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Kinetic study for adsorption of para nitroaniline (PNA) on Bentonite clay surface

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Abstract

In this study, the removal of para nitroaniline (PNA) from aqueous suspension of bentonite was investigated as a function of pH, concentration and temperature. Adsorption process was attained to the equilibrium within 65 minutes which investigated by using uv-visible spectrophotometer technique.

The adsorbed amount of para nitroaniline (PNA) decreased as the temperature and pH increased .

The Dubinin-Rasdushkevich (D-R) isotherm equation was applied to the data and values of parameters of this isotherm equation was calculated.

The mean energy of adsorption E_{ads}, was also calculated from the adsorption energy constant $K^{/}$. It's Value determined from the D-R isotherm equation.

The rate constant for adsorption and activation energy value for the adsorption process was calculated at neutral pH.

الخلاصة

في هذه الدراسة تم إزالة مركب البارا نايترو أنلين بوساطة سطح طين البنتونايت كدالة لدرجة الحرارة والتركيز والدالة الحامضية.

تم تحديد زمن الاتزان لعملية الامتزاز باستخدام تقنية مطيافية امتصاص الأشعة المرئية – فوق البنفسجية ووجد بأنه مساو الى 65 دقيقة.

ووجد ان كمية الامتزاز تقل مع زيادة درجة الحرارة والدالة الحامضية، تم تطبيق معادلة (D-R) الايسوثرمية و من خلال هذه المعادلة تم حساب معدل طاقة الامتزاز وذلك من خلال ثابت طاقة الامتزاز.

تم حساب ثابت سرعة التفاعل لعملية الامتزاز وطاقة التنشيط في الوسط المتعادل.

Introduction

Hydrophobic ionizable organic compounds such as; amines, carboxylic acids and phenols may occur both in ionised and neutral form depending on the pH value of the aqueous media(1-3).

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 sulfides, nitro and heavy metals remaining in the waste water(4)

There are different methods to purification of water such as using oxidation chemicals for water treatment by using strong oxidizing agent as ozone(5), molecular oxygen(6), and hydrogen peroxide(7).

The variation of extent of adsorption with concentration is given by an empirical isotherms. The most efficient and commonly used adsorbent is activated carbon (8). However, activated carbon is costly and has regeneration problems. Recent investigations have focused on the use of low-cost materials such as rice hulls (9), coconut husk (10), maize cobs (11), and chitin (12)

In this study, we have investigated the possibility of using bentonite clay to remove para nitroaniline (PNA) from aqueous solution.

Materials and methods

Materials:

Bentonite clay used in this study was obtained from the General Company for Geological Survey and Mining, Baghdad, Iraq, have the general structure consisting mainly $Al_2O_2.4SiO_2.H_2O$ (13), the chemical analysis of bentonite is listed in Table (1).

Table 1. The chemical analysis of bentonite

Constituent	Wt% .
SiO_2	54.66
Al_2O_3	14.65
CaO	4.77
Fe_2O_3	4.88
MgO	6
Na_2O	0.65
SO_3	1.2
Loss on ignition	13.06

Para nitroaniline (PNA) obtained from B. D. H., (92% purity),bentonite sample has been treated before using in the experiments as follows (14): it was suspended in HCl solution of pH of 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 110^0C for ten hours, ground then sieved by 90 µm sieve. The particles under 90 µm are used in present work.

Spectronic – 21 mode u.v-visible single beam with 1 cm cells Bausch and lomb (USA) was used for all absorbance measurements, pH measurements were made with Knick digital pH meter (England), Digital balance, Sartorius, (BP 3015 - Germany) and shaker water bath, SB. 4, Tecam were used.

Methods:

The adsorption isotherms have been determined by allowing PNA solution of known initial concentration to be mixed with accurately weighed amount of bentonite in a tightly closed flask at certain temperature and pH.

The amount of bentonite in the slurry has been 0.05 gm / 20ml solution. A constant mixing at a constant temperature and pH was achieved using a shaker water bath.

The adsorption rate data at different temperatures and initials pH values have been obtained by allowing the bentonite –solute (0.05 gm of clay / 20 ml of solution) to be mixed in the shaker water bath, the initial concentration of PNA was 25 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 PNA solution is measured at each time using uv- visible technique.

