

**Study the effect of pHs and temperatures on adsorption of
para nitro aniline (PNA) by Bentonite clay surface**

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Abstract:

the removal of para nitro aniline (PNA), with bentonite clay have been performed investigating by the effect of initial concentration, pH, temperature, on this process.

The equilibrium concentration have been determined spectrophotometrically using ultra violet - visible technique.

The equilibrium data are fitted to the Langmuir and Freundlich isotherm equations.

The adsorption amount of PNA increased with temperature and pHs decreased.

The temperature thermodynamic parameters like ΔG° , ΔH° and ΔS° have been calculated from the effect of temperature, the adsorption process is exothermic.

دراسة تاثير الدالة الحامضية ودرجة الحرارة على قابلية امتزاز مركب
البارا نايترو انلين باستخدام سطح طين البنتونايت

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الخلاصة:

تم دراسة ازالة مركب البارا نايترو انلين من المحاليل المائية باستخدام طين البنتونايت ودراسته كدالة للتركيز ودرجة الحرارة والدالة الحامضية. تراكيز الاتزان حددت طيفيا باستخدام تقنية الاشعة المرئية- فوق البنفسجية، ونتائج الاتزان عوملت مع كل من معادلتى لانكماير وفرندلج الايسوثرميتين ووجد ان سعة الامتزاز تزداد مع نقصان درجة الحرارة والدالة الحامضية. المكونات الترموديناميكية (ΔS^0 ، ΔH^0 ، ΔG^0) تم حسابها بواسطة تاثير درجة الحرارة على عملية الامتزاز ووجد من خلالها ان عملية الامتزاز هي باعثة للحرارة.

1. Introduction:

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 bentonite, on the other hand, may be a very good alternative to these materials. A number of investigators studied sorptive properties of various cationic organic reagents with bentonite ⁽⁷⁾, but fewer researchers studied the adsorption of anionic reagent with bentonite⁽⁸⁾.

Bentonite is hydrated aluminum silicate, consisting mainly of montmorinolite $Al_2O_3.4SiO_2.H_2O$ but usually containing some magnesium and irons together with small amount of calcium and other minerals⁽⁹⁾

The aim of the present study is to investigate the adsorption of para nitro aniline "PNA" using Bentonite clay, the effect of concentration, temperature, and pH were considered.

2. Materials and Experiments

2.1 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 $Al_2O_2.4SiO_2.H_2O$.⁽⁹⁾ the chemical analysis of bentonite is listed in table (1).

Table 1. The chemical analysis of bentonite

Constituent	Wt% .
SiO ₂	54.66
Al ₂ O ₃	14.65
CaO	4.77
Fe ₂ O ₃	4.88
MgO	6
Na ₂ O	0.65
SO ₃	1.2
Loss on ignition	13.06

Para nitro aniline (PNA) obtained from B. D. H., (92% purity) the structural formula of this compound is given in figure (1):

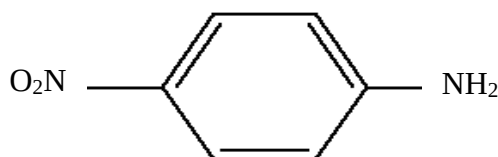


Fig. (1): Structure of Para nitro aniline

Bentonite sample has been treated before using in the experiments as follows ⁽⁵⁾: 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, (England).
- 3.Digital pH-Meter ‘Hanaa, (Roman).
- 4.Shaker Water Bath, SB. 4, Tecam.
- 5.Oven, Heracus (D-6450), Hanau, (England).

2.2 Experiments:

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 / 25ml solution. A constant mixing at a constant temperature and pH was achieved using a shaker water bath. 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 - vis) at 450 nm, the same experiment was repeated at different initial concentrations, temperatures and pH.

3. Results and discussion:

The amount of PNA adsorbed per unit weight of an adsorbent, Q_e , was calculated using the following formula:

$$Q_e = \frac{(C_o - C_e)V}{m} \dots\dots\dots(1)$$

where, C_o is the initial concentration of PNA (mg L^{-1}), C_e is the equilibrium concentration of PNA in solution (mg L^{-1}), m is the mass of the bentonite clay (mg) and V is the volume of solution (L).

