# Behavior Adsorption Study of Phenol, Picric acid and p-Amino phenol By Powder Bentonite

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## Abstract

Adsorption studies for phenol , picric acid and p- Amino phenol removal from aqueous solutions on bentonite were carried out. Batch kinetic and isotherm studies were carried out under varying experimental conditions at contact time ,initial phenol ,picric acid and p-Amino phenol concentration, adsorbent dose and pH .The adsorption data fitted the Langmuir and Freundlich isotherms equations in the whole rang of concentrations studied .The adsorption capacity of compounds was higher (12.22-27.26 $mg.g^{-1}$ )with the lower values of the temperature (18-48C°),higher values of the initial pH (3,10) and agitation rate(180rpm).The equilibrium in the solution was observed with in 45 min of opration. The equilibrium isotherm for each compound was determined to describe the adsorption processes .The results obtained shows the isotherms were ($S_3$,$L_3$) according to Giles classification .The thermodynamic parameters at compounds such as ΔG, ΔH, ΔS of adsorption were calculated.

## الخلاصة

تم دراسة امتزاز الفينول وحامض البكريك وكذلك البارا امينو فينول في المحاليل المائية على سطح البنتونايت .كما تم دراسة حركية الايزوثيرمات على اختلاف الظروف التجريبية والمتمثلة بزمن الاتزان والتركيز الابتدائي للمركبات المدروسة،كمية السطح الماز وكذلك تاثيرات الدالـة الحامـضية كانت معطيات الامتزاز تطابق معادلات ايزوثيرمات فرندلش ولانكمـاير ضـمن حـدود التراكيـز المدروسة.أما سعة الامتزاز للمركبات المدروسة كانت ضمن حدود(12.22-27.26مليغرام /غـرام) عند الدرجات الحرارية (18-48 درجة مئوية)،وقيم الدالة الحامضية (3،10) وسرعة الاتـزان 180 دورة لكل دقيقة. لوحظ ان اتزان المحلول يكون عند زمن 45دقيقة لكل عملية امتـزاز. تـم تقـدير ايزوثيرم الاتزان لكل مركب تحت الظروف الموصوفة. من النتائج المستحصلة ظهران الايزوثيرمات تبعا لتصنيف جيلز هي ($S_3$,$L_3$) .كما تم حساب القـيم الثرموديناميكيـة ΔG, ΔH, ΔS للمركبـات المدروسة.

***Key words:-*** *Bentoinite ,adsorption isotherm,phenols compounds*

## Introduction

Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins ,which are used as construction materials for automobiles and appliances ,epoxy resins and adhesives ,and polyamide for various applications [1]. Oxygen –containing functional group such as picric acid,p-Amino phenol and phenols quinines have asignificatant effect on the reaction between an adsorbate and different carbon surface[2-7]. Phenol is considered to have toxic effects ,and from chlorophenol in the presence of chlorine in drinking water[8-10].

Bentonite is along for gotten adsorbent .It was used in paraquat poisoning as a gastric decontaminant but has largely been replaced by activated charcoal.Bentonite is a cation exchange resin ,which has found applications in industry as an agent capable of removing cation impurities[11].Bentonited adsorption (absorption)properties are very useful for wastewater purification . Common enviormental directives recommend low permeability soils,which naturally should contain bentonite ,as a sealing material in the construction and rehabilitation of landfills to ensure the protection of ground water from the pollutants. Bentonite is the active protective layer of geosynthetic clay liners.

## Experimental

The adsorption of phenol,picric acid and p- amino phenol were carried out using technique at room temperature (25±0.5C º).The adsorption concentration of phenol,picric acid and p-aminophenol in aqueous solution was measured by UV-visible spectrophotometer(Double beam,shimadzu UV-1700) at wavelength of 269, 355 and 272 nm respectively.

**1. Sample collection:-**

The bentonite used as an adsorbent was obtaind from Basrah company in Iraq .The material was washed with distilled water until the pH became neutral and dried at 100Cº for two hours and pulverized at 200 µm.The three compounds were used for this study .The compounds were:phenol,picric acid and and p-amino phenol .All compounds used as an adsorbate were supplied by fluka.