The bentonite – solution have been then 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 maximum absorption for PNA at 450 nm., as shown in figure 1.

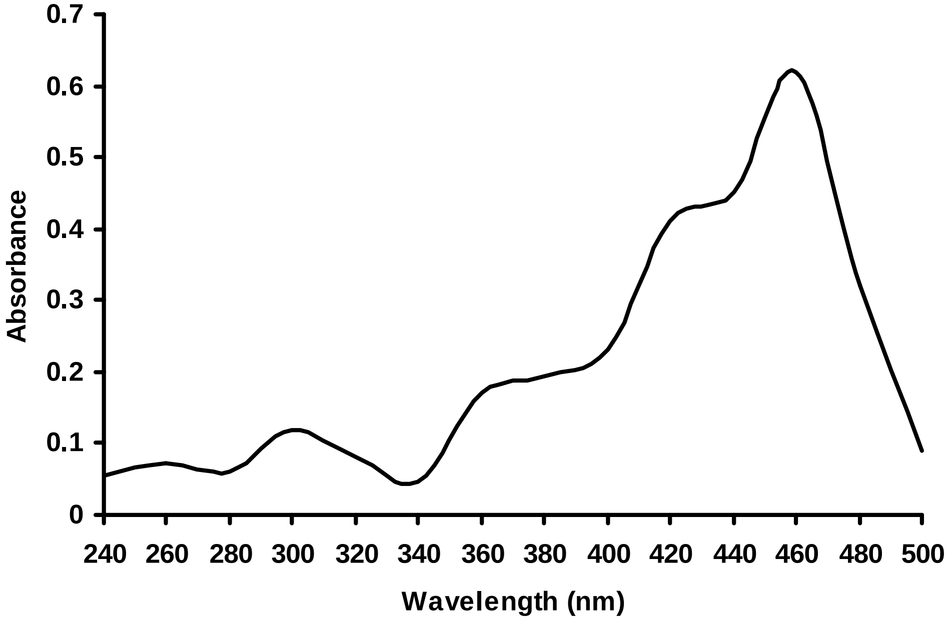

Figure 1: uv- visible spectrum of PNA

The amount of PNA retained by bentonite was calculated from the relation :

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

Where C_o is the initial concentration and C_e is the equilibrium concentration (mg/L), V(L) is the volume of PNA solution and m (gm) is the weight of bentonite clay.

Results and Discussion

Effect of initial concentration and contact time

The experimental results of adsorption of para nitroaniline on the bentonite clay at various initial concentrations (5-50 ppm) with time obtained and the equilibrium data collected in table (2 and 3), reveal that the adsorption percent decreases with the increase in the initial para nitroaniline concentration, while the actual amount of para nitroaniline adsorbed per unit mass of bentonite increased with the increase in para nitroaniline concentration.

This gives an indication that the adsorption is highly dependent on the initial concentration of para nitroaniline. Because at lower concentration, the ratio of the initial number of para nitroaniline 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(15,16).

The equilibrium is reached after 70 minutes for all the conditions applied (i.e: pH= (4, 7 and 10)), and temperature (298K, 308K and 318K), because at this time almost the active sites are found on the external surface of bentonite clay have been saturated, an example for the effect of time for a certain initial concentration of para nitroaniline [C_o= 25 mg/L] shown in figures 2 and 3 at different temperatures and neutral pH.

Table 2. adsorption isotherms values of para nitro aniline on the bentonite clay surface at different temperatures, and pH=7.

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
5	1.70	1.32	1.87	1.25	2.00	1.20
10	4.10	2.36	4.35	2.26	4.54	2.18
15	6.72	3.31	6.90	3.24	7.20	3.12
20	9.43	4.23	9.67	4.13	9.81	4.07
25	12.80	4.88	13.06	4.77	13.20	4.72
30	15.70	5.70	16.00	5.63	16.30	5.48
35	18.30	6.68	18.61	6.55	18.96	6.42
40	21.90	7.24	22.30	7.10	23.00	7.00
45	26.00	7.60	26.40	7.44	26.90	7.24
50	30.00	8.00	30.10	7.92	31.30	7.52

Table 3. adsorption isotherms values of para nitro aniline on the Bentonite clay surface at different pHs, and 298K

