# Feasibility Study on Adsorption of Some Naphthols onto the Iraqi Kaolin Clay

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## Abstract

In this investigation ,adsorption of α-and β-Naphthol onto the Iraqi kaolin clay has been studied in the temperature range 40-70ºC .The extent of adsorption were carried out as a function of contact time, adsorbate concentration ,pH and temperature .Maximum Napthol adsorption was found to occur at pH 9.0 .The percentage removal of α-and β-Naphthol was 61.43 and 60.80% respectively at 40ºC .The experimental data was analyzed by Freundlich and Langmuir equations at 40 ºC .Thermodynamic parameters ∆G,∆H and ∆S were calculated and showed that the Naphthols adsorption process onto kaolin clay were exothermic and spontaneous. Moreover the adsorption process took place with constant energy of activation regardless of the type of Naphthols .An attempt was made to calculate the sticking probability to assess the applicability of Iraqi kaolin clay as an a good adsorbed for Naphthols from aqueous solutions .

**Key words** : Adsorption , Kaolin , Naphthols , Isotherms

## Introduction

Pollution now a days is one of the most common environmental problems , which started to appear in $20^{th}$ century , due to industrial development which associated with industrial revolution , all that leads to the appearance of new classes of chemical substances that were unknown previously . So many poisoning chemical compounds reaching the water sources which were difficult to compose and may cause health hazards to human beings .In general many procedures were used for processing and removal organic pollutants and most commonly is adsorption, various adsorbents have been used ,such as agricultural wastes[(1-6)],industrial wastes[(7)],activated carbone[(8-9)],kaolin[(10-11)],Alumina[(12)] and etc.

The objective of this study was to assess the use of Iraqi kaolin for treatment and removal of α – Naphthol and ß – Naphthol from aqueous solutions , its thermodynamic parameters and sticking probability were also determined.

# Materials and Methods

## Materials

The kaolin used as adsorbent in this study is obtained from bahar –Al- najaf region in Al- najaf governorate ,Iraq .The α – Naphthol and ß – Naphthol were purchased from B.D.H company

## Kaolin preparation

Kaolin was prepared by the procedure of Espantaleon etal. [13] , for this lot of clay was washed with 150ml distilled water and the resulting clay was filtered , then washed with distilled water several time till it was free from $CO_3^{-2}$ and dried at 150°C in oven for 3hours , the dried sample was characterized by XRD .Table 1 shows the percentage of the constituent of Iraqi kaolin clay

Table :1 Iraqi Kaolin clay composition

| Constituent | Wt% |
|---|---|
| $SiO_2$ | 48.57 |
| $AL_2O_3$ | 35.05 |
| CaO | 0.60 |
| MgO | 0.77 |
| $K_2O$ | 0.08 |
| $Fe_2O_3$ | 1.34 |
| $TiO_2$ | 1.19 |
| Moisture | 0.08 |
| L.O.I | 12.32 |

## Adsorption Experiments

The stock solution was prepared by dissolving 0.1 g of each of α – Naphthol and ß – Naphthol in 200ml distilled water .Solutions of different concentrations were prepared by serial dilutions ranging from 10 to 100 $mg.L^{-1}$ .Batch adsorption experiments were carried out under magnetic stirring by adding 20ml of each concentration of α – Naphthol and ß – Naphthol to 0.1 g of kaolin when stirring was briefly interrupted for 3 hours, after decantation and filtration ,the residual α – Naphthol and ß – Naphthol concentration in the aqueous solution was evaluated by UV-visible spectrophotometer model (UV- visible - 100- 02 ) shimadzu , on the calibration curve registered at the maximum absorption wave length ($\lambda_{\alpha-\text{ Naph.}}$ = 293.5 nm and $\lambda_{ß-\text{ Naph.}}$ = 274 nm ).Figs.1,2 shows the $\lambda_{max}$ of α – Naphthol and ß – Naphthol.

