

Adsorption Study of Herbicide 2,4-Dichlorophenoxy Acetic Acid by α -Alumina Clay

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Adsorption of the herbicide 2,4-dichlorophenoxy acetic acid by α -alumina clay minerals, was investigated. Factors influencing adsorption such as pH of the solution, adsorbent dosage, particle size, herbicide concentration and temperature have been studied. The adsorption process was relatively fast and equilibrium was achieved after 2 h, maximum adsorption of 2,4-dichlorophenoxy acetic acid occurred at around pH = 8. Adsorption equilibrium data could also be described well by Freundlich models at the concentration of 2,4-dichlorophenoxy acetic acid which ranging from (40 to 200) mg L⁻¹. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) were calculated by kinetic equation.

Key Words: Adsorption, 2,4-Dichlorophenoxy acetic acid, α -Alumina, Kinetic model, Freundlich, Thermodynamic quantity.

INTRODUCTION

The selective and systemic herbicide 2,4-dichlorophenoxy acetic acid is used to control broadleaf weeds after emergence. Although 2,4-dichlorophenoxy acetic acid is one of the oldest chemical herbicides in the world it is still widely used in agricultural fields because of its excellent selectivity between the broadleaf weeds and graminaceous crops and its reasonable cost¹. The strong auxinic action of 2,4-dichlorophenoxy acetic acid is believed to persist in plants with out significant biodegradation and to disturb hormonal balance resulting in plant death. Kavanagh *et al.*² reported that geethite (iron oxyhydroxide) adsorbed 2,4-dichlorophenoxy acetic acid primarily by an ion exchange reaction, although the amount of 2,4-dichlorophenoxy acetic acid adsorption was considerably greater than would be expected purely on the basis of simple electrostatic interaction. Koskinen and Harper³ questioned the predominant role of ion exchange reactions on 2,4-dichlorophenoxy acetic acid adsorption on soils because layer silicate clays and soil organic matter are generally either uncharged or negatively charged. Bhaskar and Bhamidimarri⁴ studied adsorption kinetics of 2,4-dichlorophenoxy acetic acid on to activated carbon is presented and the equilibrium adsorption of 2,4-dichlorophenoxy acetic acid is described by a freundlich type isotherm and the batch kinetic experiments are analyzed using a surface diffusion model. 2,4-Dichlorophenoxy acetic acid⁵ chemically anchored on a silica gel has been used for Cu(II), Ni(II), Zn(II) and Cd(II) adsorption from aqueous and ethanolic solution at room temperature.

In this present study, we have investigated the possibility of the adsorption different concentration of 2,4-dichlorophenoxy acetic acid from water on to α -alumina at different temperature.

EXPERIMENTAL

Alumina is the low cost and widely used material in the family of engineering ceramics⁶. The α -alumina (α -Al₂O₃) clay was supplied from the state company for geological survey and mining-Iraq. The clay was ground and sieved to particle size less than 75 μ m. Sample of (100 ppm) 2,4-dichlorophenoxy acetic acid solution was taken and a spectrum scan was measured by using UV-VIS spectrophotometer, (T60U Spectrophotometer PG Instruments Ltd.) and showed a λ_{max} at 284 nm. The chemical structure of 2,4-dichlorophenoxy acetic acid is shown in Fig. 1¹.

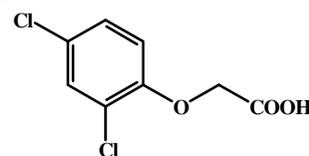


Fig. 1. Chemical structure for 2,4-dichlorophenoxy acetic acid

The adsorption isotherms have been determined by 2,4-dichlorophenoxy acetic acid solution of known, initial concentration to be mixed with accurately weighed amount of α -alumina in a tightly closed flask at certain temperature

and pH. The amount of α -alumina in the slurry has been 0.25 g/ 25 mL solution. A constant mixing at a constant temperature and pH was achieved using a shaker water bath (JEIO TECH BS-1).

The α -alumina solution have been then equilibrated for 2 h, clay suspensions have been then separated by centrifuge at 3000 rpm and the super solution was subjected to analysis using ultraviolet-visible technique (UV-VIS) at 284 nm, the same experiment was repeated at different initial concentration, temperature and pH.

RESULTS AND DISCUSSION

Effect of contact time: Adsorption study was carried out by adding a known amount of α -alumina (0.25 g) 100 ppm of 2,4-dichlorophenoxy acetic acid solution. The amount of 2,4-dichlorophenoxy acetic acid Q_e plotted against the equilibrium concentration C_e for 2,4-dichlorophenoxy acetic acid, is given in Fig. 2 and Table-1.

