Adsorption Study of Para Phenylen di amine (PPDA)On Bentonite clay surface

Asmaa Kadim Ayal*

Abstract:

   The removal of Para Phenylen di amine (PPDA), by bentonite clay surface has been Performed in investigating by the effect of initial concentration,P^H,and temperature, on this process   The equilibrium concentrations have been determined spectro photometric by using ultra violet - visible technique.The equilibrium data are fitted to the frenudlich isotherm equations.The adsorption amount of (PPDA) is increased when the temperature and P^H decreased.The thermodynamic Parameters like ΔG°,ΔH°,and ΔS° have been calculated from the effect of temperature on adsorption process,its found from the adsorption process is exothermic .The kinetic of adsorption process has been studied depending on Lagergren kinetic equation.

Key words: Adsorption (PPDA) on Bentonite clay.

Introduction:

The adsorption process is so important to understand the behavior of pesticide in the environment. Hydrophobic organic compounds such as; amines, carboxylic acids and phenols may occur both in ionized and neutral form depending on the P^H value of the aqueous media [1-3].

Organic is great concern in water treatment due to its health and environmental hazard, small quantities of soluble organic and inorganic compounds remaining in waste water [4]. Therefore the removal of pesticide residue from water by adsorption onto different types of minerlals and clays has been reported in Literature [5-7].

The adsorption of dinitrophenol herbicide from water by two reference smectite clays has been studied by shag et. al [8].The molecules formula of bentonite could be written as]9] ($Mg_2Al_{10}Si_{24}O_{60}(OH)_{12}$[Na,Ca]) .

In this present study, we have investigated the possibility of the adsorption different concentration of PPDA from water onto bentonite in different P^H solution and different temperature has been studied.

Materials:

   In this study , bentonite clay sample rich in the montmorillonite mineral was used as adsorbent the bentonite clay was supplied from the state company for geological survey and mining Iraq , the clay sample was ground , dried at ($200C^{\circ}$) for (24hr) and passed through 0.75 mesh sieve . The particles under 75 μm were used in further experiment. (PPDA).

The composition of the clay has been determined by atomic absorption which was as in the table.

Table (1) the chemical analysis of bentonite

Constituent	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	So_3	Losson ignition
Wt %	54.66	14.65	4.77	4.88	6	0.65	1.2	13.06

*Department of Chemistry, College of Science for Women, University of Baghdad

The Para Phenylenediamine was used in this study which has been obtained from BDH with Purity 97%. A sample of (100ppm) PPDA solution was taken, and a spectrum scan was measured by using UV–VIS spectrophotometer ,(T60u spectrophotometer PG in struments Ltd) And showed a λ_{max} at 233.6 nm as shown in figure (1)
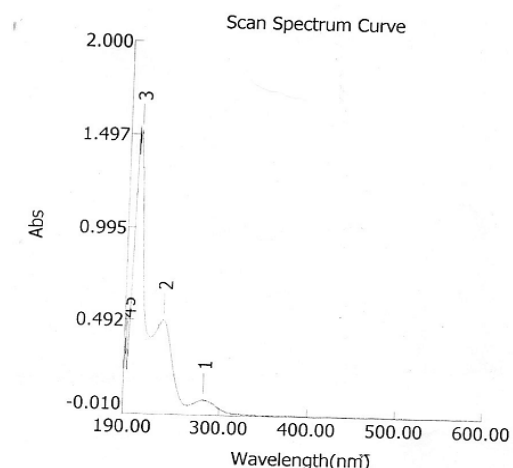

Fig. (1) U.V- Vis Spectra of (PPDA)

PH measurements were made with (Martin:Instrument,Inc) digital PH – meter (Rocky mont-Nc27804-U.S.A) Digital balance , sartor us (BP.3015 – Germany) and Skaker water bath .

Method:

The adsorption isotherms was carried out by Skaking 0.1 gm of the Bentonite with (25ml,100)ppm of PPDA in a tightly closed flask at certain temperature and PH . During the experiments, samples of the solution have been periodically with drowning at a definite time period (15, 30, 60, 90 and 120 min).
The mixtures left were filtered and the concentration of PPDA was measured at each time by using UV – Visible spectrophotometer.
The bentonite – PPDA solutions have been equilibrated for 2 hours at certain temperature . The equilibrium concentration (Ce) of PPDA solution was measured from Lambert – Beer relationship.

Then the amount of PPDA adsorbed per unit mass of Bentonite (Qe) was calculated by equation [10].

$$Qe = \frac{V(Co - Ce)}{m(gm)}$$

Where Co is the initial concentration and Ce is the equilibrium concentration (mg /L). V is the volume of PPDA in L , and m is the weight of bentonite clay in gram , Qe is the capacity of adsorption in mg / g .