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
5	1.00	1.60	1.70	1.32	2.10	1.16
10	2.89	2.84	4.10	2.36	4.60	2.16
15	5.62	3.75	6.72	3.31	7.20	3.12
20	6.11	5.55	9.43	4.23	10.20	3.72
25	6.89	7.24	12.80	4.88	13.00	4.80
30	10.21	7.92	15.70	5.70	16.10	5.56
35	14.34	8.26	18.30	6.68	19.00	6.40
40	18.70	8.52	21.90	7.24	22.20	7.12
45	23.40	8.64	26.00	7.60	26.60	7.36
50	28.00	8.80	30.00	8.00	31.00	7.44

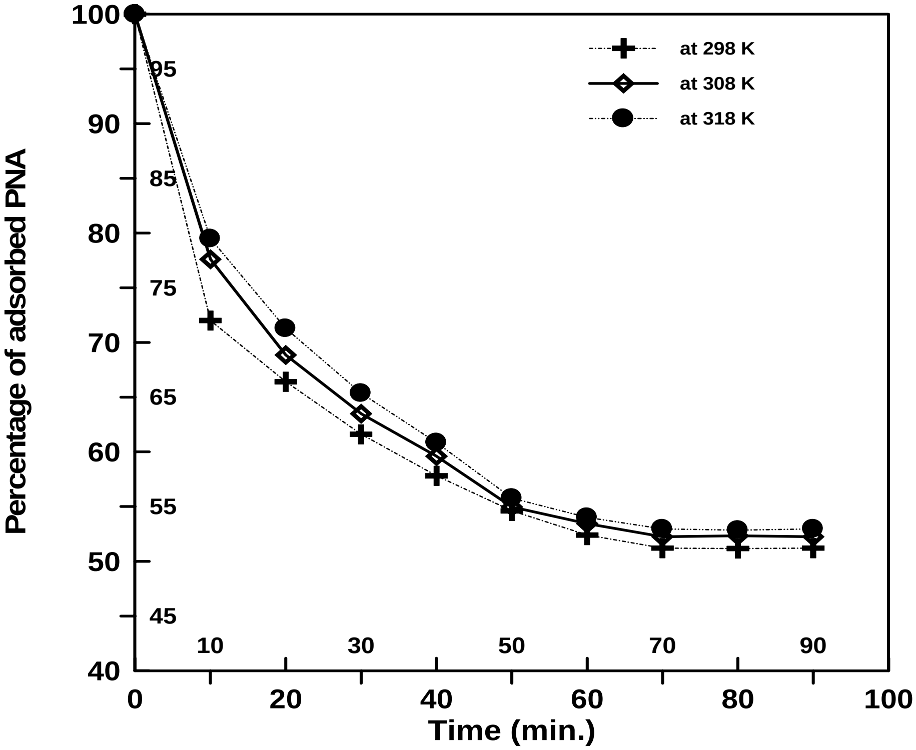

Figure 2: Effect of contact time by using adsorbed percentage of PNA (25 mg/L) on bentonite at different temperature and pH7.

