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“Kinetic and thermodynamic study on the adsorption of Para Anisidine compound by Sepiolite clay”

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Abstract:

The removal of para anisidine (PA), with sepiolite clay have been performed investigating the effect of initial concentration, pH, temperature and contact time, on this process.

The equilibrium concentration have been determined spectophotometrically using ultra violet - visible technique.The equilibrium data are fitted to the Langmuir and Freundlich isotherm equations. The rate constant and activation energy value for the adsorption process was calculated, and the equilibrium time, that’s equal to 70 minutes.

The temperature thermodynamic parameters like ΔG^o, ΔH^o and ΔS^o have been calculated from the effect of temperature. Values of enthalpy ΔH^o showed that the adsorption process is exothermic.

الخلاصة:

في هذه الدراسة تم ازالة مركب البارا انيسيديسن المستخدم في الصناعة بوساطة طين السبيولايت, حيث تم دراسة تأثير التركيز والدالة الحامضية و درجة الحرارة وزمن الاتزان على هذه العملية. وقد تم تحديد تركيز الاتزان طيفيا بوساطة تقنية الأشعة المرئية – الفوق البنفسجية, تم استخدام معادلتي لانكماير وفرندلج الايسوثرميتين على النتائج المستحصلة.

وتم حساب ثابت سرعة التفاعل وطاقة التنشيط لعملية الامتزاز, وكذلك زمن الاتزان الذي وجد بأنه يصل الى 70 دقيقة.

وجد ان ΔH^o ومن خلال قيم الانثالبي ΔS^o و ΔH^o و ΔG^o من خلال تاثير درجة الحرارة تم حساب الدوال الثرموديناميكية عملية الامتزاز هي عملية باعثة للحرارة.

Introduction :

The current theories of surface reactions are still loosely supported and only some of the background informations and treatments are available. The adsorption from solution into the solid adsorbent is a very important process and it’s represent a very extensive applications both in laboratory and industry, but is still not clearly understood(1-5). Adsorption is affected by temperature and concentration, the extent of adsorption decrease with increase of temperature (6). The variation of extent of adsorption with concentration is given by an empirical isotherms. Isotherms are relations which are used to predict how much solute can be adsorbed by clay. Minerals natural clay such as sepiolite, on the other hand, may be a very good alternative to these materials. Sepiolite has attracted remarkable attention by its sorptive, rheological and catalytic properties (7). A number of investigators studied sorptive properties of various cationic organic reagents with sepiolite (6, 8), but fewer researchers studied the adsorption of anionic reagent with sepiolite(9).

Sepiolite is a clay mineral with a unit cell formula $Si_{12}O_{30}Mg_8(OH,F)_4(H_2O)_4.8H_2O$. In some aspects sepiolite is similar to other 2:1 trioctahedral silicates, such as talc. The molecule formula is $Mg_3Si_4O_{10}(OH)_2$, but it has discontinuities and inversions of the silica sheets that give rise to structural tunnels (9,10). Sepiolite, unlike other clays, is not a layered phyllosilicate.

This chain-like structure produces needle-like particles instead of plate-like particles like other clays, Figure (1).

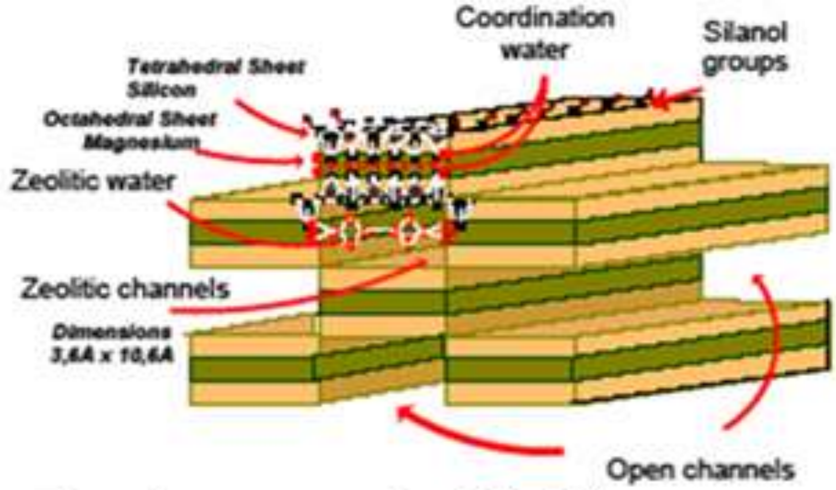

Figure 1: representation of Sepiolite structure.

In addition to that, some isomorphic substitutions in the tetrahedral sheet of the lattice of the mineral, such as Al^{3+} instead of Si^{4+}, form negatively charged adsorption sites. In an environmental engineering and especially drinking water treatment application. The most commonly used isotherm is Freundlich (11). Hydrophobic ionisable organic compounds such as; amines and phenols may occur both in an ionised and neutral form, depending on the pH value of the aqueous media, this phenomena is deeply influences their solubility in the ground waters and consequently their transport mechanisms in the aquifer. A great efforts has been directed toward understanding the adsorption of variety of hydrophobic pollutants (12). Organics are of great concern in water treatment due to their health and environmental hazard, small quantities of soluble organic and inorganic compounds such as nitro, sulfides, and heavy metals remaining in the waste water following biological or physico- chemical treatment create serious problems. The removal of such materials from waste water becomes a one of the a vital and very important tasks world (13, 14).

The aim of the present study is to investigate the adsorption of p-anisidine “Para amino anisole” using Sepiolite clay, the effect of concentration, temperature, contact time and pH were considered.

Materials and methods:

Materials:

The sepiolite sample was obtained from the general company for geological survey and mining, Baghdad (Iraq). The chemical composition of the sepiolite is given in table (1).

Table 1: Chemical composition of sepiolite clay.