Results and Discussion:

The data obtained from the adsorption of PPDA on the bentonite clay at various concentrations (20 – 120) ppm showed that a contact time of 120 min was sufficient to achieve equilibrium and the adsorption did not change with increase time .

Table (2) and figure (2) show the variation of Qe with the contact time for 100 ppm of PPDA solution at 298 K° to be in attachment with 0.1 gm of bentonite clay.

Table (2) The values of Qe and Ce at different time for 100 PPm of PPDA solutions at 298K$^{\circ}$

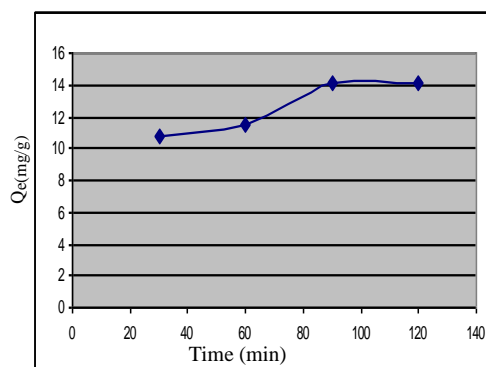| Time (min)	Ce(mg/L)	(mg/g) Qe
30	56.71	10.82
60	54.07	11.48
90	42.23	14.44
120	42.23	14.44

Fig (2) show the variation of Qe with the contact time

The equilibrium adsorption isotherms on of fundamental importance in the design of adsorption systems. [11]
Table (3) and figure (3) show the data and relationship between of frunendlich isotherm between log Qe and log Ce a various concentration of PPDA solutions at (298 , 308 , and 318) K°.

Table (3) show the data of equilibrium concentration and quantity adsorption

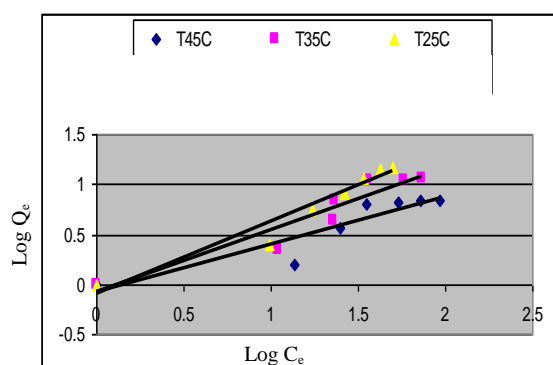| Co(mg/L)	298 K°		308 K°		318 K°	
	Log Ce	Log Qe	Log Ce	Log Qe	Log Ce	Log Qe
20	0.994	0.403	1.043	0.342	1.136	0.198
40	1.239	0.752	1.359	0.631	1.400	0.570
60	1.424	0.921	1.363	0.843	1.544	0.795
80	1.532	1.059	1.552	1.044	1.731	0.813
100	1.625	1.159	1.762	1.048	1.860	0.837
120	1.7	1.172	1.868	1.061	1.966	0.837

Fig (3) show the linear relationship of freundlich Isotherm between Log Qe and Ce

The linearized of this equation given by equation.[12]

$$Qe = k_f Ce^{\frac{1}{n}}$$

Where k_f is constant related to adsorption capacity (mg / g) , 1/n another constant related to the nature and strength of adsorption process . These parameters were determined from the slope and intercept of the linear plot between Log Qe and Log Ce .
Figure (3) shown the relationship of frunendlich, therefore fruendlich parameters determined in this work were included in table (4) .

Table (4): The values of parameters (K_f,1/n,R^2)

T(K°)	k_f (mg / g)	$\frac{1}{n}$	n	R 2
298	0.4170	0.913514	1.09467	0.9389
308	0.2444	0.914557	1.09392	0.8934
318	0.03956	1.409091	0.70967	0.8583

The fruendlich isothermal equation is an empirical equation on the sorption on a heterogeneous surface is an indication that the binding sites are not equivalent or independent. [13]
From this table we could be conclude that adsorption is highly dependent on the initial concentration of PPDA, because at lower concentration, the ratio of the initial number of PPDA molecules to the available surface area is low, the fractional adsorption become dependent on the initial concentration, however, at high concentration, the available sites of adsorption become independent on the initial concentration. [14] P^HThe equilibrium is reached after 120 minutes for all conditions applied (i . e , P^H 2.5, 7 and 11.5) and temperature (298 K°) in figure (4) and table (5) .
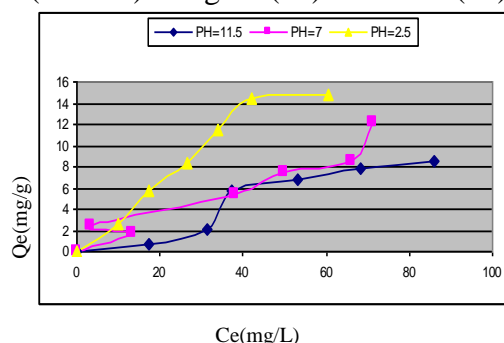