## Results and Discussion

The adsorption capacity $q_e$ (the amount of α– Naphthol and ß – Naphthol adsorbed $mg.g^{-1}$ at the equilibrium were evaluated based on the following equation [14]:

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

Where $C_o$ and $C_e$ represent the initial and equilibrium concentrations $mg.L^{-1}$ of α– Naphthol and ß – Naphthol ,$V_{sol.}$ is the volume of solution (L) and M is the amount of adsorbent (g) . The equilibrium adsorption data was analyzed by employing Langmiur and Freundlich isotherm equations . The linearized Langmuir isotherm is represented by the following equation [15]:

$$C_e / q_e = 1/kb + C_e/b$$

$C_e$ is the equilibrium concentration $mg.L^{-1}$ ,$q_e$ is the amount adsorbed at equilibrium $mg.g^{-1}$ , b is the maximum capacity $mg.g^{-1}$ and k is the energy of adsorption $mg.L^{-1}$. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor ,$R_L$ which can be defined by the equation [16]:

$$R_L = 1 / 1+bC_o$$

The isotherm is unfavourable when $R_L > 1$,the isotherm is linear when $R_L=1$,the isotherm is irreversible when $R_L=0$ and the isotherm is favourable when $0< R_L$ . The values of $R_L$ are 0.00145 , 0.000735 , 0.000489 , 0.000367 , 0.000290 , 0.000245 , 0.000219 , 0.000184 , 0.000163 and 0.000147 for α- Naphthol and 0.00203 , 0.00101 , 0.000676 , 0.000507 , 0.000406 , 0.000338 , 0.000289 , 0.000253 , 0.000225 and 0.000203 for ß- Naphthol ,when the initial concentrations ranging from 10 to 100 $mg.L^{-1}$ and the temperature is 40°C .The values of $R_L$ indicates that the Langmuir model is favourable of adsorption of α - Naphthol and ß - Naphthol onto Iraqi kaolin clay.

The linear form of Freundlich adsorption isotherm is [17] :

$$\log q_e = \log K_f + 1/n \log C_e$$

$K_f$ and n are the Freundlich constants .

As seen from Figs 3,4 the Iraqi kaolin at 40°C and pH =7 fits in to Freundlich and Langmuir isotherms.
Table 2 shows the constants parameter of α- Naphthol and ß – Naphthol for adsorption onto Iraqi kaolin clay at 40°C and pH =7.

From table 2 the correlation coefficient for the Freundlich isotherm is higher than that for Langmuir, suggesting higher probability of multilayer adsorption than momolayer adsorption .The value of n was found to be 1.027 and 0.763 of α- Naphthol and ß – Naphthol respectively which indicates that the surface heterogeneity[18] .

## Thermodynamic data determination

The effect of temperature on the adsorption of α- Naphthol and ß – Naphthol in aqueous solution by Iraqi kaolin clay were investigated in the range of 40-50°C,to confirm the adsorption nature process thermodynamic functions ΔGº, ΔHº and ΔSº were calculated from the following equations[19-20]:

$$\log Xm = \frac{-\Delta H}{2.303RT} + con.$$

$$\Delta G^o = -2.303RT \log K_d$$

$$\Delta G^o = \Delta H^o - T\,\Delta S^o$$

Where $K_d$ is the adsorption distribution coefficient ,R is the gas constant and T is the absolute temperature (K).The negative values of ΔGº reflects the feasibility and spontaneous nature of α- Naphthol and β- Naphthol adsorption onto Iraqi kaolin clay. The positive values of ΔSº show the increased randomness with some structures changes in the adsorbate .Figs 5,6 and 7 showed that the adsorption capacity decreased with increased temperature ,these results may be interpreted as ,at a higher temperature the mobility of the solute molecules increases and they will have a tendency to escape from the solid phase to the liquid phase leading to a decrease in the a mount of solute molecules held by the adsorbent[21],which suggesting exothermic mechanism (negative values of ΔHº),similar findings were recorded in previous works involving the ability of the Iraqi kaolin clay to adsorbed some poisoning compounds and drugs from aqueous solutions[11,19-22].To support that the physisorption is the predominant ,the vales of activation energy Ea and sticking probability S and surface coverage θ were calculated from the following equations[23]:

$$\text{Log } S = \log(1-\theta) - Ea/2.303RT$$

$$\theta = 1 - C_e/C_o$$

The plot of log (1- θ) against 1/T gave linear plot with intercept of log S and slope Ea/2.303R as shown in Fig 8 .The $E_a$ values were found to be - 0.149$K_{J.}mol^{-1}$ and -3.733$K_{J.}mol^{-1}$ for α– Naphthol and ß – Naphthol respectively which suggests that the adsorption process is a diffusion controlled process and exothermic ,while the S values confirm that the adsorption process is physisorption .Table 3 shows the values of ΔGº , ΔHº , ΔSº , $E_a$ ,S and θ of adsorption of α– Naphthol and ß – Naphthol at the temperature range 40°C to 70°C and pH=7.

**pH effect**

The effect of pH on the system due to its influence on the surface properties of the kaolin and α– Naphthol and ß – Naphthol solutions. The change of the adsorption capacity with pH is shown in Fig.9 ,we can observe the maximum adsorption occurred at pH =9.0 because the overall surface charge on the adsorbent became negative and the high attractive forces will be occurred between the Naphthols molecules and the surface . At pH =2.0 less adsorption extent observed because the charge on the kaolin surface became positive and the surface would be surrounded by hydronium ions which caused less attractive forces.

Table: 2 Freundlich and Langmuir constants of adsorption of α– Naphthol and ß – Naphthol onto the Kaolin clay at 40°C and pH=7 .

| Materials | Langmuir isotherm | | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|---|
| | k | b | $R^2$ | $R_L$ | $k_f$ | n | $R^2$ |
| α -Naphthol | 0.214 | 68.02 | 0.9667 | 0.000147 | 19.99 | 1.027 | 0.9902 |
| β -Naphthol | 0.141 | 49.26 | 0.9469 | 0.000203 | 8.033 | 0.763 | 0.9961 |

Table :3 Values of ΔGº, ΔHº, ΔSº, Ea, S and θ of adsorption of α– Naphthol and ß – Naphthol at the temperature range 40°C-70°C and pH=7

<table>
<tr><th rowspan="2">Temp. (Cº)</th><th colspan="5">α– Naphthol</th><th colspan="5">ß – Naphthol</th></tr>
<tr><th>-ΔGº ($K_J$.mol$^{-1}$)</th><th>-ΔHº ($K_J$.mol$^{-1}$)</th><th>ΔSº (J.mol$^{-1}$K$^{-1}$ )</th><th>-Ea $K_J$.mol$^{-1}$)</th><th>S</th><th>-ΔGº ($K_J$.mol$^{-1}$)</th><th>-ΔHº ($K_J$.mol$^{-1}$)</th><th>ΔSº (J.mol$^{-1}$K$^{-1}$ )</th><th>-Ea ($K_J$.mol$^{-1}$)</th><th>S</th></tr>
<tr><td>40</td><td>8.093</td><td rowspan="4">6.753</td><td rowspan="4">33.5</td><td rowspan="4">0.149</td><td rowspan="4">1.36</td><td>7.164</td><td rowspan="4">6.339</td><td rowspan="4">20.6</td><td rowspan="4">3.733</td><td rowspan="4">0.367</td></tr>
<tr><td>50</td><td>7.854</td><td>6.877</td></tr>
<tr><td>60</td><td>7.909</td><td>6.542</td></tr>
<tr><td>70</td><td>8.007</td><td>6.624</td></tr>
</table>

## Conclusion

1- The present study shows that the Iraqi kaolin clay is an effective adsorbent for the removal of α and ß –Naphthol from aqueous solutions.

2- The results shows that the equilibrium time for removal is 180min and the maximum percentage removal of α and ß –Naphthol occurs at pH=9 and 40ºC .

3-The equilibrium data agrees with the Langmuir and Freundlich isotherms,in which the Freundlich is the best

4-The values of activation energy and sticking probability supports to suggest that the adsorption process is a diffusion controlled and physical adsorption process.

5-Thermodynamic study revealed that adsorption is an exothermic and spontaneous process.