The results concerning PNA adsorption for bentonite are presented in Figs. 2. at 298K and pHs (4, 7 and 10).

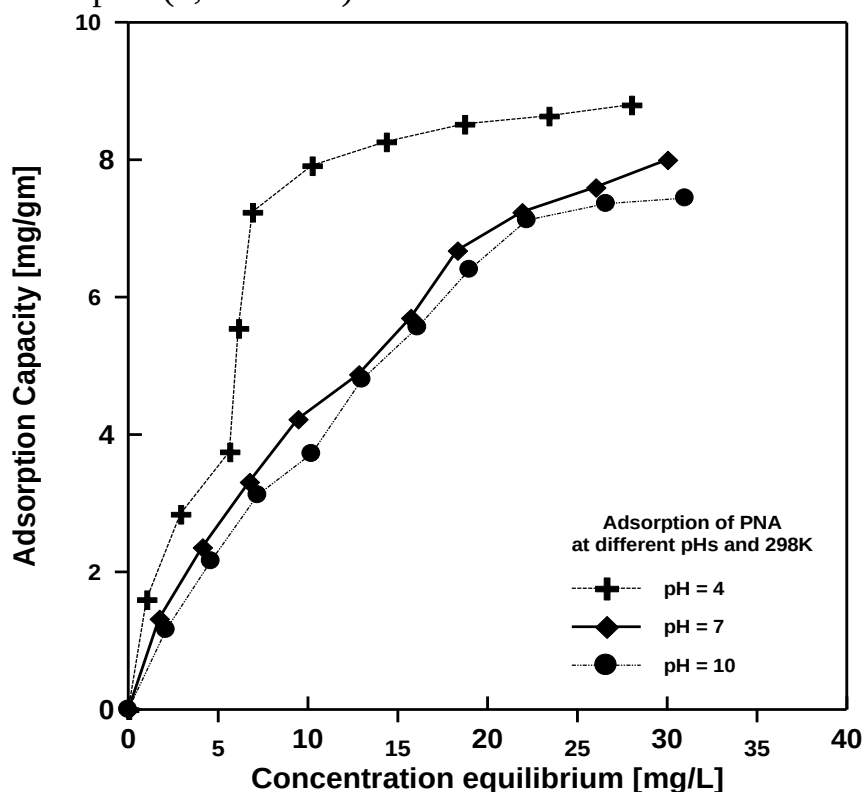


Figure 2 : adsorption isotherm of PNA on bentonite surface at different pHs and at room temperature 298K.

It is obvious from Figs. 2 that the adsorption isotherms of PNA on bentonite are S-type according to the Giles classification ⁽¹⁰⁾.

In this type of isotherm, the initial portion provides information about the availability of the active sites to the adsorbate and the plateau signifies the monolayer formation^(11, 12).

The initial curvature indicates that a large amount of PNA is adsorbed at a lower concentration as more active sites of bentonite are available, as the concentration increases, it becomes difficult for a PNA molecule to find vacant sites, and so monolayer formation occurs.

The types of system which give this curve do in fact fulfill these conditions. Thus they have one of the following characteristics: (i) the adsorbed molecules are most likely to be adsorbed flat or (ii) if adsorbed end-on, they suffer little solvent competition.

Examples of (ii) are: (a) systems with highly polar solute and adsorbent, and a non polar solvent; and (b) systems with mono functional ionic substances with very strong intermolecular attraction. It is possible that in the system (b) cases the adsorbed ions may have become associated into very large clusters and just adsorption takes place. Where the sites are few and widely separated, the surface has large hydrophobic regions⁽¹³⁾.

Solid-liquid equilibrium can be easily described by adsorption isotherms.