Component	Weight %
SiO_2	51.47
MgO	23.55
Al_2O_3	1.19
Fe_2O_3	1.16
CaO	0.71
NiO	0.43
Loss on ignition	21.49

Para anisidine (para amino anisole) obtained from B. D. H., (91% purity) the structural form of Para anisidine is given in figure (2):

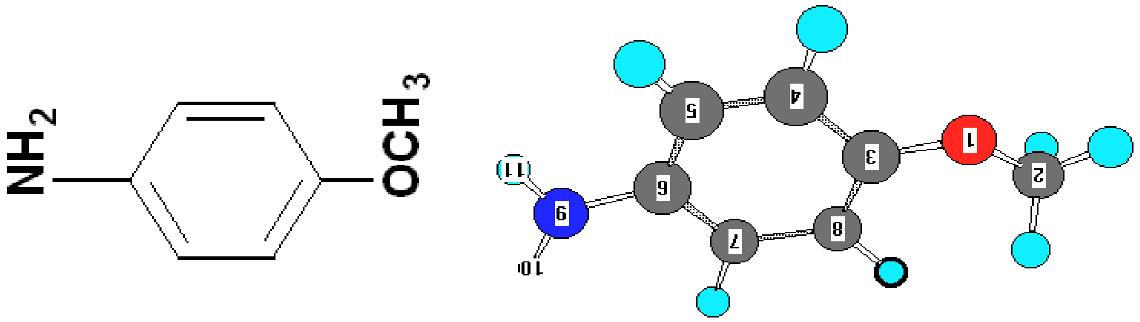

Figure 2: Structure of Para anisidine

Sepiolite sample has been treated before using in the experiments as follows $^{(15)}$: it was suspended in HCl solution of pH=3 to remove carbonate of, it was washed with an excess amount of distilled water to remove soluble materials. Then it was dried in the oven at 383K for ten hours, ground then sieved by 90 µm sieve. The particles under 90 µm are used in further experiment.

The following instruments were used in this study:

1.Digital balance, Sartoris ,BP 3015 (Germany).
2.Uv-Visible Spectrophotometer, Single Beam, Pye Unicam-8700.
3.Shaker Water Bath, SB. 4, Tecam.
4.Digital pH-Meter ,Hanaa, Roman
5.Oven, Heracus (D-6450), Hanau, (England).

Methods:

The adsorption isotherms have been determined by allowing PA solution of known initial concentration to be mixed with accurately weighed amount of sepiolite in a tightly closed flask at certain temperature and pH.The amount of sepiolite in the slurry has been 0.3 gm / 250ml solution. A constant mixing at a constant temperature and pH was achieved using a shaker water bath. The sepiolite – solution have been equilibrated for 2 hours, clay suspensions have been then filtered and the supernatant solution was subjected to analysis using ultraviolet – visible technique (uv - visible), the amount of PA retained by sepiolite was calculated from the relation :

$$Qe=\frac{(C_o-C_t)*V(L)}{m(gm)}..........(1)$$

Where C_o is the initial concentration and C_e is the equilibrium concentration (mg/L), V(L) is the volume of PA and m (gm) is the weight of sepiolite clay. The same experiment was repeated at different initial concentrations, temperatures and pH. The adsorption rate data at different temperatures and initials pH values have been obtained by allowing the sepiolite –solute (0.3 gm of clay / 250 ml of solute) to be mixed in the shaker water bath, the initial concentration of PA was 4 mg/L. During the experiments, samples of the solution have been periodically withdrawn at a definite time period (10, 20, 30, 40, 50, 60, 70 and 80 min.), filtered and the concentration of PA is measured at each time using uv- visible technique at 390 nm.

Results and Discussion:

Effect of initial dye concentration and contact time:

The experimental results of adsorption of para anisidine on the sepiolite clay at various initial concentrations (1, 2, 3, 4, 5, and 6 mg/L) with time were obtained and the equilibrium data collected (table 2 and 3), reveal that the percent adsorption decreases with the increase in the initial para anisidine concentration, while the actual amount of para anisidine adsorbed per unit mass of sepiolite increased with the increase in para anisidine concentration. This gives an indication that the adsorption is highly dependent on the initial concentration of para anisidine. Because at lower concentration, the ratio of the initial number of para anisidine molecules to the available surface area is low, the fractional adsorption become independent on the initial concentration. However, at high concentration the available sites of adsorption become independent on the initial concentration(16).

Initial Con. C_o(mg/L)	**298K**		**308K**		**318K**	
	C_e mg/L	**Q_e mg/g**	**C_e mg/L**	**Q_e mg/g**	**C_e mg/L**	**Q_e mg/g**
1	0.248	0.626	0.36	0.533	0.44	0.466
2	0.76	1.03	0.82	0.983	0.91	1.09
3	1.11	1.575	1.32	1.4	1.41	1.325
4	1.645	1.962	1.73	1.891	1.91	1.74
5	2.01	2.49	2.2	2.33	2.44	2.133
6	2.65	2.79	2.89	2.59	3.02	2.483

Table (2) adsorption isotherms values of para anisidine on the Sepiolite clay surface at different temperatures, and pH=7.

Initial Con. C_o(mg/L)	**pH = 4**		**pH = 7**		**pH = 10**	
	C_e mg/L	**Q_e mg/g**	**C_e mg/L**	**Q_e mg/g**	**C_e mg/L**	**Q_e mg/g**
1	0.134	0.721	0.248	0.626	0.461	0.449
2	0.57	1.191	0.76	1.03	1.02	0.816
3	0.91	1.74	1.11	1.575	1.42	1.316
4	1.42	2.15	1.645	1.962	1.98	1.683
5	1.84	2.63	2.01	2.49	2.43	2.14
6	2.33	3.05	2.65	2.79	3.04	2.46

Table (3) adsorption isotherms values of para anisidine on the Sepiolite clay surface at different pHs, and 298K

The equilibrium is reached after 70 minutes for all the conditions applied (i.e: pH= (3, 7 and 10)), and temperature (298K, 308K and 318K). an example for the effect of time for a certain initial concentration of para anisidine [C_O= 4 mg/L] is shown in figure 3.