**2. Dependence on pH and batch adsorption**:-

Sample of 0.1gm of bentonite were placed in a conical flask ,with 25cm$^3$ of compound solution .The pH was adjusted to the desired value by the addition of acid or alkaline solution .The flask was then closed and placed in a bath controlled by a thermostat (25±0.5Cº) for four hour. The samples were reciprocted in a rotary shaker with a controlled agitation (180rpm).The phenol, picric acid and p-amino phenol were then centrifuged and the residual concentration was determined at the wavelengths of 269,355 and 272 nm using ethanolic aqueous solution as a blank.In order to reduce measurement errors ,the UV absorption intensity of each equilibrium solution sample was measured three times and the average value was used to calculate the equilibrium concentration based on a standard calibration curve, whose correlation coefficient($R^2$) was 0.998. The adsorption capacity $q_e$ was calculated from the difference between the initial and equilibrium adsorbate (compounds) concentration which is as follows:[12,13]

$$q_e = \frac{(C_o - C_e)}{M} . V_{sol} \ldots\ldots\ldots\ldots (1)$$

Where:qe is the adsorption capacity ($mg.g^{-1}$),Co and Ce are the initial and equilibrium concentration($mg.L^{-1}$) respectively,M is the adsorbent dosage (g) and V is the solution volume (L). The adsorption capacity was determined with the effects of contact time, initial concentration of compounds solutions and pH ,Temperature and agitation rate.The equilibrium concentration ,adsorption capacity at equilibrium were determined to fit in the adsorption isotherms.

**Results and discussion**

**1.Adsorption isotherms:-**

Analysis of Equlibrium isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes .The Langmiur and Freundlich models are the most frequently employed models. The Freundlich isotherm has been widely adopted to characterize the adsorption capacity of phenol compounds pollutants using different adsorbents by filting the adsorption data .The Freundlich isotherm has the general from such as[14]:-

$$q_e = K_f . C_e^{1/n} \quad \text{……..(2)}$$

This equation can be modified as:-

$$q_e = \frac{(C_o - C_e)}{M} . V_{sol} = K_f . C_e^{1/n} \quad \text{……(3)}$$

Where: $K_f$ and 1/n are the adsorption capacity and intensity of adsorption respectively .The value of $K_f$ and 1/n can be determined from the intercept and slope ,respectively of the logarithmic plot in Eq.3

$$\ln q_e = \ln K_f + 1/n \ln C_e \text{ ----------(4)}$$

The linear Lagmuir adsorption isotherm modle can be represented by the following relation[15].

$$Ce/qe = \frac{1}{K_1 q_m} + \frac{1}{q_m} C_e \text{……(5)}$$

Where: qe is the amount of dye adsorbed at equilibrium ($mg.g^{-1}$ ),$C_e$ is the equilibrium concentrations of phenol compounds ,$K_1$($mg.L^{-1}$) and $q_m$ ($mg.g^{-1}$) are the Langmuir constants ,representing the maximum adsorption capacity for the soild phase loading and the energy constant related to the heat of adsorption. The constants $q_m$ and $K_1$ can be determined from the intercept and slope of the linear plot of the experimental data of $C_e/q_e$ against $C_e$ .The linearized Freundlich and Langmuir adsorption isotherms at initial phenol concentration and pH 100 ($mg.L^{-1}$) and 3,10 respectively, Temperatur 18C°,agitation rate 180rpm were used to compare the adsorption capacity of bentonite for three phenolic compounds. The adsorption constant evaluated from the isotherms with correlation coefficients are shown in Table (1).

The values showed that the equilibrium data for all compounds fitted well to both the Langmuir and Freundlich isotherms in the studied concentration ranges.

Based on the correlation coefficients ($R^2$) ,the equilibrium data was fitted in the Freundlich adsorption isotherm than the Langmuir equation Table(1).Many authers have used these isotherms to evaluate the adsorption capacity by different adsorbent with different phenolic compounds [16-19].The results showed that the adsorption of phenol and picric acid and p-amino phenol on to bentonite was found to be effective at pH 3 and 10 Fig(1,2).The Freundlich and the Langmuir equations were used to study data concering the dependence of the adsoption on the phenolic compounds concentrations at pH 3 and 10 Fig(3,4,5,6).