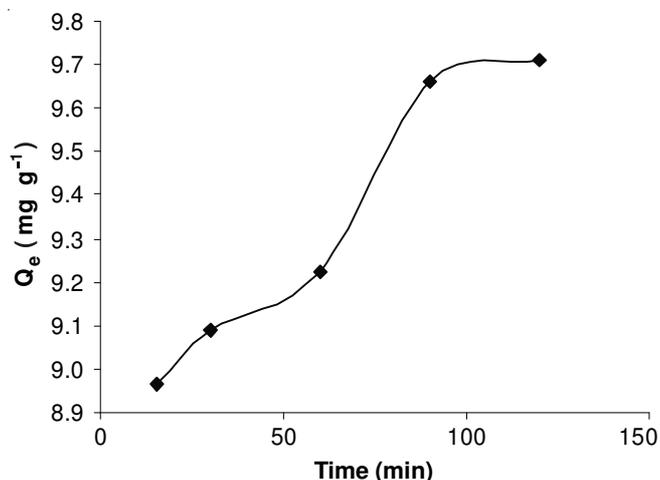


Fig. 2. Variation of Q_e with equilibrium time for 100 ppm 2,4-dichlorophenoxy acetic acid solution at 298 K

C_e (mg L ⁻¹)	Q_e (mg g ⁻¹)	Time (min)
10.344	8.965	15
9.122	9.087	30
7.788	9.221	60
3.344	9.661	90
2.900	9.710	120

Most of the maximum quantity adsorption of 2,4-dichlorophenoxy acetic acid was attained after about 3 h of shaking time at different initial concentration. The increasing contact time increased the 2,4-dichlorophenoxy acetic acid adsorption and it remains constant after equilibrium reached for different initial concentrations.

Adsorption isotherms: Freundlich isotherm is the most frequently employed models to describe the equilibrium characteristics of adsorption isotherm. The linearized form of the Freundlich equation⁷⁻⁹ is as follows:

$$\log Q_e = \log K_f + 1/n \log C_e \quad (2)$$

The Freundlich isotherm constants K_f and $1/n$ can be calculated from the plot between $\log Q_e$ and C_e , K_f (mg/g), $1/n$ (L/g) and n are the Freundlich constant. Table-2 shows the Freundlich data which are indicators of adsorption capacity and adsorption intensity, respectively. Table-3 shows the Freundlich constants at different temperature.

298 K				
C_o (mg L ⁻¹)	C_e (mg L ⁻¹)	Q_e (mg g ⁻¹)	$\log C_e$	$\log Q_e$
40	4.254	3.574	0.628	0.553
50	4.418	4.558	0.645	0.658
60	6.139	5.386	0.788	0.731
70	6.319	6.368	0.8	0.804
80	8.27	7.173	0.917	0.855
90	9.188	8.081	0.963	0.907
100	9.86	9.014	0.993	0.954
110	11.09	9.891	1.044	0.995
120	12.483	10.751	1.096	1.031
130	12.68	11.732	1.103	1.069
140	14.139	12.586	1.15	1.099
150	15.057	13.494	1.177	1.13
160	16.073	14.392	1.206	1.158
170	16.959	15.304	1.229	1.184
180	17.598	16.24	1.245	1.21
190	19.27	17.074	1.284	1.232
200	19.434	18.056	1.288	1.256
303 K				
40	4.27	3.573	0.63	0.553
50	5.073	4.492	0.705	0.652
60	6.188	5.381	0.791	0.73
70	6.795	6.32	0.832	0.8
80	8.418	7.158	0.925	0.854
90	9.5	8.05	0.977	0.905
100	10.155	8.984	1.006	0.953
110	11.254	9.874	1.051	0.994
120	12.549	10.745	1.098	1.031
130	13.04	11.696	1.115	1.068
140	14.516	12.548	1.161	1.098
150	15.434	13.456	1.188	1.128
160	16.204	14.379	1.209	1.157
170	17.139	15.286	1.233	1.184
180	17.811	16.218	1.25	1.21
190	19.418	17.058	1.288	1.231
200	19.827	18.017	1.297	1.255
308 K				
40	4.68	3.532	0.67	0.548
50	5.532	4.446	0.742	0.648
60	6.565	5.343	0.817	0.727
70	7.467	6.253	0.873	0.796
80	8.713	7.128	0.94	0.853
90	9.532	8.046	0.979	0.905
100	10.631	8.936	1.026	0.951
110	11.696	9.83	1.068	0.992
120	11.959	10.804	1.077	1.033
130	12.942	11.705	1.112	1.068
140	13.926	12.607	1.143	1.1
150	15.024	13.497	1.176	1.13
160	16.352	14.364	1.213	1.157
170	17.27	15.273	1.237	1.183
180	18.008	16.199	1.255	1.209
190	18.729	17.127	1.272	1.233
200	20.385	17.961	1.309	1.254

