obtained by means of a coupling relationship (16)

$\Delta G° = \Delta H° - T\,\Delta S°$

To find the adsorption temperature (ΔH°), the following equation was used:

$\text{Log } X_m = (-\Delta H/2.303RT) + C$………..

As:

Log Xm = the largest quantified logarithm (mg/g)

C= Constant equation of Van Huff

T= Temperature (Calvin)

R = the general constant of the gases (8.314 J.mol-1 deg-1

The change in energy (ΔG°)can be :obtained from the following equation

$\Delta G° = - RT \ln (Q_e / C_e)$**.. ....**

Ce: Concentration at equilibrium (mg / L)

Qe: Amount of absorbent material (mg/g)

Composite material is a system consisting of two or more material and the physical dimension between them is greater than about (1) micrometer equivalent (1x10-6) meters and these materials are linked together to the atom or molecule (17)

Substrate	Source	Mw (g/mol)	Chemical formula	Purity
Melamine	BDH	126.12	NH2,C:N,C(NH2):N, C(NH2):N	99 %
Urea	Hannover	60.06	H2NCONH2	99 %
Sodium Hydroxide	BDH England	39.99	NaOH	96 %
Hydrochloric Acid	Riedel-De Haen	36.46	HCl	34 %
Lead nitrate	MERCK	331.3	$Pb(NO_3)_2$	99 %

Attapulgite

The Attapulgite used in this study was obtained from the General Company for Geological Survey and Table (1-2) showing the analysis of the chemical elements of ethyls by EDS (Energy Dispersive X-ray Spctroscopy).

Table (1-2) Chemical analysis of the clay of the used attapulgite

Compounds	Wt %
SiO_2	60.531
MgO	11.348
Al_2O_3	10.136
Fe_2O_3	6.782
CaO	4.952
K_2O	2.358
MnO	2.220
TiO_2	1.126
Na_2O	0.547

Configure the attapulgite

The clay was then washed and grinded. After that, it was washed with distilled water, several times to remove the dust and suspended materials. The mud was then immersed in the distilled water for two days to ensure surface washing. It was then washed with 10% dilute hydrochloric acid to purify it and remove all ions on its surface. Then the

FTIR (Fourier Transform Infrared Spectrophotometer)

Type (shimadzu 8400) Japan

2-Atomic absorption spectrometer

Atomic Absorption Spectrophotometer

Shimadzu AA-6200, Japan-type

3-Sensitive Balance Type: Electronic Balance Kern Lab CE, Germany

4 - water bath equipped with a temperature controlled temperature of type:

BS-11 degetal, JEIO TECH, Korea.

5. pH meter of type:

pH 84, Research pH meter Radiometer, Cobenhagen, Denmark

6-Laboratory Thermal Oven Type: Gallen KampVacuum Drying Oven, Dp61 Yamato HITEC, Japan (25-630) C^o

7-mortar ceramic (mortar)

Used chemical

The chemicals whose types, purity and composition are listed in Table 1.1 below

Table (1.1) Chemicals used, sources and purity equilibrium time of the adsorbent material was determined by following the change of absorbance with time. 90 min.

Effect of material weight

The effect of the weight of the adsorbent was studied in the adsorption process at constant temperature (25C °), 50ppm concentration and 50ml size after adding different weights of the adsorbent material (1.5, 0.1, 0.5 and 0.1) respectively

Effect of temperature

The effect of temperature on the adsorption process was studied at five degrees of temperature and the effect of temperature was recorded on the process of adsorption of lead nitrate

Effect of acidic function

The adsorption conditions were stabilized from a 50ppm concentration and a temperature of 25 ° C. The acid function was arranged within range (2-9) and contact with a 2g weight of the overlapped and a contact time of 90 minutes. The acidic function values were controlled using diluted solutions of HCl (0.1M) and (0.1M) NaOH to modify the acidity and use of the pH device.

Isotherm adsorption

Five concentrates of lead-absorbing material were prepared with concentrations ranging from 10-50 ppm. Add 50ml of each solution to clay is washed with distilled water to remove the traces of acid and then dried in the oven temperature of 80 ° C for three hours and then re-grind it again and dried and then placed in the container

Preparation of the Composite (AMU)

This composite was brought from a mixture of 40gm of clay with 4gm of both urea and melamine. The above materials were placed in a mortar and a few drops of water were added to it to complete the interference. The mixture was then heated for half an hour and then left for one week to complete the tangle

Preparation of the standard solution of lead nitrate solution

The standard solution for the lead nitrate used in this study was prepared at a concentration of (1000 ppm) of dissolving (1.598) of lead nitrate in one liter of distilled water, from which I attended solutions with different concentrations.