**2.Contact time:-**

The relation ship between contact time and adsorption capacity of phenolic compounds (phenol,picric acid,p-amino phenol) by the bentonite was conducted through batch experiments to achieve the equilibrium as shown in Fig(7). The results showed that the equilibrium time was reached with in (45)min of operation .The adsorption capacity was constant there after for case of all organo phenolic compounds observed. The compounds of picric acid and p-amino phenol were found to be more effective for bentonite compared to the phenol.

**3. Adsorbent dosage:-**

In order to study the effect of adsorbent dosage on organo phenolic compounds removal as the adsorption capacity with afixed initial concentration of (phenol, picric acid and p-amino phenol) and PH, Temperature,agitation rate,bentonite was used as an adsorbent .The maximum removal of phenol, picric acid and p-amino phenol was observed with the dosage of 0.1 gm.

**4. Effect of pH:-**

The adsorption of phenol, picric acid and p-amino phenol by bentonite was studied at various pH vales .Different initial concentrations of organo phenolic compounds were prepared based on the reseaches concentrations in industrial effluents[20] in the range of 90-180 $mg.L^{-1}$ and adjusted to different pH values of 3,10 .The results are displayed in Fig[8].As was expected, the adsorbed amount of phenol, picric acid and p-amino phenol at pH 3 .This can be attributed to the dependency of phenolic compounds ionization on the pH value[1].The adsorption capacity of compounds was increased at PH 10.The higher adsorption capacity ($27.26mg.g^{-1}$) was recorded in aqueous solution of phenol ,where as for p-amino phenol and picric acid ($26.02mg.g^{-1}$),($12.22mg.g^{-1}$),respectively .It may be related to the surface properties of bentonite are depended on pH of the solution.

**5. Effect of temperature:-**

The effect of temperature ranges 291-321 K on the adsorption of phenol, picric acid and p-amino phenol by bentonite is shown in Fig(9,10).The uptake of compounds increased with an increase in temperature. The compound ($26.4mg.g^{-1}$for phenol) was recorded with in the temperature of 321K.The adsorption capacity was increased from 27.26 to 27.8 $mg.g^{-1}$,26.02 to 26.4$mg.g^{-1}$ ,12.22 to12.48$mg.g^{-1}$ for the compounds of phenol, p-amino phenol and picric acid respectively at pH 3

The adsorption capacity was increased from 27.44 to28.3$mg.g^{-1}$, 27.34 to28.22 $mg.g^{-1}$ ,12.88 to13.82 for phenol, p-amino phenol and picric acid respectively at pH 10 in the solution . The result indicated that the process is indothermic in nature.The thermodynamic factors $\Delta H$, $\Delta S$ and $\Delta G$ of compounds were calculated by using the following equations [21,22]:

$$\log X_m = \frac{-\Delta H}{2.303\ RT} + Con \quad \ldots\ldots\ldots\ldots (6)$$

Where : log Xm =higher adsorption capacity, R= gas constant and T =room temperature

$$\Delta G = -RT \ln\left(\frac{Qe}{Ce}\right) \quad \ldots\ldots\ldots (7)$$

Where: $Q_e$ is the amount of dye adsorbed at equilibrium and $C_e$ is the equilibrium concentrations.

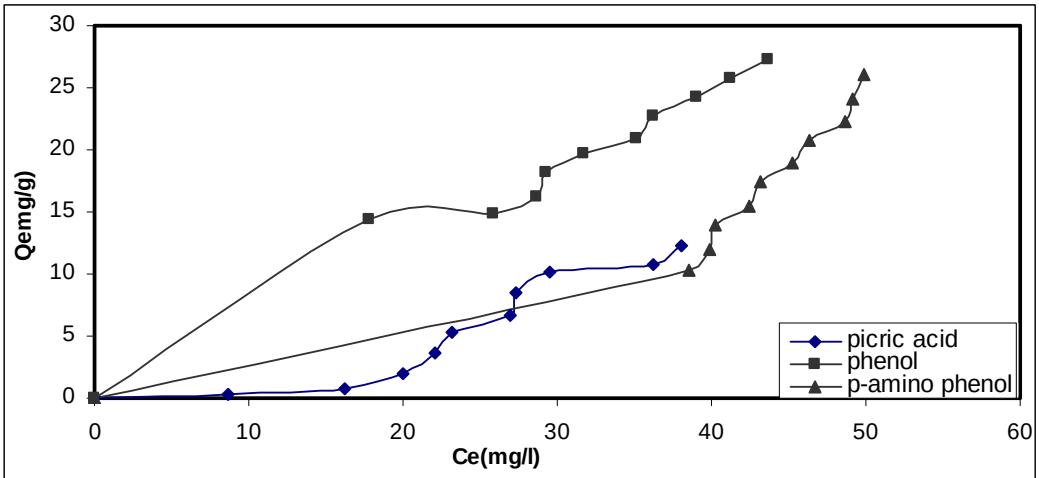
The thermodynamic factors evaluated from the isotherms are shown in Table(2).