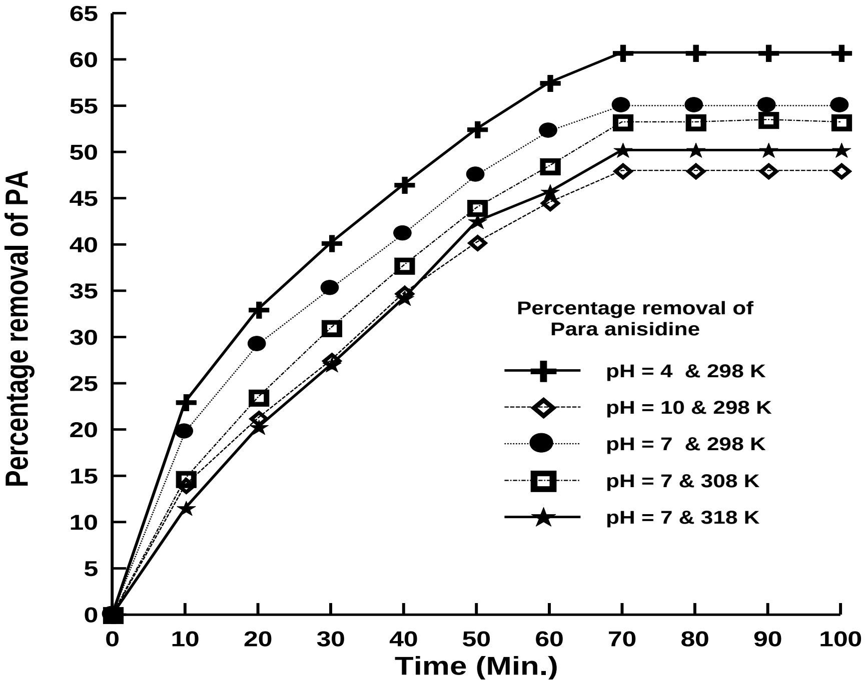

Figure 3 : Effect of contact time on the adsorption of PA (4 mg/L) by sepiolite surface with variable temperature and pH.

Adsorption isotherm:

The experimental data are analyzed according to the linear form of the Langmuir and Freundlich isotherms.

The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{Q_e} = \frac{b}{Q_m} + \frac{C_e}{Q_m} \text{..........(2)}$$

Here C_e is the equilibrium concentration (mg/L), Q_e is the amount adsorbed at equilibrium (mg/gm) and Q_m and b are Langmuir constants related to the adsorption efficiency and energy of adsorption, respectively. The linear plots of $\frac{C_e}{Q_e}\cdot$ versus C_e suggest the applicability of the Langmuir isotherms as shown in figures (4 and 5). The values of Q_m and b are determined from the slope and intercept of the plots and the results are shown in table (4), from the results, it is clear that the values of adsorption efficiency Q_m is decreasing with temperature increasing. From the values we can conclude that the maximum adsorption corresponds to a saturated mono layer of adsorbate molecules on an adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface occurs. The trend shows that the adsorbent prefers to bind acidic ions and that specially predominates on sorbent characteristics, when ion exchange is the predominate mechanism.

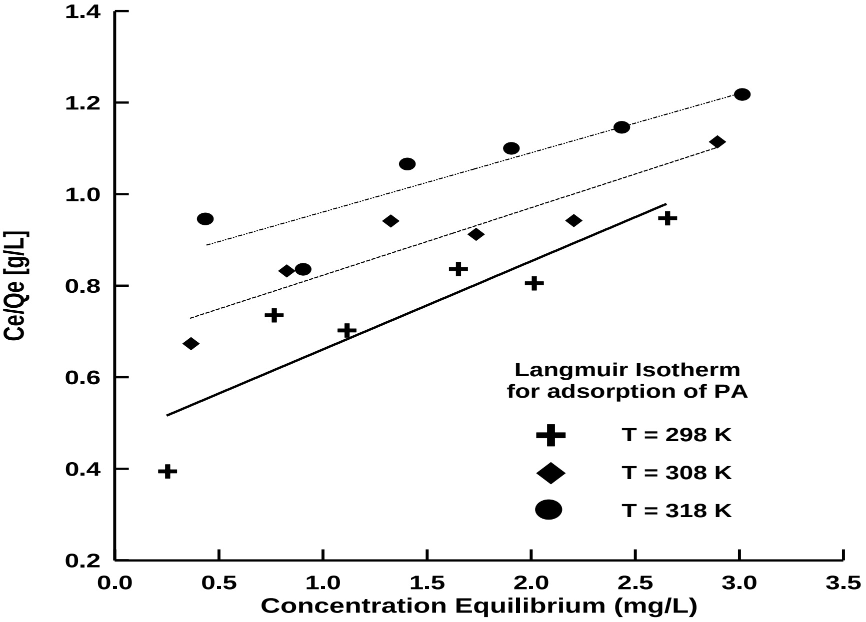

Figure 4: linearized Langmuir plot for PA on sepiolite surface at different temperatures.