Determining the time required for equilibrium to occur

To determine the time required for the stability of the lead nitrate on the composite powder, 250 ml of the lead solution was taken at 50ppm and 25C °. The solution was distributed evenly over five flasks of each 50ml flask. Add 2g of the adsorbent to each flask. The solutions were then placed in a vibrating water bath (120rpm). (15,30,45,60,75,90,120 min) and its absorbance measurements after the separation and filtration process. The

Results and discussion

identification of adsorbent (composite)

Infrared spectrum for attapulgite

Figure (1-1) refers to the infrared spectrum of the pulses. The 3618.58cm-1-3408.19cm-1 frequencies are indicated to the bacterial vibration of 0H hydroxyl group in different environments (20). The amplitude of the beam is due to the formation of the hydrogen atom with the internal water molecules. Frequency 1637.62cm-1-1631.83 cm-1 is due to the bending vibration of the water molecule. The package at 1435.09cm-1 indicates the presence of calcite as an impurity. The beam at 1008.80cm-1 refers to the asymmetric tee frequency of the unit {Si-O-Si (Al)}

2gm of powdered material in five flasks, all placed in a sprayed water bath at 25 ° C for 90 min. At the end of the equilibrium time, 5ml of each flask was loaded and placed in a test tube with a sealed seal and then placed in the centrifuge for 15min. After separation, the absorption of the solution is calculated by the atomic absorption spectrometer. Calibration curves, from which the quantity of the absorbent substance Qe was calculated in mg / g units and according to the relationship

$$Qe = \frac{Vsol\,(Co - Ce)}{m}$$

Qe = amount of absorbed substance(mg \ g)

Vsol = the total solution volume of the solution of the absorbent material L)

Co = primary concentration of solution(mg / L)

Ce = concentration of the solution at equilibrium(mg / L)

m = weight of the adsorbent(g)

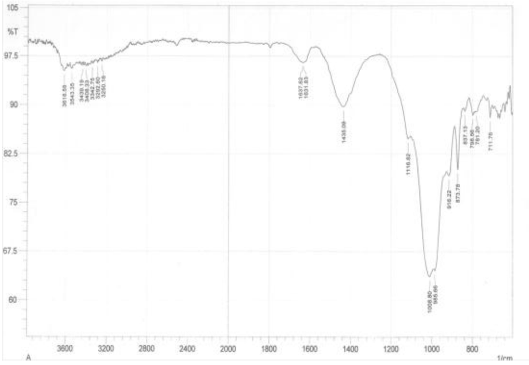

Figure (1-1) Infrared spectrum of the attapulgite

1539.25-143316 cm-1)) due to the bending vibration of the NH frequency in the secretary. The top of cm-1 810.13 goes back to the ring of trazine (21)

Infrared spectrum of melamine

Figure (1-2) shows the infrared spectrum of melamine, where we observe the appearance of peaks at 3470.06-3327.32 cm-1) due to the mass vibration of the NH2 group. The cap at 1694.19 cm-1 is due to the mass vibration of C = N (Cm-1) (1197.83-1022.31) is due to the temporal vibration of the CN (vertices at

3431.48-3338.89 cm-1 indicate the NH2 vibration. The peak at 1678.13 cm-1 indicates the mass vibration of the carbonyl group C = O. The peak at 1460.16 cm-1 returns to the C-N tattoo.