**Table(1): Langmuir and Freundlich isotherms for three different compounds in aqueous solution using bentonite**

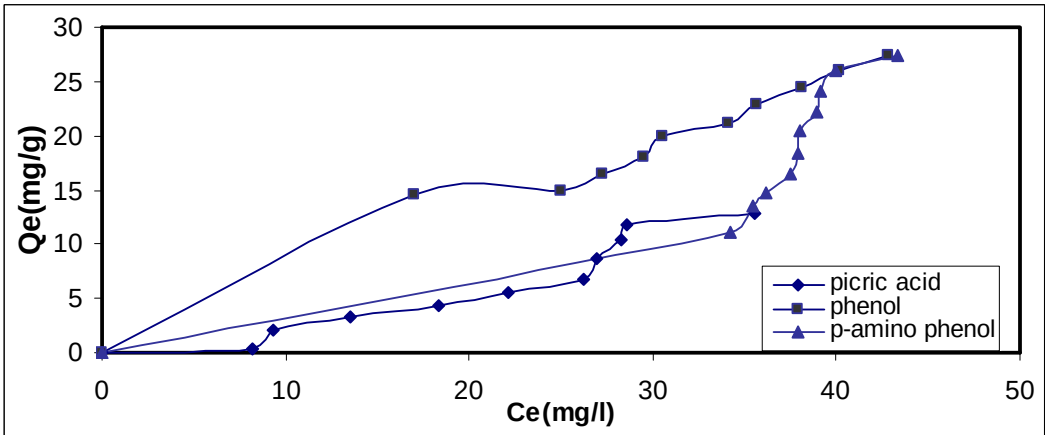
| *compounds* | *n($mg^{-1}$)* | *$K_f$($mg.g^{-1}$)* | *$R^2$ (F)* | *qm ($mg.g^{-1}$)* | *K1($mg.L^{-1}$)* | *$R^2$(L)* |
|---|---|---|---|---|---|---|
| **phenol** | **1.300** | **2.296** | **0.8681** | **116.2** | **0.0063** | **0.2202** |
| **Picric acid** | **0.744** | **-0.431** | **0.9645** | **13.73** | **0.0139** | **0.759** |
| **p-amino phenol** | **0.229** | **$1.20.10^{-13}$** | **0.8895** | **15.17** | **0.0154** | **0.9527** |

**Table(2): Thermodynamic values of compounds in aqueous solution using bentonite**

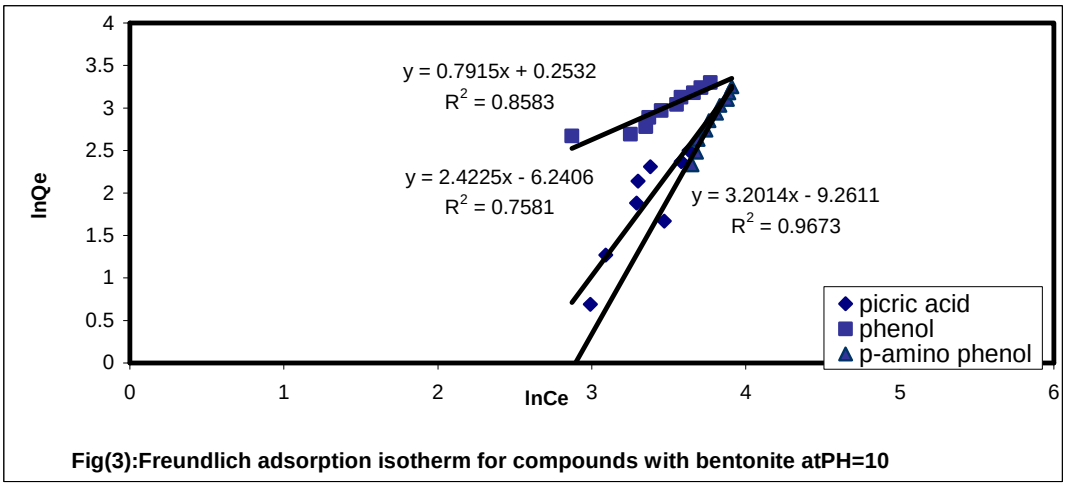
| *compounds* | *$\Delta H(k_j.mol^{-1})$* | *$\Delta G(k_j.mol^{-1})$* | *$\Delta S(j.mol^{-1})$* |
|---|---|---|---|
| **phenol** | 15.28 | 1.0754 | 48.81 |
| **Picric acid** | 71.76 | 2.459 | 238.1 |
| **p-amino phenol** | 15.233 | 1.116 | 48.51 |