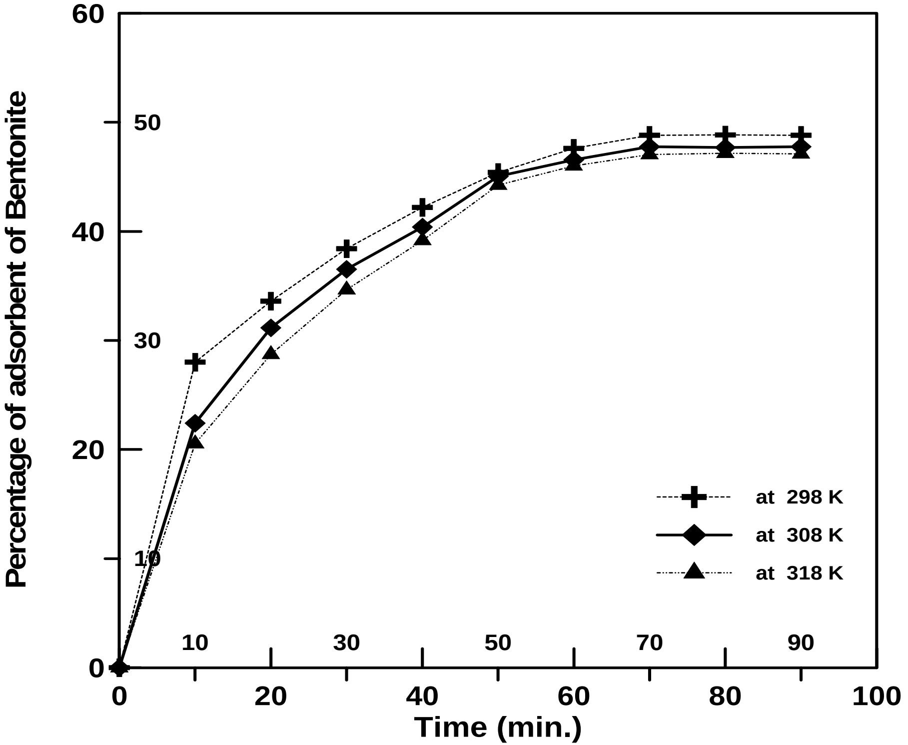

Figure 3 : Effect of contact time by using adsorbed percentage of bentonite for removal of PNA (25 mg/L) at different temperature and pH7.

Mechanism behavior of adsorption of para nitroaniline

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$^{(17)}$:

$$\frac{dQ_t}{dt} = k(Q_e - Q_t)..........(2)$$

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 Q_t=0 to Q_t=Q_t, the integrated form of eq(2) becomes:

$$\ln(Q_e - Q_t) = \ln Q_e - kt..........(3)$$

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 nitroaniline into bentonite clay according to eq (2), results are shown in figure (4) and values of rate constants are illustrated in table (4).

Effect of temperature on adsorption kinetics

The adsorption experiments were repeated at different temperatures [298, 308 and 318 K] with the bentonite clay at neutral pH.

The equilibrium adsorption capacity Q_e of para nitroaniline decreases from 4.88 mg/gm to 4.72 mg/gm with increasing temperature from 298 to 318 K, which indicate at low temperature the removal of para nitroaniline is favored by sorption onto bentonite clay sorbent.

This may be due to the tendency for the para nitroaniline molecules to escape from the solid phase to the bulk phase with an increase in temperature of the solution.

The value of rate constant K_{ad}, are calculated experimentally from figure (4) , were found to be increased when temperature increased from 298 to 318K, and the values of rate constants are illustrated in table (4).