Thermodynamic parameters:

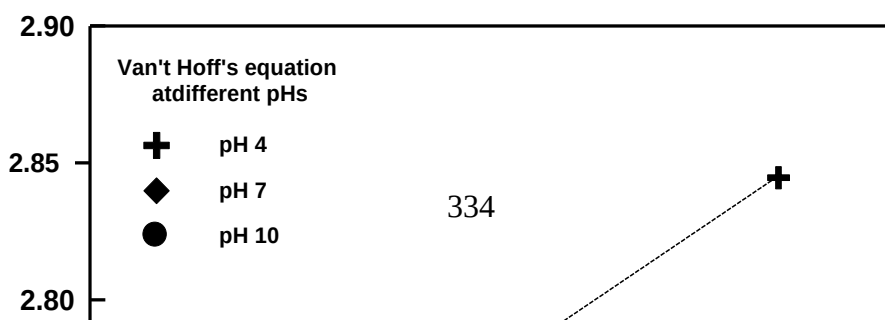
The thermodynamic parameters for the adsorption of PNA by bentonite such as the enthalpy change (ΔH^0), the Gibbs free energy change (ΔG^0) and the entropy change (ΔS^0) can be calculated from the variation of maximum adsorption with temperature (T) using the following basic thermodynamic relations ⁽¹⁴⁾:

$$\ln K_e = A - \frac{\Delta H^0}{RT} \dots\dots\dots(2)$$

$$\ln K_e = - \frac{\Delta G^0}{RT} \dots\dots\dots(3)$$

$$\Delta S^0 = \left(\frac{\Delta H^0 - \Delta G^0}{T} \right) \dots\dots\dots(4)$$

According to equation 2, the mean value of the enthalpy change due do the adsorption of PNA by bentonite over the temperature range studied can be determined graphically by the linear plotting of $\ln k_e$ against $1/T$ using the least squares analysis, see figure 3.



The mean enthalpy change can be determined from the slope of the straight line. The variation of Gibbs free energy and entropy change with temperature can be calculated using equations 3 and 4, respectively, the results are arranged in table 2.

An important result can be obtained from table 2 is that the Gibbs free energy (ΔG°) is small and negative with its value decreases with increasing temperature.

This indicates that the adsorption processes of PNA by bentonite can be enhanced by decreasing temperature.

The values of entropy change (ΔS°) are positive and remain almost constant with temperature. This gives an evidence that structural changes in PNA and bentonite occur during the adsorption process. The negative values of enthalpy change (ΔH°) show the exothermic nature of the adsorption process of PNA by bentonite.

table 2: Thermodynamic parameters for the adsorption of PNA on the Bentonite.

pH 4	Thermodynamic parameters		
	ΔH° (kJ/mole)	ΔG° (kJ/mole)	ΔS° (J/K.mole)

T/K	Mean value		Mean value
298	-5.509	-7.048	5.165
308		-7.099	
318		-7.151	
pH 7 T/K	ΔH° (kJ/mole) Mean value	ΔG° (kJ/mole)	ΔS° (J/K.mole) Mean value
298	-4.135	-6.900	9.275
308		-6.990	
318		-7.085	
pH 10 T/K	ΔH° (kJ/mole) Mean value	ΔG° (kJ/mole)	ΔS° (J/K.mole) Mean value
298	-5.029	-6.706	5.975
308		-6.803	
318		-6.964	

The adsorption curves were applied to the Langmuir, the Langmuir equation is the mathematical function most commonly used to describe this process⁽¹⁵⁾.

The Langmuir isotherm can be expressed as

$$Q_e = \frac{X_m k C_e}{1 + k C_e} \dots\dots\dots(5)$$

where Q_e =amount of PNA adsorbed per unit weight of adsorbent (mgg^{-1}), C_e =concentration of PNA remaining in solution at equilibrium (mgL^{-1}), X_m =amount of PNA adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface (mgg^{-1}) and $k = a$ constant related to the energy or net enthalpy (k).

By plotting Q_e versus C_e , a curve is obtained which is linear at low equilibrium concentrations, followed by a curvature (concave to the x-axis), and with an asymptotic tendency to saturation corresponding to a monolayer covering.

The linear form of the Langmuir isotherm equation is represented in equation (5).

$$\frac{C_e}{Q_e} = \frac{1}{k X_m} + \frac{C_e}{X_m} \dots\dots\dots(6)$$

Straight lines were obtained by plotting C_e / Q_e against C_e for the adsorption of PNA onto bentonite illustrated in figures (4, 5, and 6) at different temperatures and pHs.