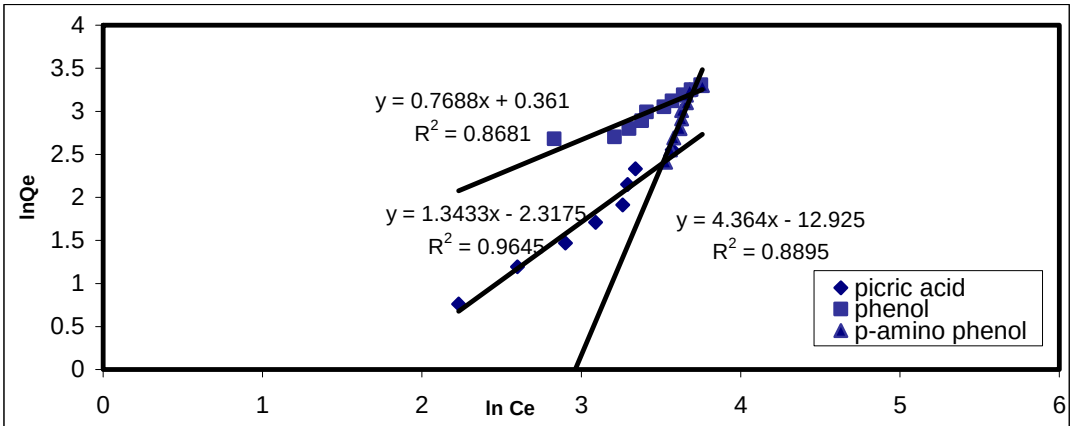

**Fig(1):isotherm adsorption for compounds with benonite at PH=3**



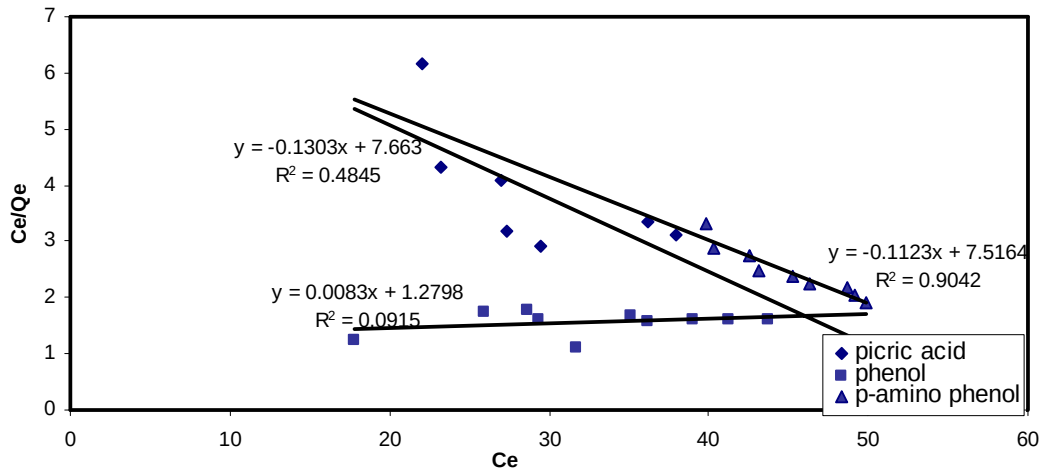

**Fig(2):isotherm adsorption for compounds with bentonite at PH=10**



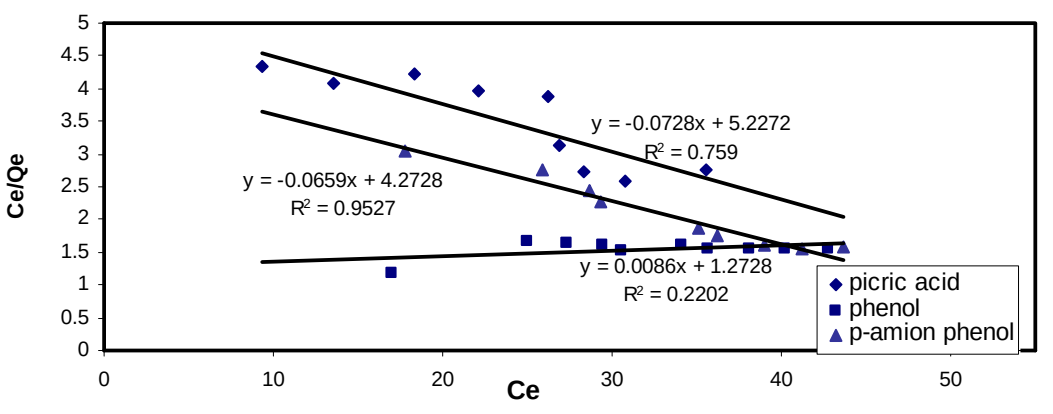

**Fig(3):Freundlich adsorption isotherm for compounds with bentonite atPH=10**



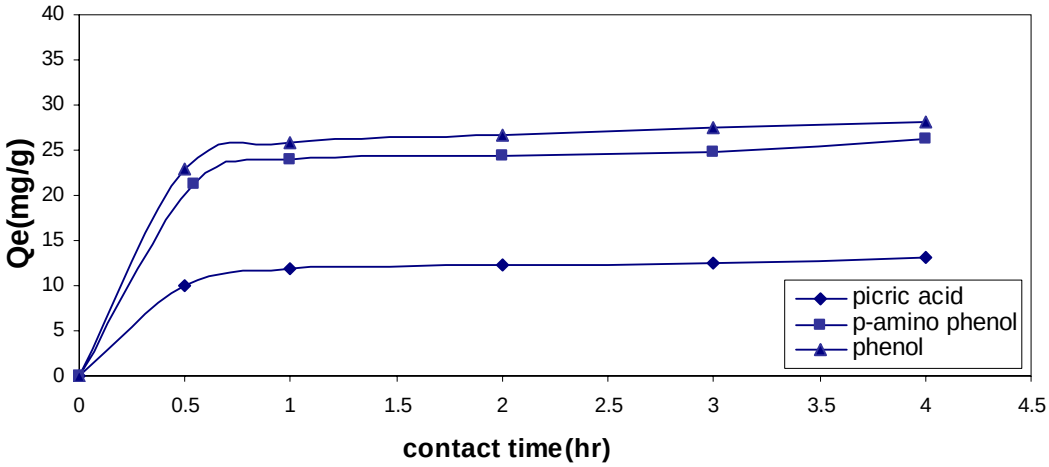