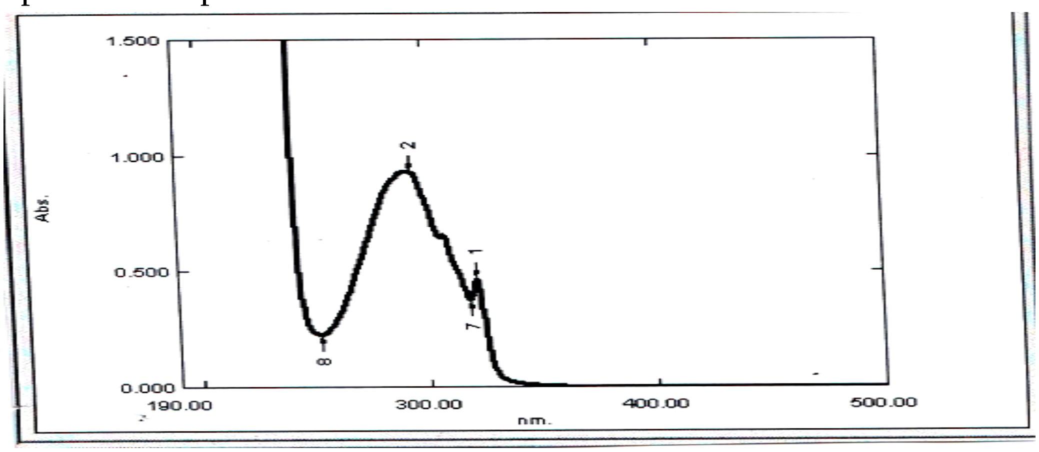


Fig. 1 $\lambda_{max}$ of α – Naphthol

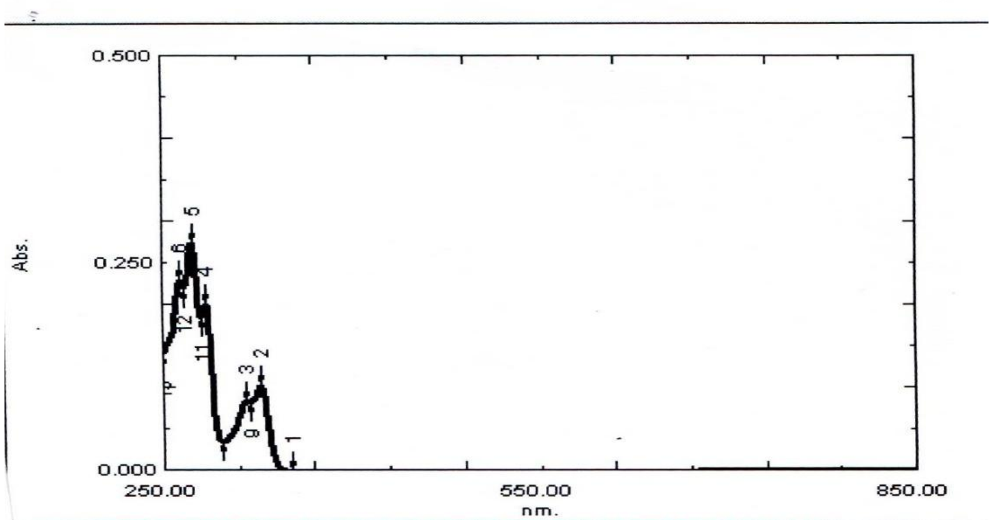


Fig. 2 $\lambda_{max}$ of β – Naphthol

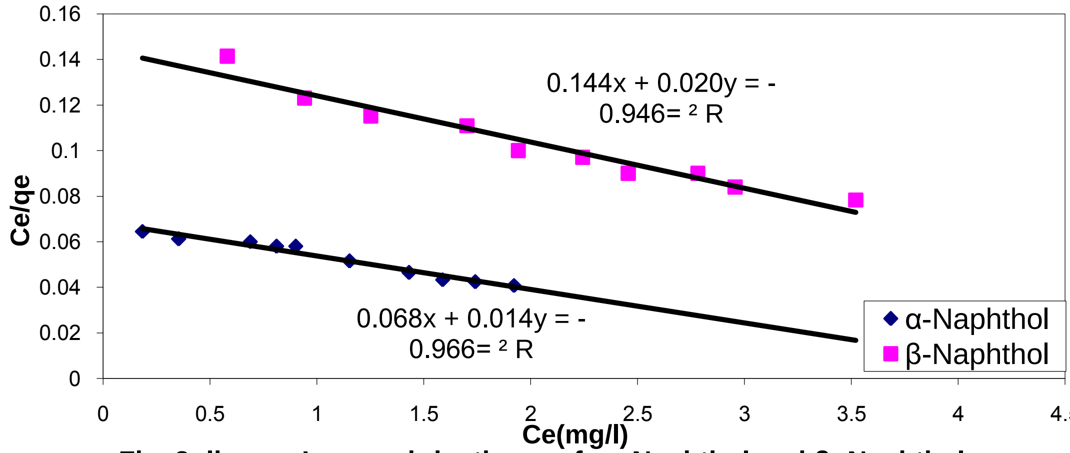


**Fig. 3 :linears Langmuir isotherm of α- Naphthol and ß- Naphthol onto the kaolin clay at 40°C and pH=7**

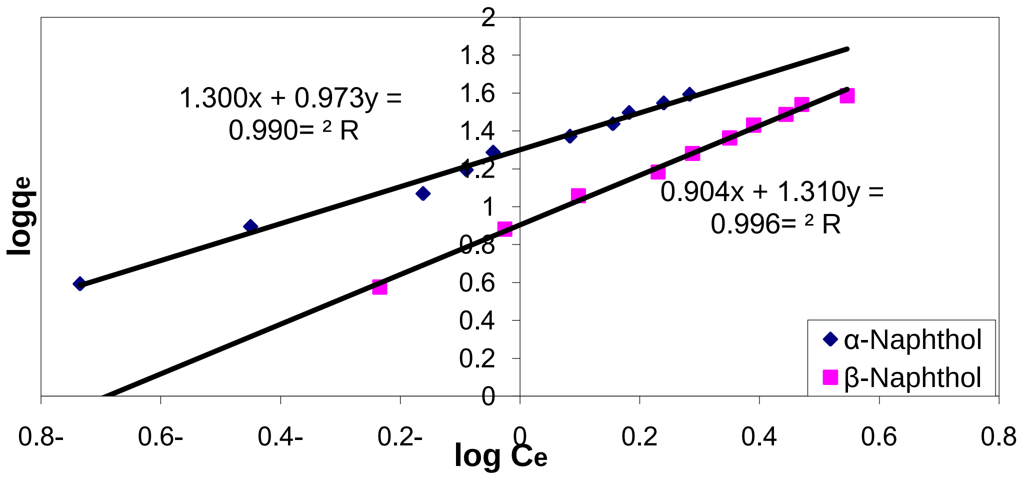