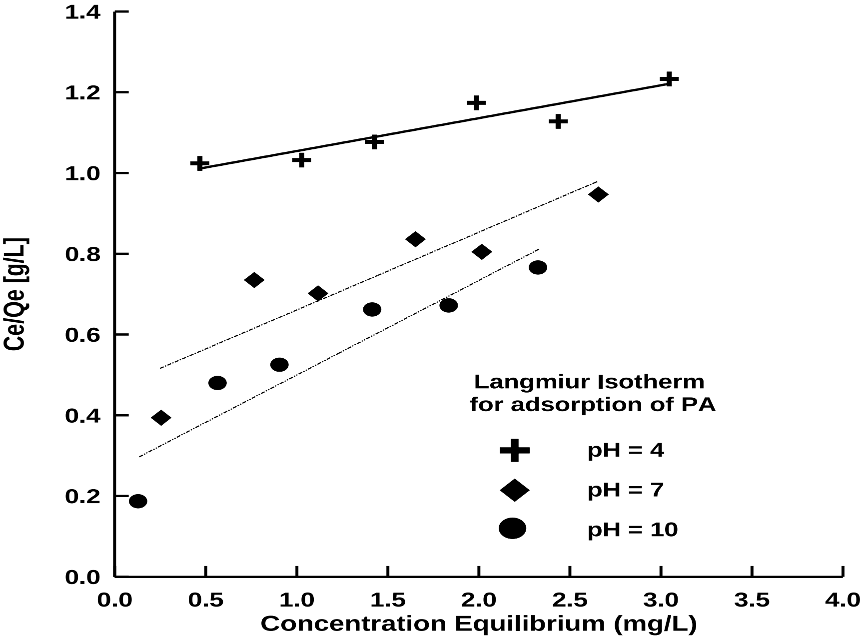

Figure 5: linearized Langmuir plot for PA on sepiolite surface at different pHs.

The Freundlich equation is also applied to study the behavior of the adsorption of para anisidine on the adsorbent. The Freundlich isotherm is represented as:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \text{..........(3)}$$

Here Q_e is the amount of para anisidine adsorbed (mg/gm), C_e is the equilibrium concentration of para anisidine in the solution (mg/L) and K_f and n are constants, incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plot of ln Q_e versus ln C_e as shown in figures (6 and 7) shows that the adsorption of para anisidine follows also the Freundlich isotherm. The values of **K_f** and **n** are given in table (4).

Table4. Freundlich and Langmuir constants for different PHs, and temperatures of para anisidine on the sepiolite surface.

Temp (K)	pH	Freundlich constants of para anisidine			Langmuir constants of para anisidine		
		1/n	K_f	R^2	b	Q_m	R^2
298	**7**	0.657	1.450	0.9759	2.429	5.192	0.7972
308	**7**	0.788	1.170	0.9937	4.580	6.780	0.8753
318	**7**	0.842	1.010	0.9819	6.430	7.754	0.8013
298	**4**	0.935	0.894	0.9728	11.955	12.28	0.8674
298	**10**	0.509	1.850	0.9896	1.133	4.269	0.8678

The intensity of adsorption gives an indication for the bond energies between para anisidine and the adsorbent predicting the possibility of a slight chemisorption rather than physisorption, and the possibility of multilayer adsorption of para anisidine cannot be related out.

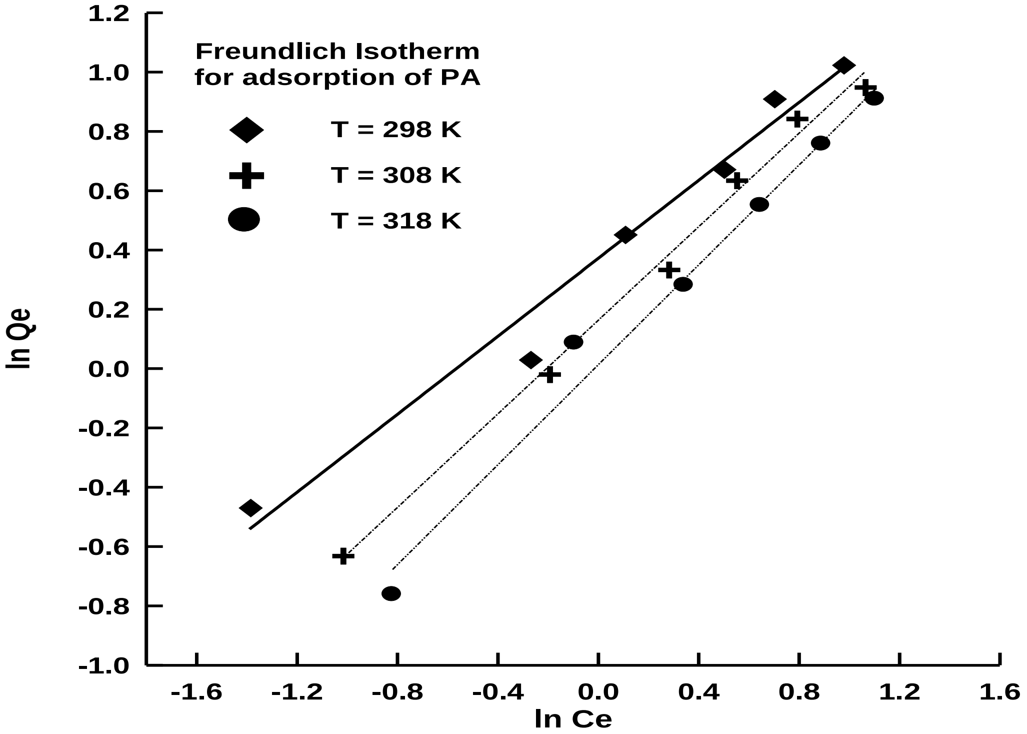

Figure 6: Linearized Freundlich plot of PA adsorption on Sepiolite surface at different temperature.