Co (mg L ⁻¹)	C _e (mg L ⁻¹)	Q _e (mg g ⁻¹)	log C _e	log Q _e
313 K				
40	4.647	3.535	0.667	0.548
50	5.385	4.461	0.731	0.649
60	6.745	5.325	0.829	0.726
70	7.581	6.241	0.879	0.795
80	8.581	7.141	0.933	0.853
90	9.68	8.032	0.985	0.904
100	10.516	8.948	1.021	0.951
110	11.336	9.866	1.054	0.994
120	12.27	10.773	1.088	1.032
130	13.532	11.646	1.131	1.066
140	14.352	12.564	1.156	1.099
150	15.27	13.473	1.183	1.129
160	16.434	14.356	1.215	1.157
170	16.926	15.307	1.228	1.184
180	17.991	16.2	1.255	1.209
190	19.139	17.086	1.281	1.232
200	19.844	18.015	1.297	1.255
318 K				
40	4.663	3.533	0.668	0.548
50	5.483	4.451	0.793	0.648
60	6.549	5.345	0.816	0.727
70	7.68	6.232	0.885	0.794
80	8.5	7.15	0.929	0.854
90	9.516	8.048	0.978	0.905
100	10.614	8.938	1.025	0.951
110	11.155	9.884	1.047	0.994
120	12.336	10.766	1.091	1.032
130	13.598	11.64	1.133	1.065
140	14.352	12.564	1.156	1.099
150	15.204	13.479	1.181	1.129
160	16.5	14.35	1.217	1.156
170	16.762	15.323	1.224	1.185
180	18.385	16.161	1.264	1.208
190	19.303	17.069	1.285	1.232
200	19.909	18.009	1.299	1.255

T	R ²	n	K _f
25	0.9891	1.0204	0.9499
30	0.9971	0.9802	0.8373
35	0.9975	0.9026	0.6613
40	0.9987	0.9062	0.6657
45	0.9959	0.8880	0.6244

It is noted from isotherms adsorption on the surface of α -alumina the amount of adsorption was increased of 2.4 by low temperature namely that the type of adsorption process exothermic as less than the amount of adsorbent high temperature because the thickness of adsorption was layer will be reduced with increasing temperature. This is due to increase the solution temperature that leads to increase in kinetic energy of the ions adsorbed on the surface adsorbent which leads to separate from the surface of adsorbent and return to the solution¹⁰.

Effect of pH: The effect of initial pH on α -alumina was examined over pH values from 2 to 10 and the result are present in Fig. 3 and Table-4. The adsorption amounts of 2,4-dichlorophenoxy acetic acid were higher at low pH It is a common observation that anions are favourably adsorbed on the surface of adsorbents at low pH because the presence of hydrogen ion renders the surface active for the adsorption of cations at high pH values¹¹.

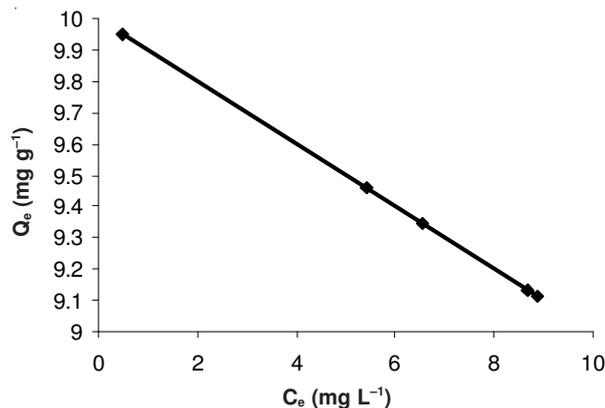


Fig. 3. Quantity of adsorption at different pH value, using α -alumina at 298 K for 100 ppm 2,4-dichlorophenoxy acetic acid solution

pH	Q _e (mg g ⁻¹)	C _e (mg L ⁻¹)
2	9.9515	0.4850
4	9.4564	5.4352
6	9.3468	6.5315
8	9.1309	8.6910
10	9.1142	8.8571

Effect of ionic strength: Study of the effects of strength ion by adding different concentrations of NaCl and found that the amount of material adsorbed on all surfaces decreases with increases concentration of NaCl solution, because the added concentration of NaCl solutions cause an increase in competition between ions of the 2,4-dichlorophenoxy acetic acid and electrolyte ions on the adsorption sites on the surface¹² (Fig. 4). The adsorption isotherm of 100 ppm 2,4-dichlorophenoxy acetic acid are given in Table-5.