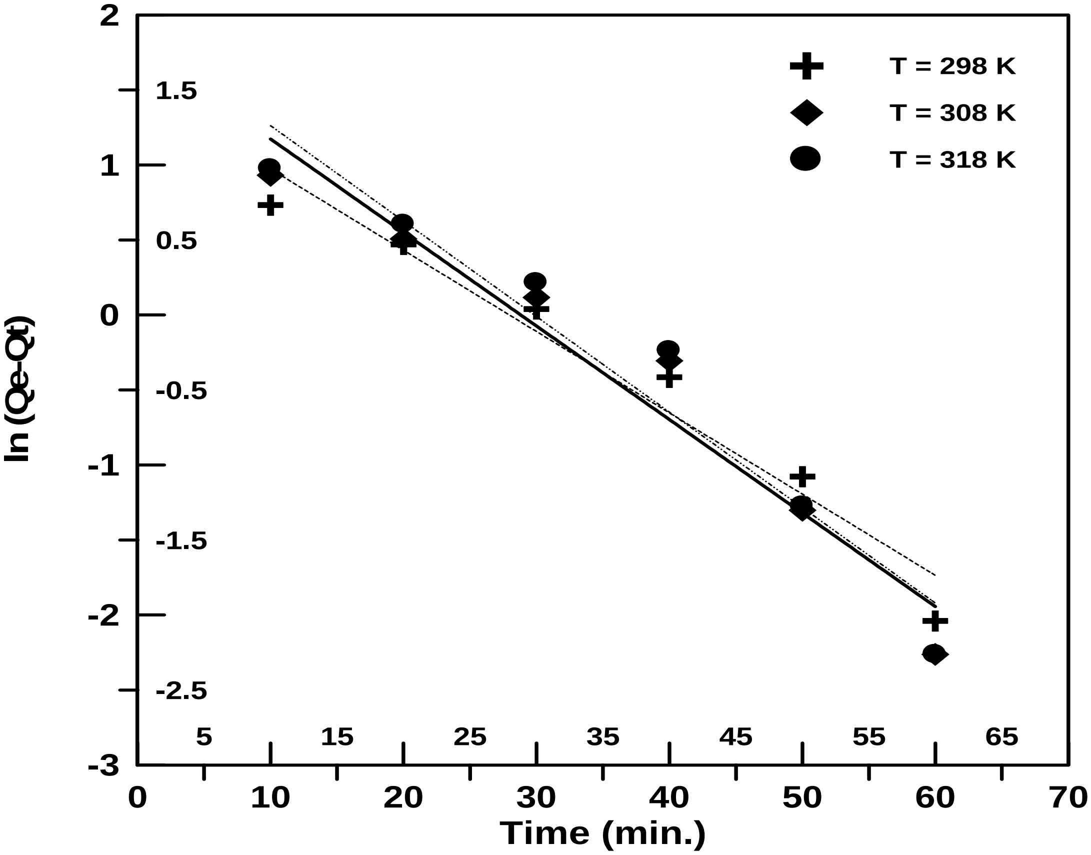

Figure 4 : Pseudo- first order adsorption kinetic of Para nitro aniline on the bentonite surface at different temperature and pH7.

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

$$\ln k_a = \ln A - Ea / RT..........(4)$$

Where k is the rate constant of sorption (min^{-1}), Ea is the activation energy of sorption (kJ.mol^{-1}), R is the gas constant (0.008314 kJ K^{-1} mol^{-1}), T is solution temperature (K).

The ln k_{ad} 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 (5)

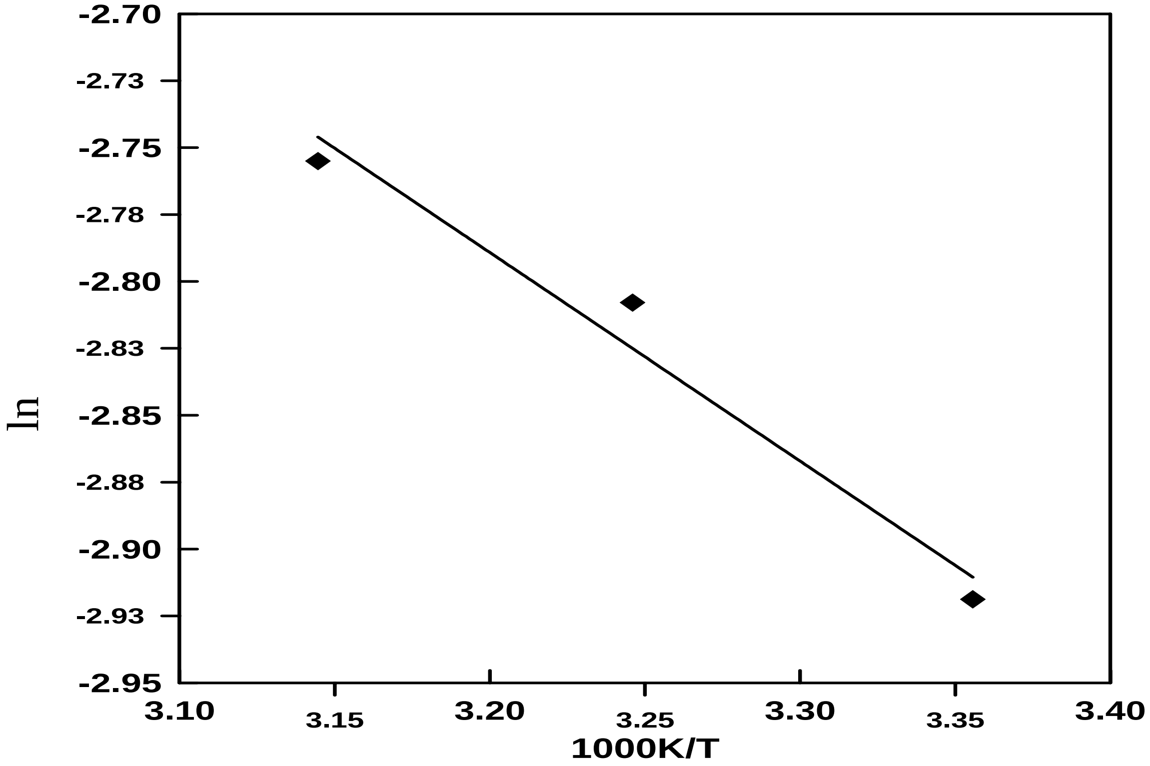

Figure 5: Relationship for Arrhenius equation to calculate the activation energy for pseudo first order reaction by effect of temperature at pH of 7.