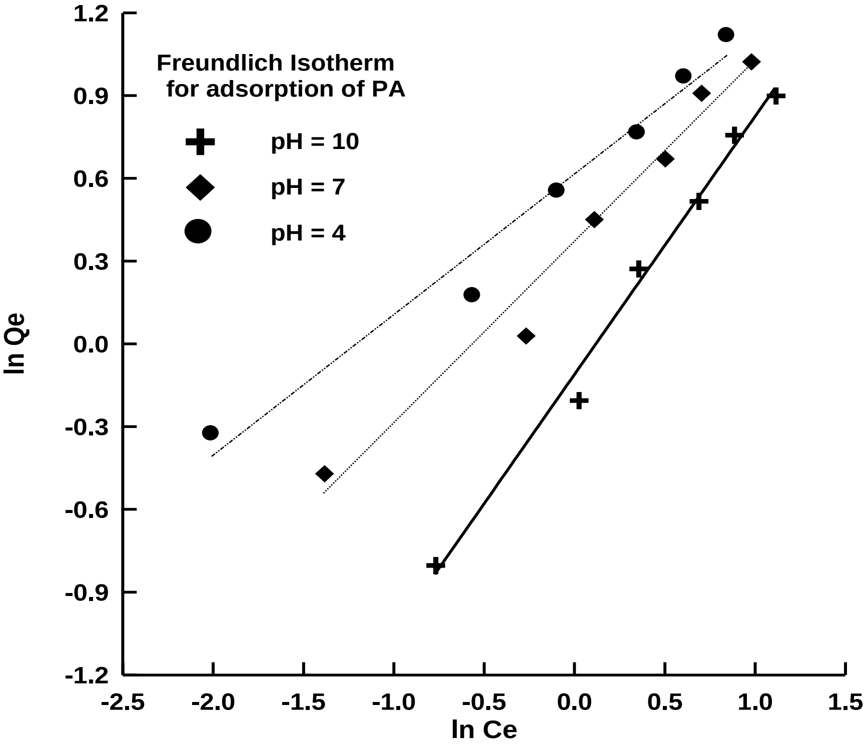

Figure 7: Linearized Freundlich plot of PA adsorption on Sepiolite surface at different pHs .

The adsorption isotherms of para anisidine from aqueous solution on the sepiolite surface at (298, 308, and 318 K) and pH=7 is shown in figure 9 also various and that at pH values (4, 7, and 10) and temperature equal to 298 K is shown in figure 9.

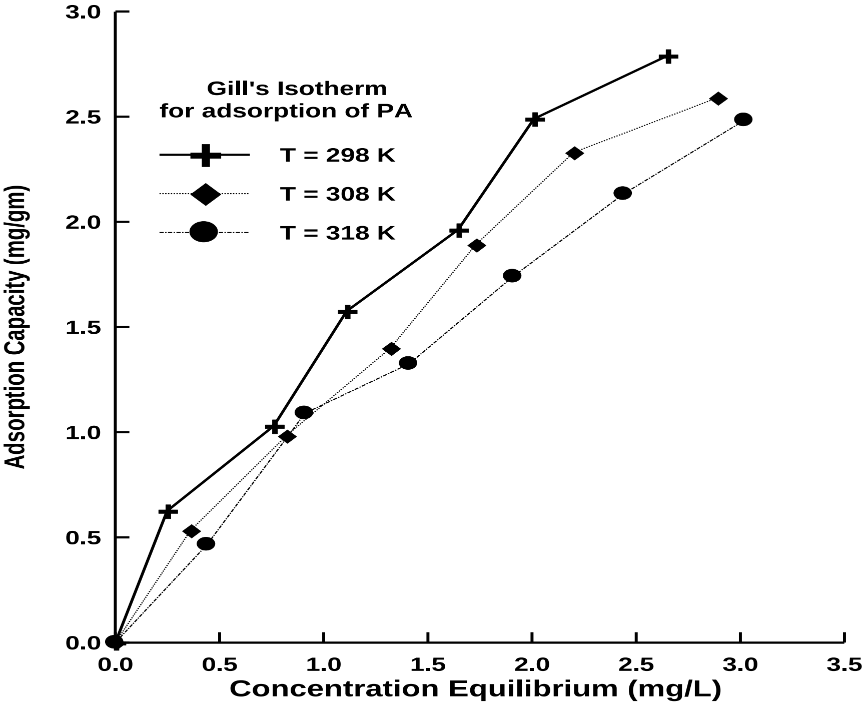

Figure 8. adsorption isotherm of para anisidine by sepiolite clay at different temperatures.

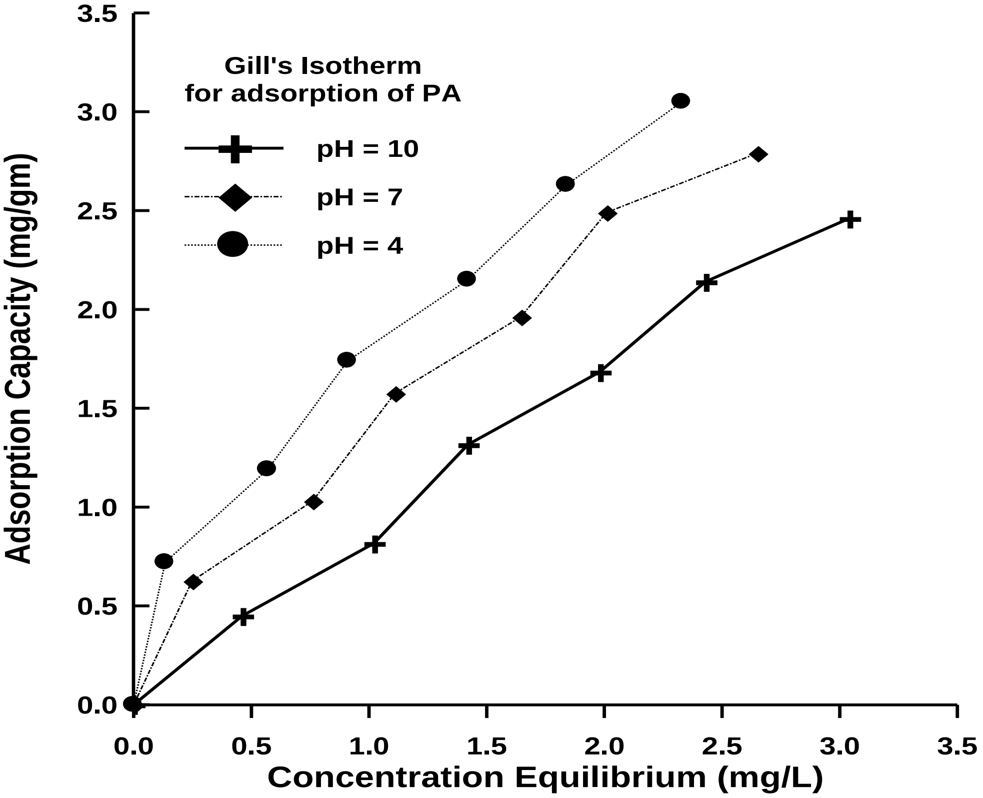

Figure 9. adsorption isotherm of para anisidine by sepiolite clay at different pH values.