**Fig. 4 :linears Freundilch isotherm of α- Naphthol and ß- Naphthol onto the kaolin clay at 40°C and pH=7**

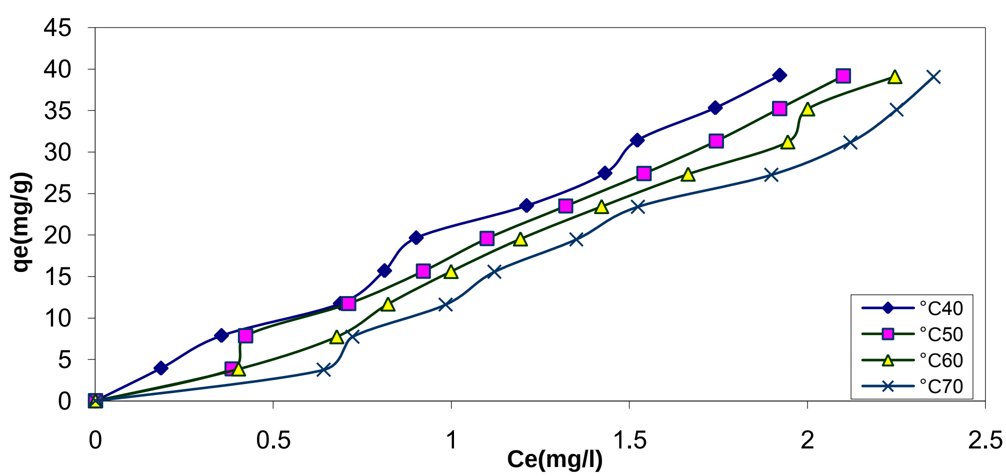


**Fig. 5:Effect of temperature of adsorption of α-Naphthol onto the kaoiln clay at pH=7**

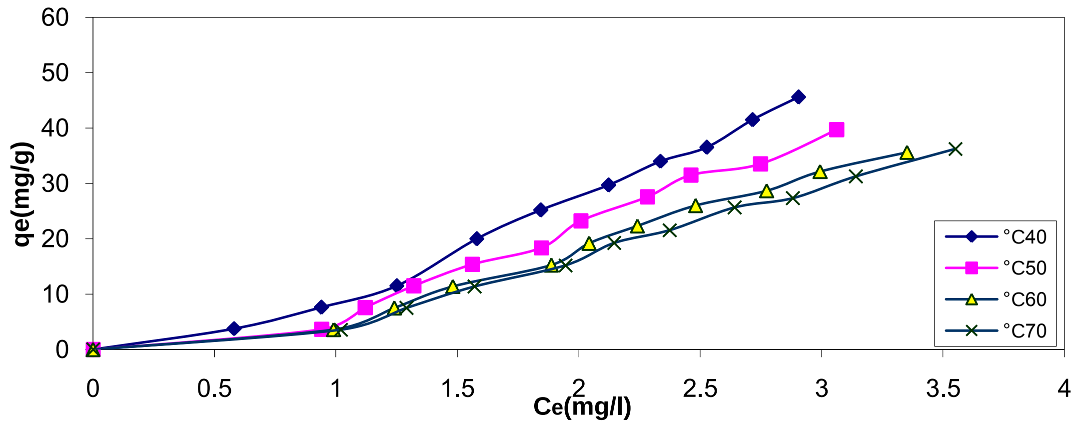