The value of activation energy of adsorption obtained is **(6.4765 kJ.mol^{-1})**, Since sorption is an exothermic process, it would be expected that an increase in solution temperature would result in a decrease in adsorption capacities.

Table 4. Rate constants and equilibrium adsorption capacities for effect of different temperatures on the sorption of para nitroaniline (25 mg/L).

pH	**Temperature (K)**	**Q_e (mg/gm)**	**K_{ads}(min^{-1})*10^2**
7	298	4.880	5.410
7	308	4.776	6.033
7	318	4.720	6.360

The adsorption data thermodynamically were tested by Dubinin-Radushkevich (D-R)(18) adsorption isotherm.

This isotherm is more general than the Langmuir isotherm since it does not assume a homogenous surface or constant sorption potential. The D-R equation is

$$Q_e = X_m^{/} \exp(-K^{/}\varepsilon^2) \text{.............}(5)$$

where ε (polanyi potential)= RT ln (1+1/C$_e$), Q$_e$ is the amount of PNA adsorbed per unit weight of bentonite (mg g^{-1}) at equilibrium, $X_m^{/}$ is the adsorption capacity (mg g^{-1}), C$_e$ is the equilibrium concentration of PNA in solution (mg L^{-1}), $K^{/}$ is the constant related to the adsorption energy (mol^2 kJ^{-2}), R is the gas constant (kJ. deg^{-1} mol^{-1}) and T is the absolute temperature (K), the D-R isotherm can be linearized as

$$\ln Q_e = \ln X_m^{/} - K^{/}\varepsilon^2 \text{..........(6)}$$

The data are summarized in figures (6, 7, and 8) and the constants are illustrated table 5.

The mean energy of adsorption, E_{ads}, can be calculated from the $K^{/}$ values (18) using the relation

$$E_{ads} = (2K^{/})^{-0.5} \text{.............(7)}$$

The determined values of E_{ads} are presented in table 5, the calculated mean energy of adsorption, E_{ads}, from the D-R isotherm, gives information about the chemical or physical properties of the sorption.

The calculated mean energy values of adsorption of the PNA by bentonite are very small and this implies that the type of adsorption is physical.