Thermodynamic parameters such as standard enthalpy (ΔH^o), standard free energy (ΔG^o), and standard entropy (ΔS^o) for using para anisidine adsorption by sepiolite were calculated using the following equations:

$$\ln X_m = \ln \bar{X}_m - \frac{\Delta H^o}{RT} \text{..........(4)}$$

$$\ln X_m = -\frac{\Delta G^o}{RT} \text{...........(5)}$$

x_m is the maximum adsorption , T is the temperature in (Kelvin) and R is the gas constant 0.008314 $Kj.K^{-1}.mole^{-1}$, the value of standard enthalpy (ΔH^o) is determined graphically by plotting ln x_m versus 1/T which gives a straight line (figure 10) and the values of standard free energy (ΔG^o), and standard entropy (ΔS^o) computed numerically are presented in table (5).

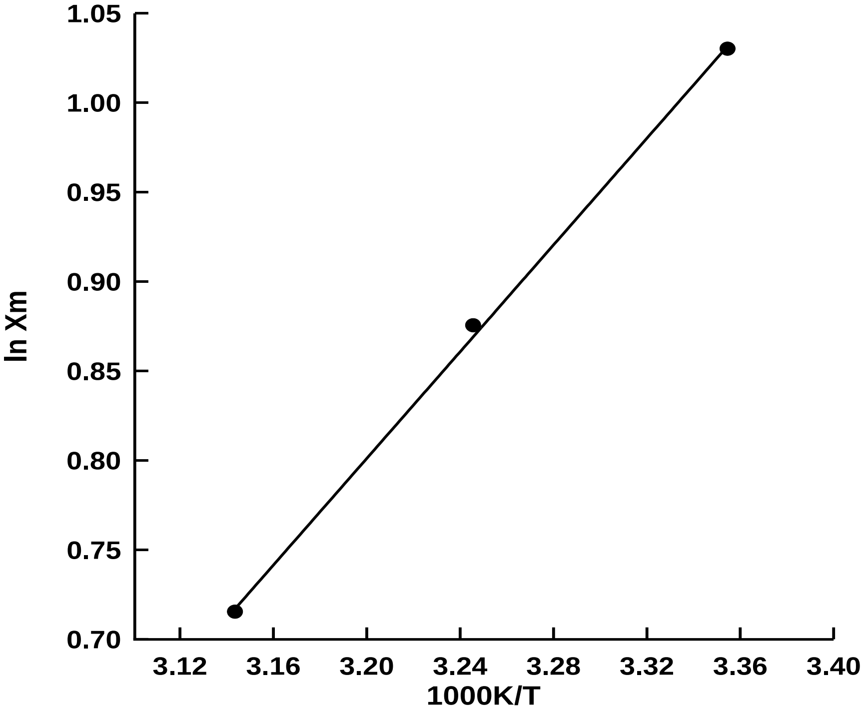

Figure 10: Plot of ln Xm versus 1000 K/T of PA on Sepiolite surface surface.

Table 5. Thermodynamic functions ΔG^o, ΔS^o and, ΔH^o of para anisidine on the adsorbent surface sepiolite clay at pH=7 and 298 K.

ΔG^o (kJ mole^{-1})	**ΔS^o (J mole^{-1} K)**	**ΔH^o (kJ mole^{-1}) x 10^3**
- 0.127	0.384	- 12.393

It has been shown from table 5 that the standard free energy (ΔG^o) is very small and negative, which indicates that better adsorption is obtained at low temperature. The positive value of standard entropy (ΔS^o) may be due to some structural changes in both of the adsorbents and adsorbates during the adsorption process.

Mechanism behavior of adsorption of para anisidine

In order to investigate the mechanism of sorption, kinetic models have been used to test experimental data. The kinetic model in this study includes the pseudo – first order equation.
The pseudo–first order equation of Lagergreen is generally expressed as follows(17, 18):

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)..........(6)$$

Where Q_e and Q_t are the sorption capacity at equilibrium and at time t, respectively (mg.gm^{-1}) and k is the rate constant of pseudo first order sorption (min^{-1}). After integration and applying boundary conditions t=0 to t = t and Qt=0 to Qt=Qt, the integrated form of eq(6) becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - kt..........(7)$$

The value of rate constant for the pseudo first order reaction is calculated experimentally by plotting $\ln(Q_e - Q_t)$ against time of the adsorption of para anisidine into sepiolite clay according to eq (7), results are shown in figure (11) and values of rate constants are illustrated in table (6).