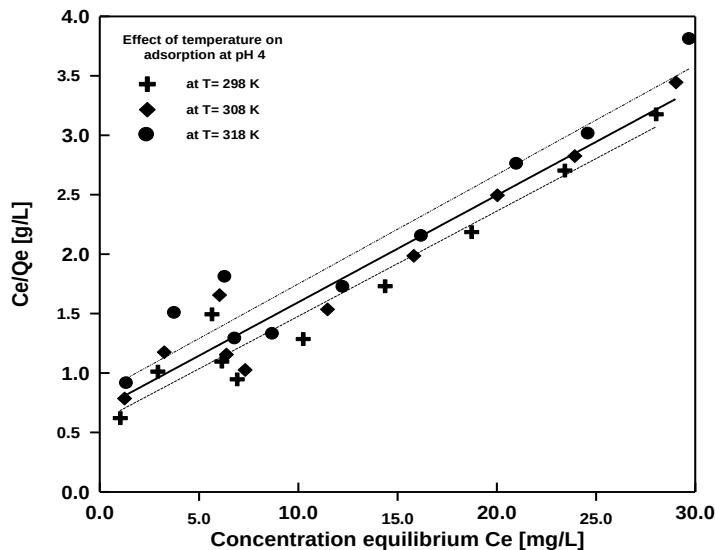


Figure 4: Langmuir plots bentonite

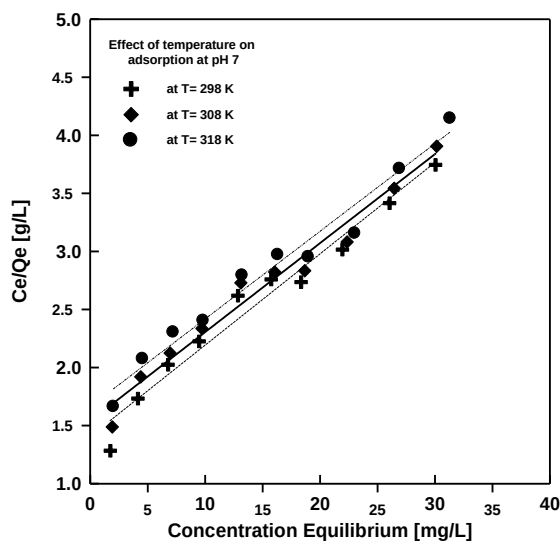
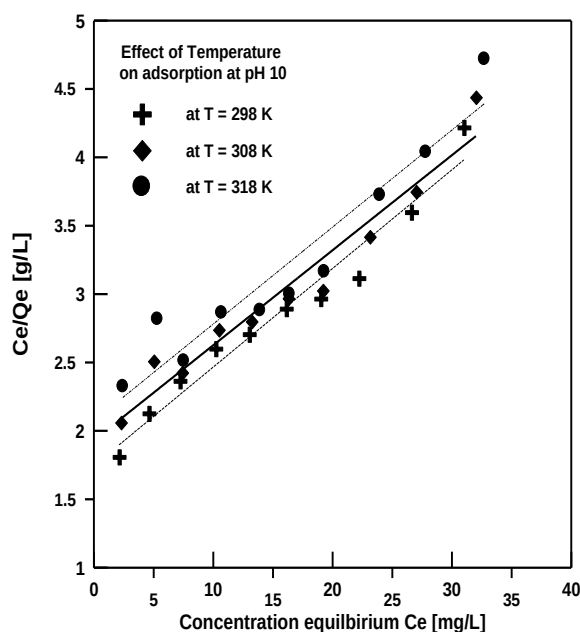


Figure 5: Langmuir plots



**Figure 6: Langmuir plots
bentonite / PNA at different**

The values of X_m and k calculated from the slopes and intercepts of the Langmuir plots and correlation coefficients R^2 ; are reported in Table 3.

As it can be seen most of the adsorption isotherms obeyed the Langmuir equation with correlation coefficients $R^2 > 0.913$. Many experimental isotherms conforming to a Langmuir isotherm involve monolayer coverage⁽¹⁵⁾.

The value of monolayer coverage of bentonite by this PNA increased in the order $pH4 > pH7 > pH10$.

The equilibrium adsorption density Q_e increased with the increase in PNA concentration.

the equilibrium adsorption densities Q_e of the bentonite reach almost the same Q_e as those at high equilibrium PNA concentrations.