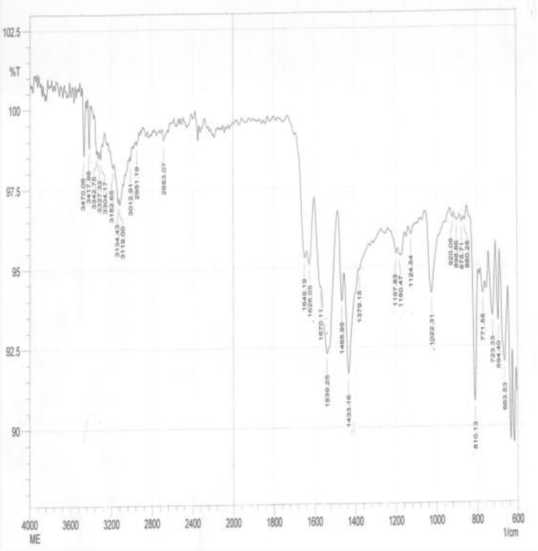

Figure (1-2) Infrared spectrum of melamine

Infrared spectrum of urea

Figure (1-3) shows the infrared spectra of the urea where the numbers

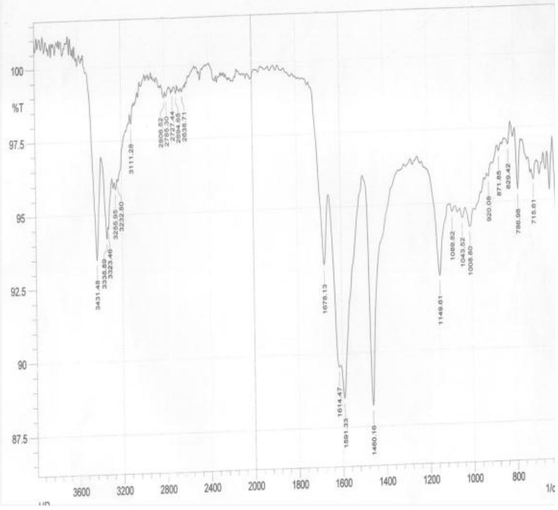

Figure (1-3) Infrared spectrum of urea

Infrared spectrum of (AML)

Figure (1-4) shows the infrared spectra of the AMU spectra where we see the shift of the NH2 to Melamine and Urea to a frequency greater than 3470.06-3327.32cm-1 for melamine and 3431.48-3338.89 cm-1. This is due to the emergence of a positive charge on the nitrogen atom due to the contribution of the electronic double on it by a certain kind of sequence, such as being hydrogenated with the acid protons on the surface of the attapulgite. The emergence of this positive charge on the nitrogen atom increases the constant strength of the NH signal by attracting the current electron density towards the positively charged nitrogen atom, which leads to the compression of the atom and then increases its constant force. This happens for both symmetric and asymmetric frequencies. Carbonyl group C = O is less than 1678.13cm-1 for urea and 1,649.19cm-1 for melamine due to the formation of the hydrogen atom between the oxygen atom of the carbonyl group and the hydroxyl endotracheal of the bacterium, which gives the carbonyl group a single,

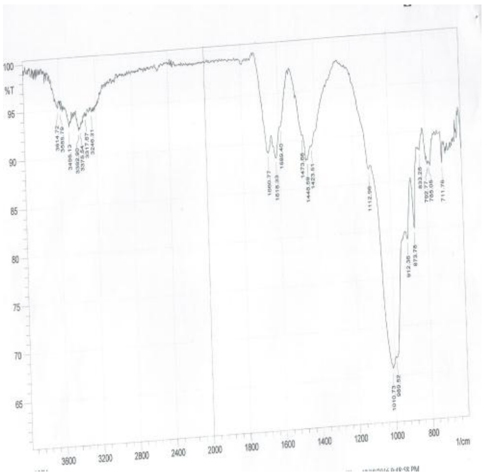

Figure (1-4) Infrared spectra of the composite

Effect of acidic pH function

The effect of pH on the process of adsorption of lead ion on the surface of the composite was studied in different acidic media. (1-5) that the process of adsorption of lead ion dioxide increases with increasing acid pH values. The reason is that the high pH will reduce the concentration of H + ions in the solution, reducing the competition with the ion of the lead on the two sites of bonding the surface of the composite and preferably adsorption Cation on the surface (114) which raises the percentage values for the removal of

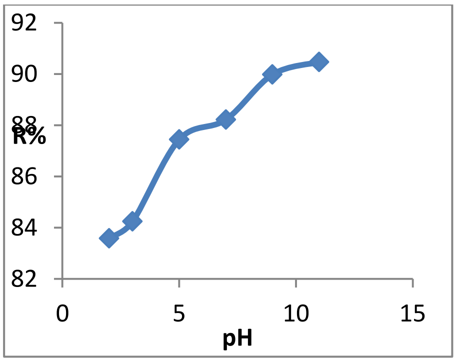

Figure (1-5) The effect of the acidic function in the percentage of the removal of the binary lead ion on the surface of the composite

Effect of weight of adsorbent (composite)

The effect of the weight of the adsorbent was studied on the process of ionization of the lead lead. Various weights ranging from 0.1-2 gm were used. It should be noted from Figure (1-6) that the removal ratio increases with the increase of the weight of the adsorbentza material. This is due to the increase of the surface area and thus the increase in the number of effective adsorption sites on the surface which are ready for adsorption of ions(24)