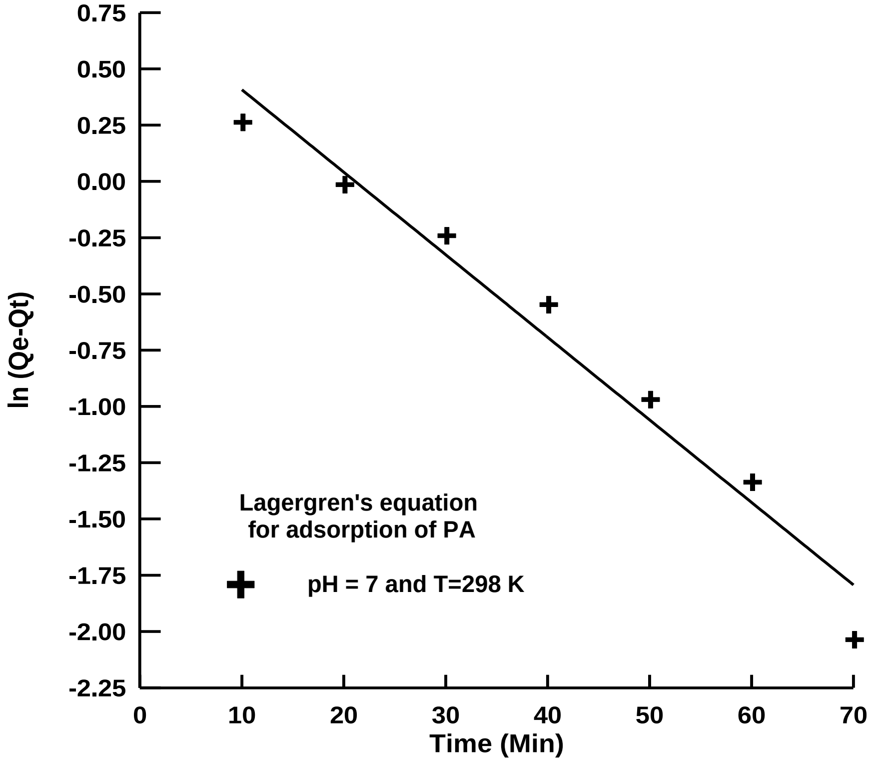

Figure 11: Pseudo- first order adsorption kinetic of Para anisidine on the sepiolite surface at 298 K.

Effect of temperature :

The adsorption experiments were repeated at various temperatures in the range of 298 to 318 K with the sepiolite clay at neutral pH. The equilibrium adsorption capacity Q_e of para anisidine decreases from 1.96 to 1.75 mg/gm with increasing temperature from 298 to 318 K, which indicate at low temperature the removal of para anisidine is favored by sorption onto sepiolite clay sorbent. This may be due to the tendency for the para anisidine molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution.(19, 20) The value of rate constant K, (0.036675 to 0.0456014 min^{-1}) that determined from figure (12) , were found to be increased when temperature increased from 298 to 318K, and the values of rate constants are illustrated in table (6).

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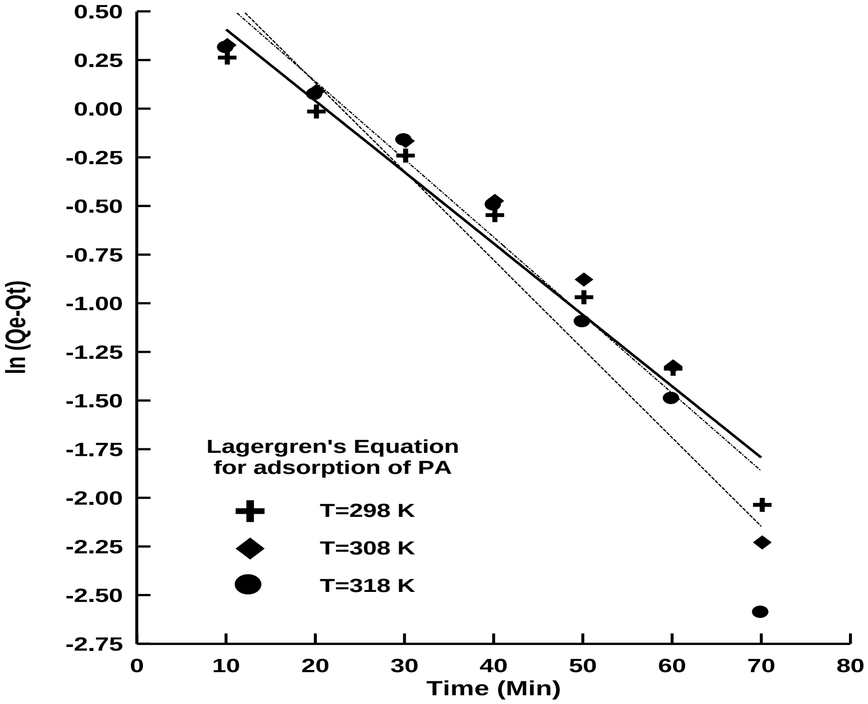

Figure 12 : Pseudo- first order adsorption kinetic of Para anisidine on the sepiolite surface at different temperature.

The sorption rate constant may be expressed as a function of temperature by following the relationship:

$$\ln k = \ln A - Ea / RT \text{..........}(8)$$

Where k is the rate constant of sorption (min^{-1}), Ea is the activation energy of sorption (KJ/mole), R is the gas constant (0.008314 $\text{KJ.K}^{-1}.\text{mole}^{-1}$), T is solution temperature (K). The k_a values for the pseudo first order were plotted as a function of reciprocal of the Kelvin temperature. Linear variation were observed as shown in figure (13)