**Fig(4):Freundlich adsorption isotherm for compounds with bentonite at PH=3**



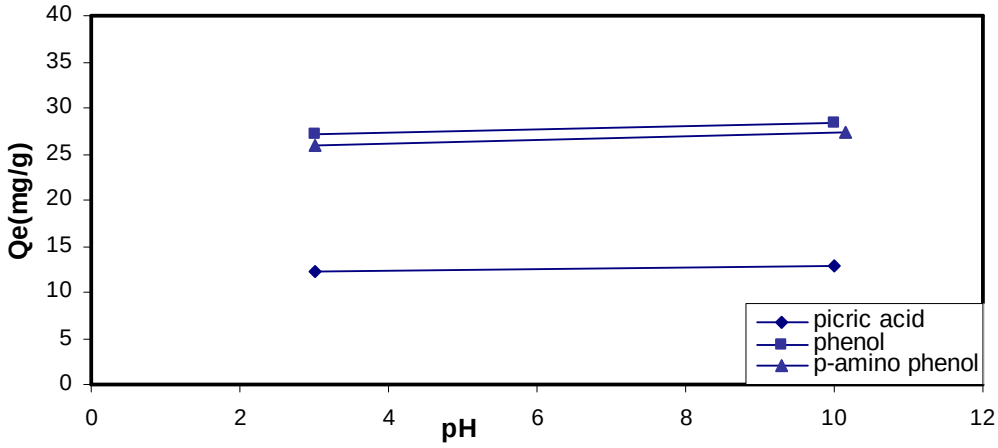

**Fig(5):Langmuir adsorption isotherm for compounds with bentonite at PH=3**



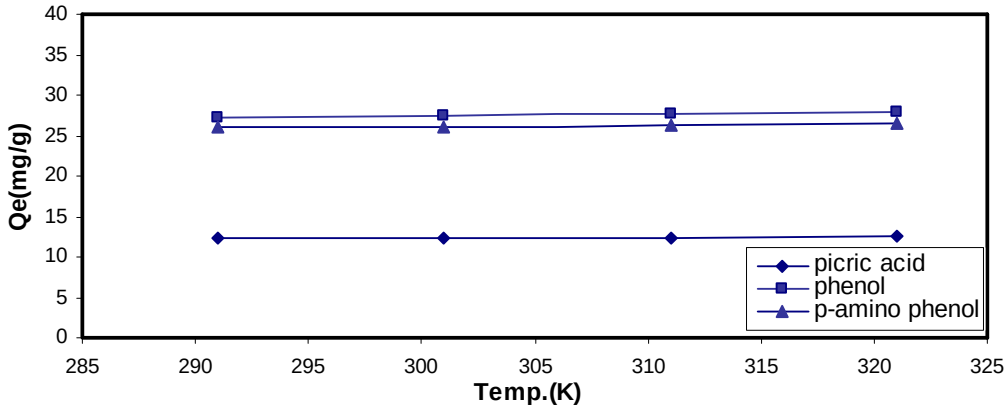

**Fig(6):Langmuir adsorption isotherm for compounds with bentonite at PH=10**



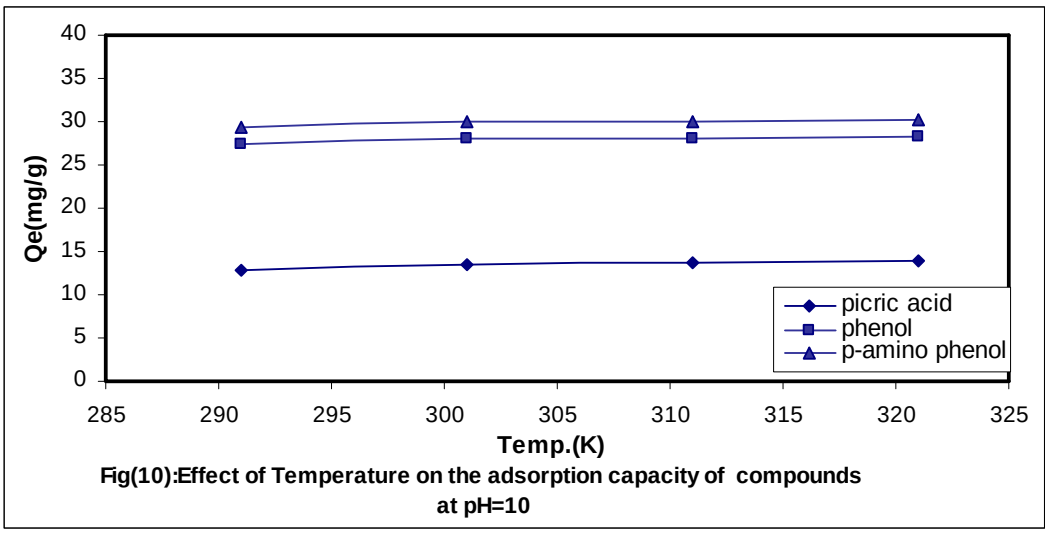

**Fig(7):Effect of contact timefor the removal organo by bentonite in organo concentrations**




**Fig(8):Effect of pH on the adsorption capacity of compounds**




Fig(9):Effect of Temperatura on the adsorption capacity of compounds at pH=3




**Fig(10):Effect of Temperature on the adsorption capacity of compounds at pH=10**

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