It indicates that the bentonite have high adsorption density even at low equilibrium PNA concentrations^(16, 17).

The adsorption curves were also applied to Freundlich equation. The Freundlich isotherm is given as

$$Q_e = K_f C_e^{1/n} \dots\dots\dots(7)$$

where K_f is roughly an indicator of the adsorption capacity and $(1/n)$ of the adsorption intensity all data are illustrated in figures (7, 8, and 9).

Values $n > 1$ represent a favorable adsorption condition⁽¹⁶⁾ K_f and $1/n$ can be determined from the linear plot of $\ln(Q_e)$ vs. $\ln(C_e)$. Parameters of the Freundlich isotherm was computed in Table 1.

The Freundlich isotherm fits quite well with the experimental data (correlation coefficient $0.884 < R^2 < 0.996$).

Table 3 indicates that the computed maximum monolayer capacity Q_e on the bentonite has a large value, Table 3 also shows that the bentonite studied in this work have a very large adsorption capacity at pH 4, 298K.

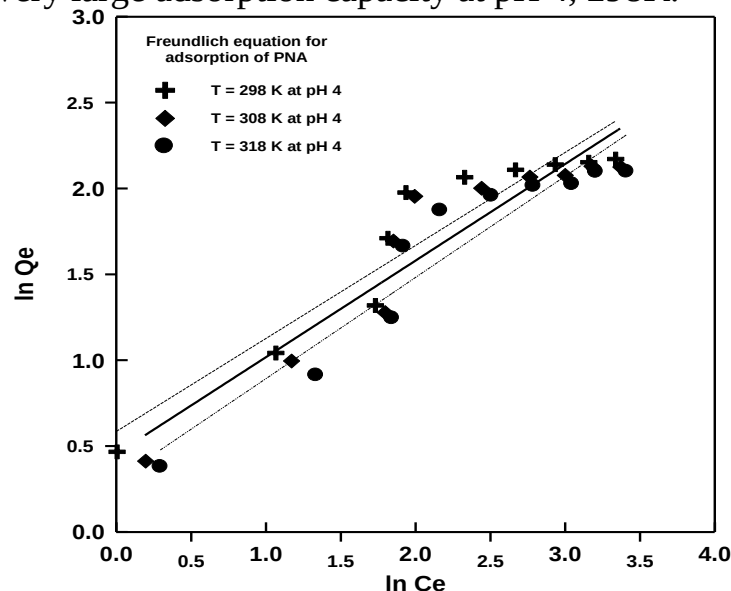


Figure 7: Freundlich plots bentonite / PNA at different temperature and pH 4

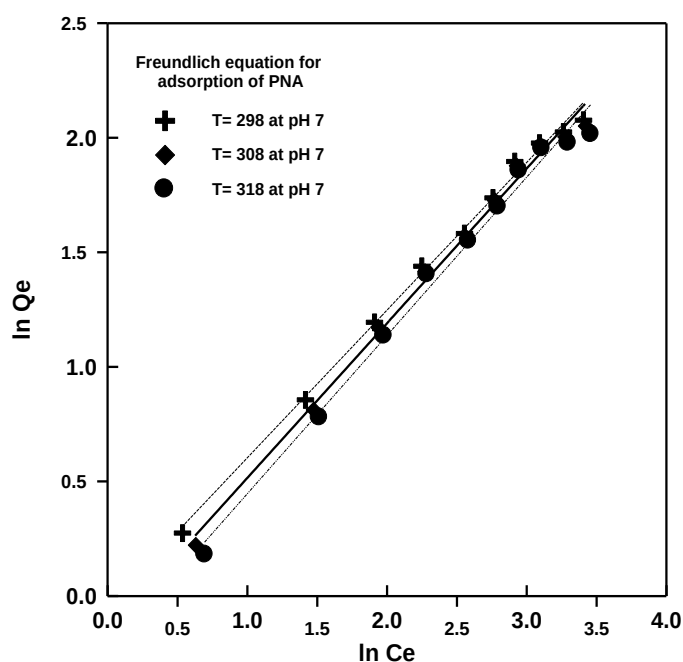


Figure 8: Freundlich plots bentonite / PNA at different temperature and pH 7.