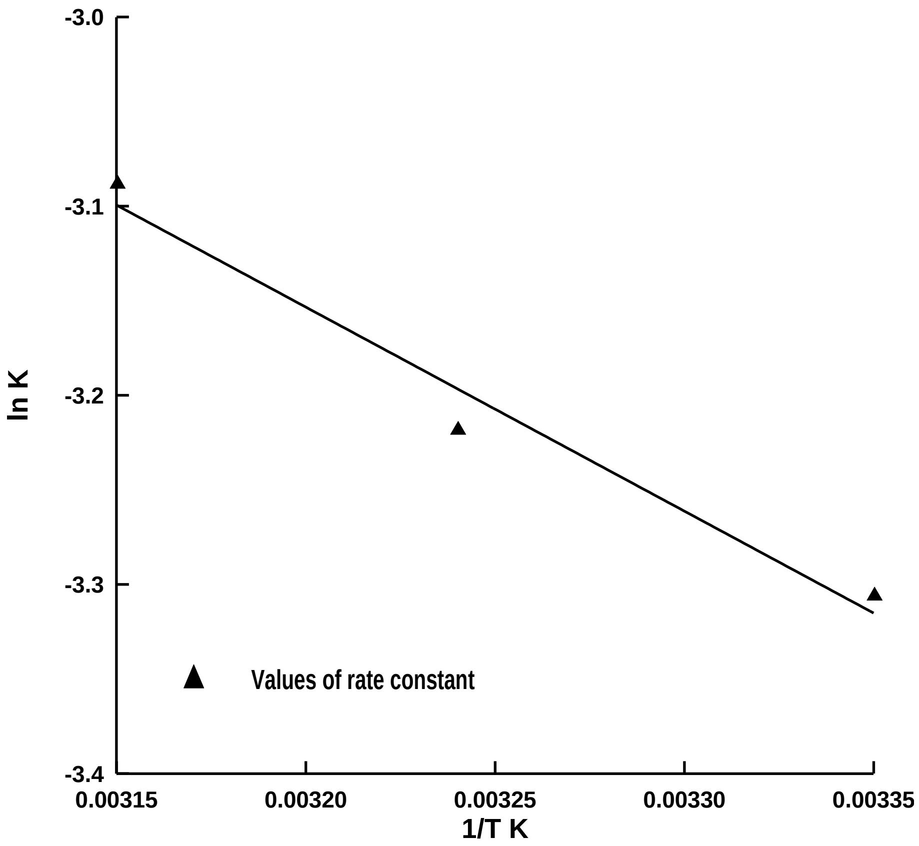

Figure 13 : Relationship for Arrhenius equation to calculate the activation energy for pseudo first order reaction by effect of temperature.

The value of activation energy of adsorption obtained is (1.078 KJ/mole), Since sorption is an exothermic process, it would be expected that an increase in solution temperature would result in a decrease in adsorption capacities.

Effect of pH:

The rate of para anisidine sorption onto sepiolite clay sorbent will be varied on varying the pH values of the solution when.

The pH values used in these studies are 4, 7 and 10 for the adsorption of para anisidine (4 mg/L) with sepiolite clay sorbent.

The rate constant, k, of sorption at different pH values has been calculated from figure (14) and the results are illustrated in table (6).

Y
Y

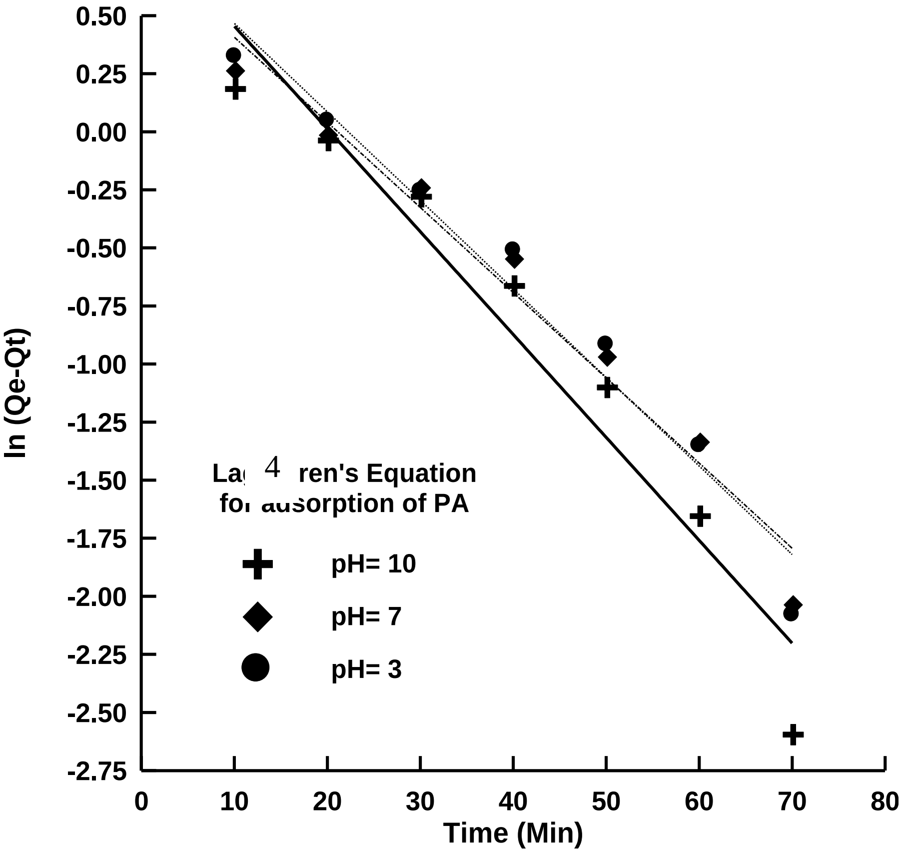

Figure 14: Pseudo- first order adsorption kinetic of Para anisidine on the sepiolite surface at different pHs.

Table 6: Rate constants and equilibrium adsorption capacities for effect of initial pHs and different temperatures on the sorption of para anisidine (4 mg/L).

pH	**Temperature (K)**	**Q_e (mg/gm)**	**K_{ads}(min^{-1})**
7	298	1.962	0.03667
7	308	1.891	0.04003
7	318	1.74	0.04560
4	298	2.63	0.03811
10	298	2.14	0.04427

Conclusions:

The equilibrium and the dynamics of the adsorption of para anisidine on the sepiolite clay surface, have been investigated. The sepiolite clay shown very high adsorption capacities to remove the para anisidine, whose maximum monolayer adsorption capacity ranged from 0.62 to 2.49 (g/kg) at 298K and pH=7 . The adsorption capacities were significantly affected by the initial para anisidine concentration and pH. The uptake increased with the increase in the initial para anisidine concentration and with decreases in pH. The Freundlich equation agrees very well with the equilibrium isotherm also Langmuir equation give accepted linearity. The pseudo first-order kinetic model fits very well with the dynamical adsorption behavior of this compound in solution with different parameters such as temperatures and pHs. From the values of thermodynamic parameter indicates this adsorption process is physisorption.

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