Fig. (4): adsorption isotherm of PPDA on bentonite Surface at different PHs and at 298

Table (5): data Ce and Qe at different P^H at 298 K°

P^H =2.5			P^H =7.00			P^H = 11.5		
Co	Ce	Qe	Co	Ce	Qe	Co	Ce	Qe
20	9.868	2.532	20	13.157	1.71	20	17.236	0.69
40	17.368	5.657	40	3.394	2.401	40	31.447	2.138
60	26.578	8.355	60	38.157	5.46	60	37.368	5.657
80	34.078	11.48	80	49.868	7.532	80	53.026	6.743
100	42.236	14.44	100	65.921	8.519	100	68.421	7.894
120	60.526	14.868	120	71.052	12.236	120	86.052	8.486

The thermodynamic functions, ΔH, ΔG, and ΔS can be estimated using equilibrium constant charging with temperature. The free energy change of the sorption reaction is given by the following equation. [15, 16]

$$\Delta G^{°} = - R\ T\ lnka \text{------- (1)}$$

$$lnka = A - \frac{\Delta H}{RT} \text{-------(2)}$$

$$\Delta G^{°} = \Delta H^{°} - T\Delta S^{°} \text{--------- (3)}$$

WhereK is the maximum adsorption quantity for various PPDA solution at different temperature. The equation (2) was used to calculate the $\Delta H^{°}$, by plotting against 1/T.

Table (6) and figure (5) showed a linear relationship and the slope represent $-\Delta H /R$ where R is the gas constant (8.314 J .K^{-1}. mole^{-1}) and $\Delta H^{°}$ ads were calculated.

Table (6): The values of the reciprocal of temperature and lnk

T(K$^{°}$)	1\ T(K^{-1}) $\times 10^{-3}$	Ln k
298	3.35	6.89
308	3.24	6.6
318	3.19	6.06

$1/T \ (^{°}K^{-1})$
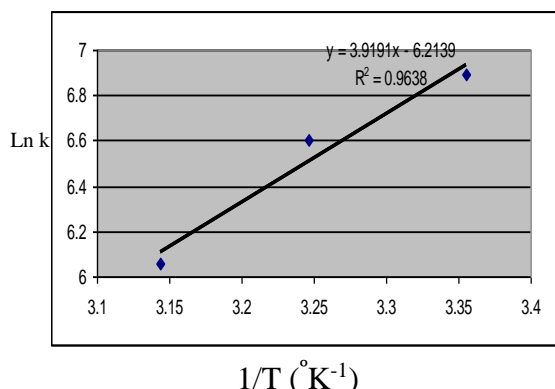
Fig (5): The plot of ln k vs . The reciprocal of temperature

The $\Delta G^{°}$ and $\Delta S^{°}$ values at different temperature (298 , 308 , 318 K) and initial P^{H} (2.5) were given in table (7) .

Table (7) show the thermodynamic functions of the Adsorption process

T (K$^{°}$)	$\Delta H^{°} \times lo^{-3}$ K J . mole^{-1}	$\Delta G^{°}$ K J . mol^{-1}	$\Delta S^{°} \times lo^{3}$ J.mole^{-1} . K^{-1}
298		$- 17.07$	$+ 46. 79$
308	$- 3.1249$	$- 16 . 9$	$+ 44. 72$
318		$- 16 . 02$	$+ 40. 55$

As seen in table (7), the negative values of ΔG confirm the feasibility of the process and the spontaneous nature of sorption, The negative values of ΔH indicate the exothermic nature of the process while the positive ΔS corresponds to increase disorder of the system increase, the system becomes more disordered process and diffusion of PPDA in the bentonite pores.

To investigate the mechanism of adsorption, kinetic model has 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 gene rally expressed as follows. [17]

$$In (q_{e} - q_{t}) = lnq_{e} - k\ t \text{------- (4)}$$

Where q_{t} and q_{e} are the amount of PPDA adsorbed at time (min), and at equilibrium time respectively, and k is the rate constant of pseudo first order adsorption (min^{-1}). The value of rate constant for the pseudo first order reaction is calculated experimentally by plotting

In (q_{e} – q_{t}) against time of the adsorption of PPDA on to bentonite clay according to equation (4) , results are shown in figure (6) and values of rate constants are illustrated in table (8) .