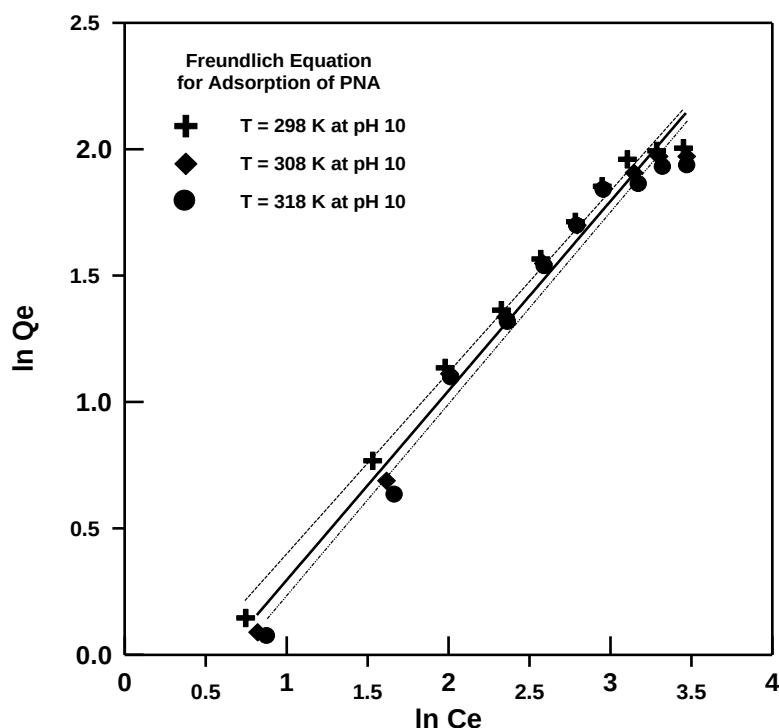


Figure 9: Freundlich plots bentonite / PNA at different temperature and pH 10.

For the adsorption of removing PNA from aqueous solution, by bentonite appears to be much more efficient than commercial activated carbon^(17, 18). at lower pH more protons will be available to protonate amino groups of PNA molecules to form groups -NH_3^+ , thereby increasing the electrostatic attractions between negatively charged of clay surface sites and positively charged adsorbent and causing an increase in PNA adsorption.

This explanation agrees with our data on pH effect. It can be seen that the pH of aqueous solution plays an important role in the adsorption of PNA onto bentonite .

Table 3: Langmuir and Freundlich constants for adsorption of PNA at different temperatures and pHs.

pH 4 T/K	Langmuir constants			Freundlich constants		
	X _m (mg/gm)	K _L (L/gm)	R ²	K _f (L/gm)	n	R ²
298	11.315	0.1487	0.9450	1.795	1.847	0.8923
308	11.12	0.129	0.9404	2.195	1.778	0.8859
318	10.88	0.11	0.9271	1.355	1.698	0.9056
pH 7 T/K	X _m (mg/gm)	K _L (L/gm)	R ²	K _f (L/gm)	n	R ²
	X _m (mg/gm)	K _L (L/gm)	R ²	K _f (L/gm)	n	R ²
298	13.25	0.0558	0.9683	0.960	1.552	0.9955
308	13.04	0.0497	0.9725	0.852	1.483	0.9931
318	12.72	0.0453	0.9691	0.783	1.448	0.9891
pH 10 T/K	X _m (mg/gm)	K _L (L/mg)	R ²	K _f (L/gm)	n	R ²
	X _m (mg/gm)	K _L (L/mg)	R ²	K _f (L/gm)	n	R ²
298	14.49	0.1204	0.9614	0.727	1.393	0.9880
308	14.19	0.136	0.9482	0.635	1.334	0.9826
318	13.87	0.149	0.9141	0.591	1.318	0.9728

Conclusions

The equilibrium of the adsorption of para nitro aniline on the bentonite clay surface, have been investigated.

The bentonite clay shown very high adsorption capacities to remove the para nitro aniline, 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 nitro aniline concentration and pH.

The uptake increased with the increase in the initial para nitro aniline concentration and with decreases in pH, also when temperature increased the adsorption capacity decreased.

The Freundlich equation agrees very well with the equilibrium isotherm also Langmuir equation give accepted linearity.

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