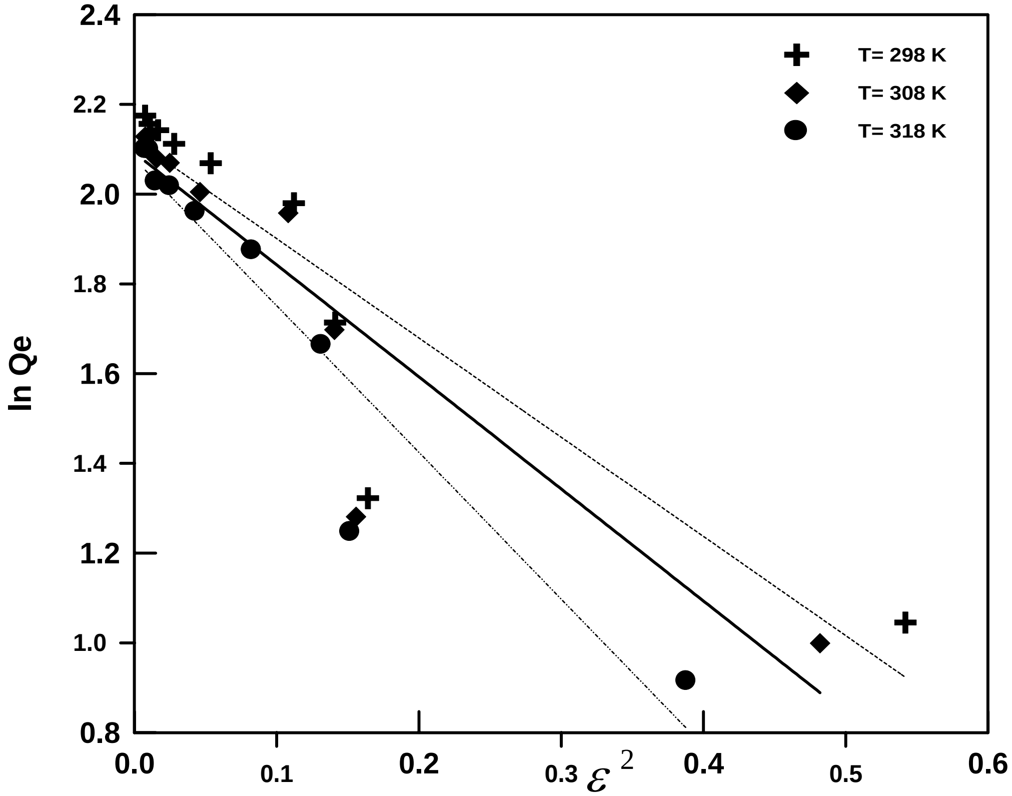

Figure 6: D-R plots bentonite / PNA at different temperatures and pH4

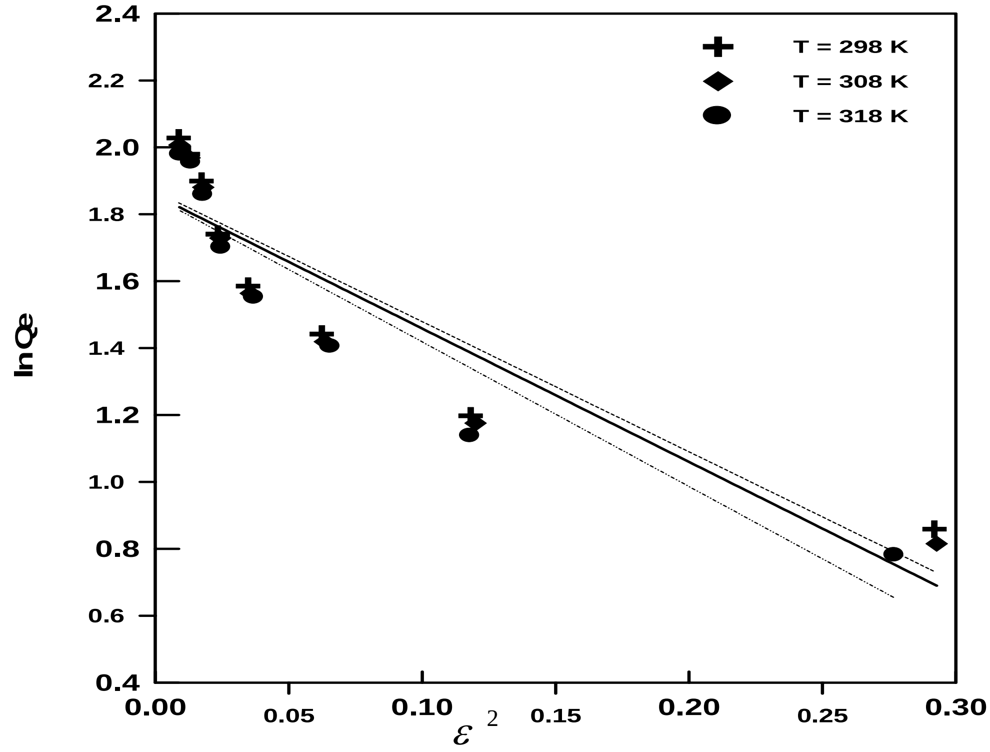

Figure 7: D-R plots bentonite / PNA at different temperatures and pH7

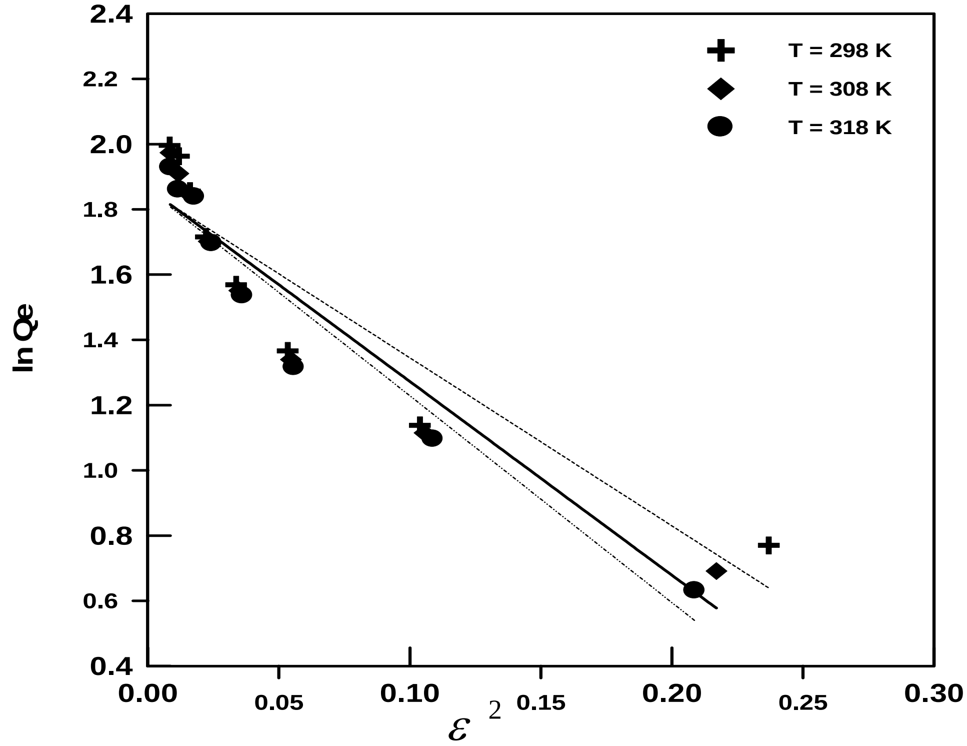

Figure 8: D-R plots bentonite / PNA at different temperatures and pH 10.

Table 5. D-R isotherm parameters and mean energy of the adsorption for different PHs, and temperatures of PNA on the bentonite surface.

pH 4 **T/K**	**D-R constants**			
	$K^{/}$ **(mol^2.kJ^{-2})**	**E$_{ads}$ (kJ.mol^{-1})**	**Xm (mg/gm)**	**R^2**
298	2.2107	0.4755	8.342	0.8204
308	2.4959	0.4475	8.097	0.8366
318	3.2681	0.3911	7.989	0.9046
pH 7 **T/K**	**D-R constants**			
	$K^{/}$ **(mol^2.kJ^{-2})**	**E$_{ads}$ (kJ.mol^{-1})**	**Xm (mg/gm)**	**R^2**
298	3.8890	0.3580	6.4739	0.8378
308	3.9849	0.3540	6.4014	0.8482
318	4.3220	0.3401	6.3630	0.8661
pH 10 **T/K**	**D-R constants**			
	$K^{/}$ **(mol^2.kJ^{-2})**	**E$_{ads}$ (kJ.mol^{-1})**	**Xm (mg/gm)**	**R^2**
298	5.1504	0.3115	6.460	0.8617
308	5.9370	0.290	6.437	0.9093
318	6.3370	0.281	6.422	0.9374

Conclusion

The PNA was accepted sorbed on bentonite. This could be explained by adsorption interaction between the adsorbed PNA molecules and bentonite. The uptake increased with increase in initial PNA concentration and with decreases in pH. The strong electrostatic interaction between the –NH_3^+ of PNA with the negative charge of bentonite surface can be used to explain the high adsorption capacity of PNA bentonite.

The pseudo first-order kinetic model fits very well with the dynamical adsorption behavior of this compound in solution with different temperatures at neutral pH. From the values of D-R equation indicates this adsorption process is physisorption. At the end of the adsorption studies, it can be said that -bentonite may be used as an adsorbent for adsorption or removal of some aromatics amino compounds such as PNA from waste water solutions.

Nomenclature:

PNA	Para nitroaniline
C_o	Initial solution concentration, mg/L.
C_e	Equilibrium solution concentration, mg/L.
C_t	Concentration of solution at time t, mg/L.
k_a	Rate constant
$K^{/}$	Adsorption energy constant
E_{ads}	Mean adsorption energy
D-R	Dubinin- Rasdushkevich equation
X_m	Maximum monolayer adsorption.
R^2	Correlation coefficient

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