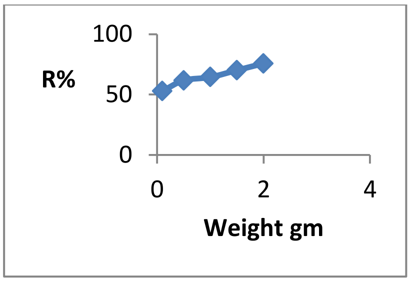

Figure (1-6) The effect of the difference in the weight of the adsorbent material in the percentage of the removal of the lead lead ion on the surface of the composite

Effect of contact time

The time required to reach the equilibrium state in the process of adsorption of binary lead ion on the surface of the adsorbent material at different times (15,30,45,60,75,90,120min) was observed. Figure(1-7) shows that after 90min 78.40% lead was removed. Where we notice that the removal rate increases with increasing time and this explains with the availability of effective sites for adsorption at the beginning of the process. The number of active sites available for adsorption on the surface is high, but the number of the adsorption process is constantly decreasing until all the active sites are covered with lead ions, thus stopping the adsorption process(25).

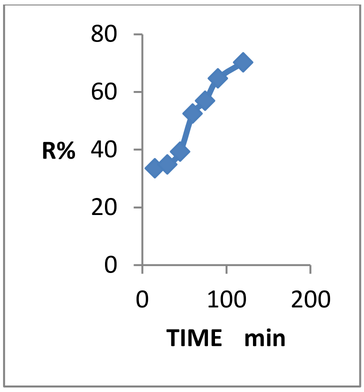

Figure (1-7) The effect of the difference in the contact time in the percentage of the removal of the binary lead ion on the surface of the composite

Effect of temperature

The effect of temperature on ion adsorption of lead biodegradable at different temperatures (25,35,45,55,65 C °) was studied on the surface. As shown in Figure (1-8), ion adsorption of the double lead increases with the decrease of temperature, ie, the process is exotherm. This is due to the increase of the temperature of the solution, which increases the kinetic energy of the lead ion, which is absorbed on the surface of the gas which leads to its separation and return. From surface to solids (26)

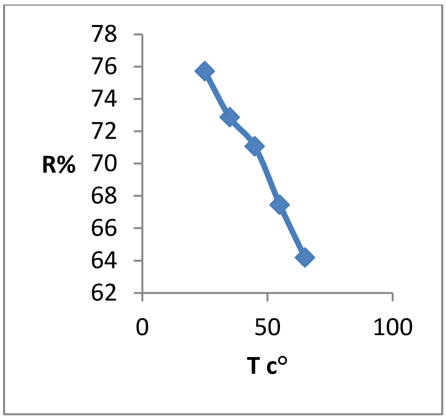

Figure (1-8) Effect of temperature difference in percentage to remove lead ion ion on the surface of the composite

Thermodynamic studies

The study of the effect of temperature in estimating the values of the basic thermodynamic functions is the free energy (ΔG°) and the (ΔH°) and the (ΔS°).

figure (1-9) shows the temperature of the thermodynamic stability of the binary lead ion adsorption On the surface of the composite.

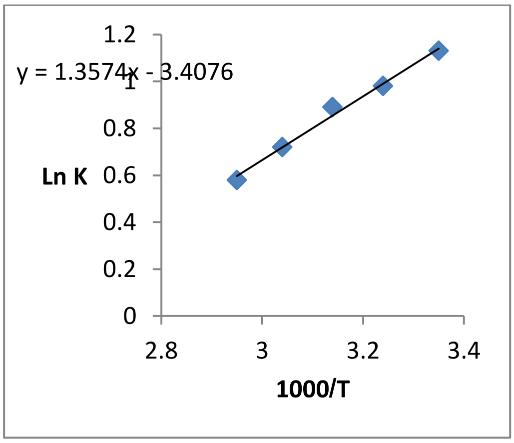

Figure (1-9) Values Ln k vs. 1000 / T for ion adsorption of lead-binary on the composite surface

Table (1-3): Effect of temperature in the static equilibrium of the ionic adsorption of the lead on the surface of the composite

C_e (mg/l)	T(°C)	T(K)	1000/T (K^{-1})	Q_e (mg/g)	Equilibrium constant (K)	ln K
12.15	25	298	3.35	0.946	3.11	1.13
13.57	35	308	3.24	0.910	2.68	0.98
14.47	45	318	3.14	0.888	2.45	0.89
16.28	55	328	3.04	0.843	2.07	0.72
17.91	65	338	2.95	0.802	1.79	0.58

The thermodynamic functions above were calculated using the following equations:

$\Delta G° = - RT \ln K$ ....