Table (8) show the rate constants of the adsorption process

Temp(K$^{°}$)	Qe (mg / g)	K (min^{-1})
298	14.440	0.01333
308	11.184	0.126
318	6.87	0.0185

The value of rate constant kad were found to be increased When temperature increase from 298 to 318 K°.
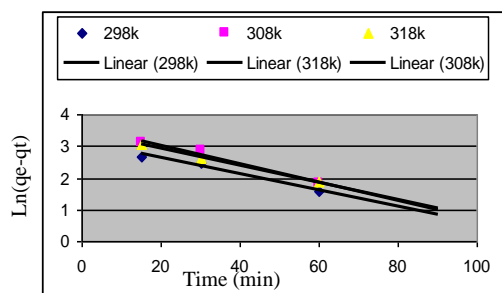

Fig (6) the lagergren model for a series (PPDA) solution at (298,308 and318) K°

References:

1-Fariba amir, M.SC. 2000.Thesis institute of water chemistry, Dresden University of Technology Germany.

2-R.albert, 1987, physical chemistry, 7th edition, John Wiley and Sons:314-315.

3-A.Pala, E.Tokat and H.Erkay, 2003, is international conference environmental research and assessment, Bucharest, Romania, March:114.

4-V.T.Favera, E. Pozza, F. Furlan,L. Sanchez,1998,effects of PH and contact time on adsorption of reactive dyes on chitosan microsphers,J, Braz.chem, soc, 4(5):435.

5-L.Clausen, I. Fabricius and L. Madsen, 2001, Adsorption of pestiudes onto quartz ,calcite, Kaolinite and Alumina,J,of Environment of quality 30(3):846.

6-L.Clausen, I.Fabricius, 2001, Adsorption of pestiudes onto quartz,Calcite, Kaolinite and Alumina, J, of Environment quality, 30(3):825.

7-E.Ayranci and M.Hoda, 2004, Adsorption of bentazon and propanil from aqueous solutions at the high area activatd carbon-cloth , chemosphere,57:755.

8-G.Sheng, G.T. Johnston, 2000, B.J.Teppen and S.A.Boyd, clays and clay minerals 50 (1): 25

9-Al.Gohara, O.Lyull, J, and Marray, J.B, 1987, Aproximacion ale studio de complejos male to detimololsepiolita pars en farmacia, pharm. Acta. Helv, 62(30): 66-72.

10-W.L.Moore, 1972, physical chemistry, 4th Ed, prentice-Hall, INC: 495.

11-W.J.Laidre, J.H.MISEN, 1982, physical chemistry, Bensamiu Cummings publishing company, California.

12-A.Hussien, H.Falah, 1993, "Thermodynamic of liquid and solution", Al-Qadisiayah University.

13-Jalal.R. Chafourian, H.Asel.Y. Davapanah.S.J.Spehy, 2002, Chromium(III) removal from tannery effluent by streptomyces sp (MB3) waste biomass of fermentation process, J.Haz.Mater, 92:253-262.

14-A.Al-Kaim, M.SC, 2005, Thesis College of science, Babylon University.

15-C.Chem.X.Wang,2000,"Adsorption of Ni(Π)from aqueous solution using oxidized mutual carbon Nanotubes"Ind.Eng .chem.Res.,45:9144-9149.

16-S.Karaca, A.Gures, M.Acikyildiz, M.Ejder, 2008, Adsorption of cationic dye from aqueous solution by activated carbon, Microporous Mesoporous mater,115:376-382.

17-M.H.Entizari, T.R. Bastami, 2006, "sons-sorption as anew method for the removal of lead ion from aqueous solution ", J, Hazaral. Mater,137:959-964.

دراسة امتزاز بارافينل داي امين على سطح طين البنتونايت

اسماء كاظم عيال*

*قسم الكيمياء – كلية العلوم للبنات – جامعة بغداد

الخلاصة :

تم دراسة ازالة مركب البارافنيل داي امين من المحاليل المائية باستخدام طين البنتونايت ودراسته كدالة للتركيز ودرجة الحرارة والدالة الحامضية. حددت تراكيز الاتزان طيفياً باستخدام تقنية الاشعة المرئية فوق البنفسجيةوعوملت نتائج الاتزان مع معادلة فرندلج ووجد ان سعة الامتزاز تزداد مع نقصان درجة الحرارة والدالة الحامضية .تم حساب الدوال الثرموديناميكية($\Delta H°$, $\Delta G°$, $\Delta S°$) بوساطة تأثير درجة الحرارة على عملية الامتزاز وجد من خلالها ان عملية الامتزاز هي باعثة للحرارة .و تم كذلك دراسة حركية الامتزاز اعتمادا على معادلة لاكركرين .