**Fig. 6 :Effect of temperature of adsorption of ß -Naphthol onto the kaolin clay at pH=7**

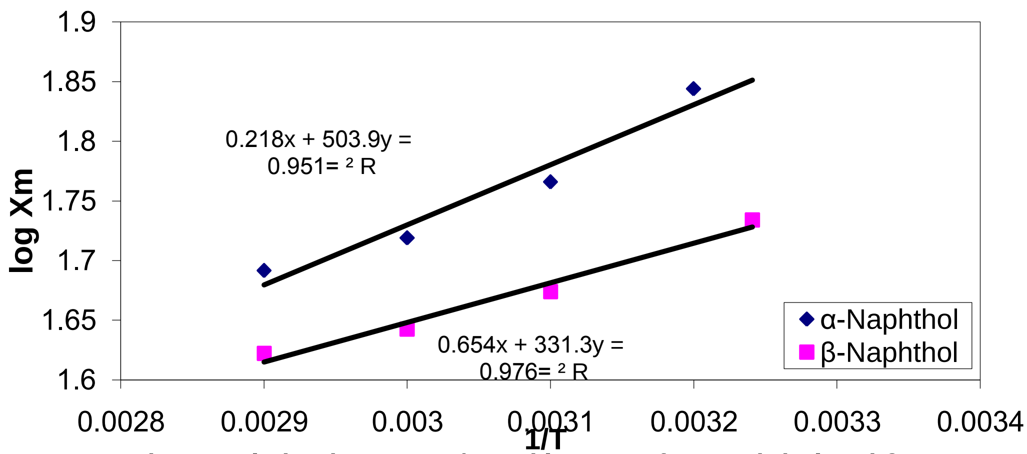


**Fig. 7 :Relation between 1/T and log Xm of α- Naphthol and ß- Naphthol onto the kaolin clay**

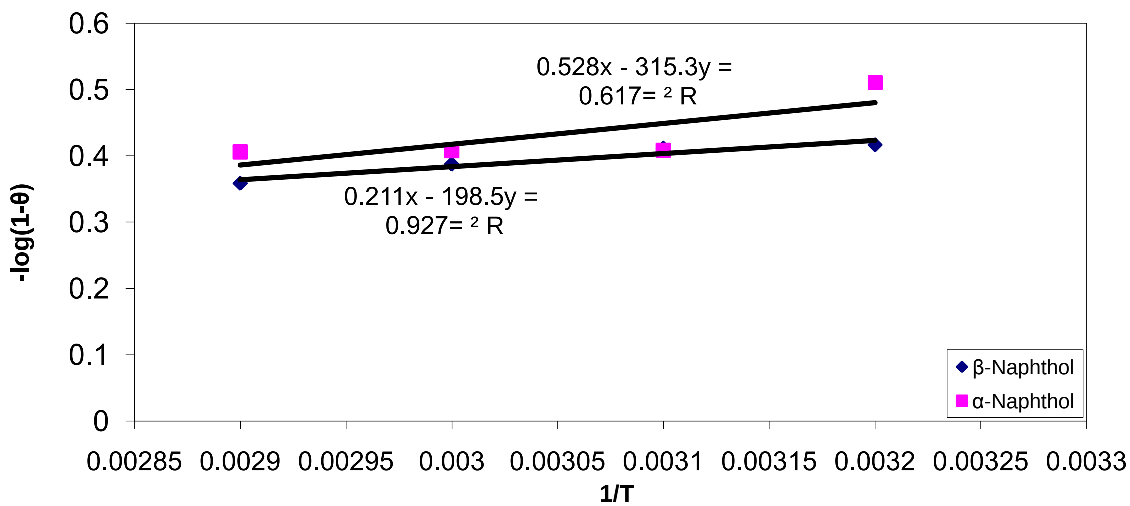