$\ln k = (-\Delta H°)/ RT +$ constan

$\Delta G° = \Delta H° - T \Delta S°$

Where the constant R of the gases (8.314 J.mol-1. Deg-1) K is the equilibrium constant of the adsorption process at each temperature.

Table (1-4) shows the values of thermodynamic functions of lead ion adsorption on the surface of the composite

Temp(°C)	ΔH KJ/mole	ΔG kJ/mole	ΔSKJ/ mole
25	-11.28	-2.799	-0.0378

Table (1-4) shows the values of the thimodynamic functions of ion adsorption of the lead on the surface of the body. Where the negative adsorption temperature of ΔH° indicates that the adsorption process is exothermic. The negative value of the change in free energy ΔG° °indicates that the adsorption is spontaneous. The negative value of the entropy ΔS° indicates that the absorbed ions are more uniform on the surface of the superconductor when the adsorption is obtained from the solution (26)

Isotherm adsorption

The adsorption of adsorption adsorption gives important information about the adsorption process and its conditions, and the knowledge of the adsorption capacity of the adsorption material and its concentration at the time of the adsorption process. Figure (1-10) Isotherm shows the biodegradation of the lead on the surface of the composite at a temperature of 298K and the acid function 2. According to the Giles classification, when comparing the general form of adsorption of adsorption, it is observed that (S) is achieved in the case of heterogeneous surfaces (27).

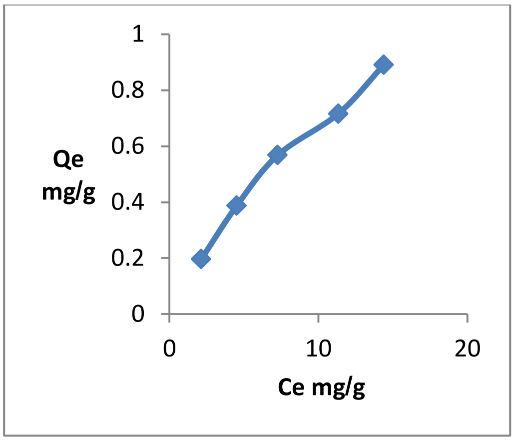

Figure (1-10) Isotherm adsorption of lead ion-on the surface of the composite at 90-minute equilibrium time and acidic function 2

The binary lead ion adsorption data were treated according to the Freundlich Equation formula by the following equation:

$$log\ Q_e = log\ k_f + \frac{1}{n} log\ Ce \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(-)}$$

In this equation we calculated the experimental FRENDLES constants and correlation coefficient as shown in Table (1-5). The log relationship between log qe and log ce was obtained and Figure (1-11) is obtained, which shows the linear relation of the FRINDLESH equation.

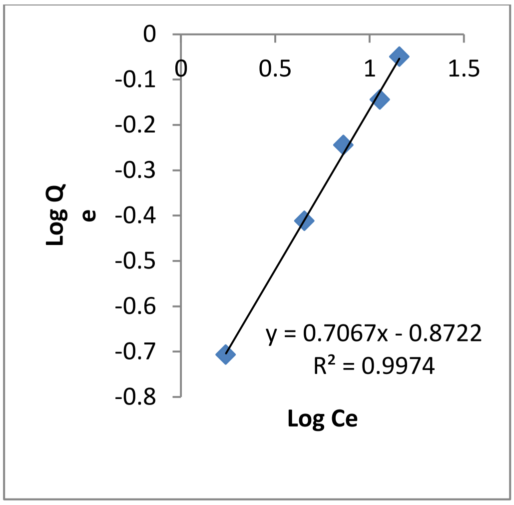

Figure (1-11) The linear of Isotherm FRENDLECH for ion adsorption of lead ion on the composite surface

Table (1-5): Determination of the FRENDLES constants and correlation coefficients for ion adsorption of lead on the surface of the composite

N	**K_f**	**R^2**
1.415	0.059	0.9974

Where (n) represents the efficiency of adsorption, and when the value is greater than one, adsorption is preferred and physical in nature. Kf is the adsorption capacity of the surface and (R2) represents the lead ion correlation coefficient with the surface.

Conclusions

- The process of adsorption ion-lead binary increase in temperature decrease, that is exothermic.

- The percentage of binary lead ion removal is increased when the acid function decreases.

- The percentage of binary lead ion removal is increased when the weight of the adsorbent is increased.

- The results of Isotherm Ion ion adsorption on the surface of the body Adsorbent corresponds to the model Frenaldsh and similar to the class (s) according to the classification of Giles.

- The value of change in free energy is negative, indicating that the process of adsorption is spontaneous

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