**Fig. 8 :The relationship between temperature and sticking probability for adsorption of α- Naphthol and ß- Naphthol onto the kaolin clay**

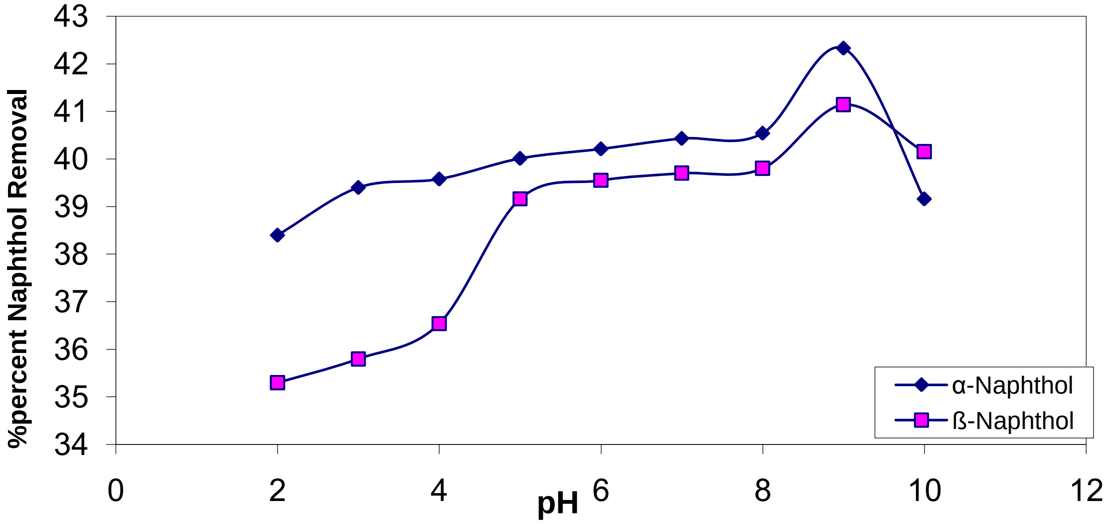


**Fig: 9 Influence of pH on adsorption of Naphthols 100mg/l onto kaolin clay (0.1g/100ml) temperature 40ºC ,contact time 180min**

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