C/M of Na Cl	C _e (mg L ⁻¹)	Q _e (mg g ⁻¹)
0.001	0.0046	9.9995
0.01	0.0150	9.9985
0.1	0.0994	9.9900

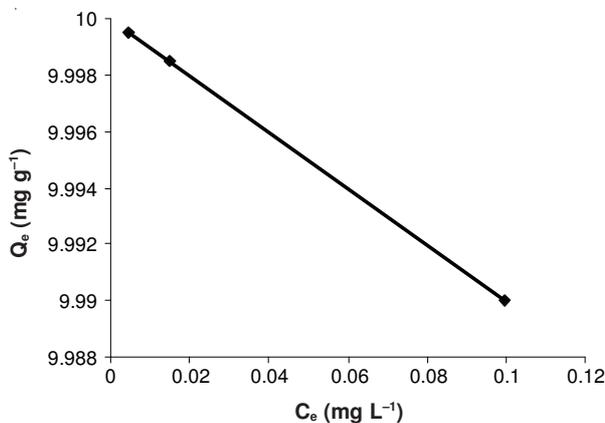


Fig. 4. Plot of Q_e against concentrations of NaCl for the adsorption of 100 ppm 2,4-dichlorophenoxy acetic acid solution at 298 K

Thermodynamic parameters: 2,4-Dichlorophenoxy acetic acid adsorption decreases with increasing temperature, showing the exothermic nature of the process. The thermodynamic functions ΔH , ΔG and ΔS were calculated using the following formulas¹³⁻¹⁵:

$$\log X_m = \frac{-\Delta H}{2.303RT} + \text{constant} \quad (3)$$

$$\Delta G = -RT \ln (Q_e/C_e) \quad (4)$$

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

where X_m is the maximum adsorption quantity for various 2,4-dichlorophenoxy acetic acid solution at different temperature.

The equation (3) was used to calculate the ΔH , by plotting against $1/T$. In the equation (4), where ΔG is the change in the value of free energy (KJ mol^{-1}), R is the gas constant [$8.314 \text{ (J mol}^{-1} \text{ deg}^{-1})$] (Fig. 5).

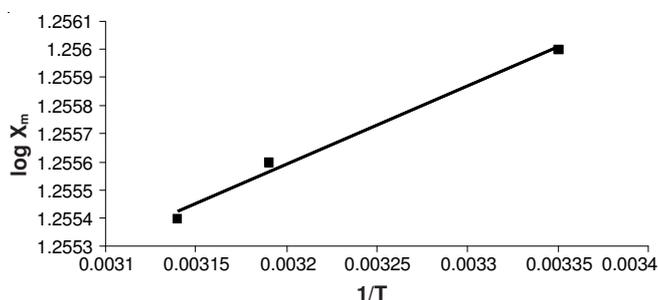


Fig. 5. Plot of $\log X_m$ against $1/T$

From Table-6, it's clear that ΔH has the negative values, which indicates the ideal and maximum value of physico-adsorption process. All values of ΔG were positive, these value indicate that the adsorption process accompanied the process of absorption.

T (K)	ΔH (kJ mol^{-1})	ΔG	ΔS ($\text{J mol}^{-1} \text{ K}$)
298		182.215	-6.1153
303		186.728	-6.1634
308	-0.02303	202.494	-6.5752
313		197.303	-6.3043
318		201.335	-6.3385

As the spreading molecules adsorbed inside the pores of the α -alumina and increases speed of deployment with increasing temperature and this behaviour is attributable to additional absorption. ΔS had the negative value, which indicates that the adsorbed molecules are arranged on the surface as a results of its association with α -alumina. This is the normal consequence of the physical adsorption phenomenon, which takes place through electrostatic interactions.

Kinetic model: 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 generally expressed as follows¹⁶:

$$\ln (q_e - q_t) = \ln q_e - K_{\text{ads}} \cdot t \quad (6)$$

where q_t and q_e are the amount of 2,4-dichlorophenoxy acetic acid adsorbed at at time (min) and at equilibrium time respectively and $K_{\text{ads}}/\text{min}^{-1}$ is the rate constant. The linear relationship was obtained *via* plotting $\ln q_e - q_t$ values t/min as shown in Fig. 6, q_t and q_e values are given in Table-7.

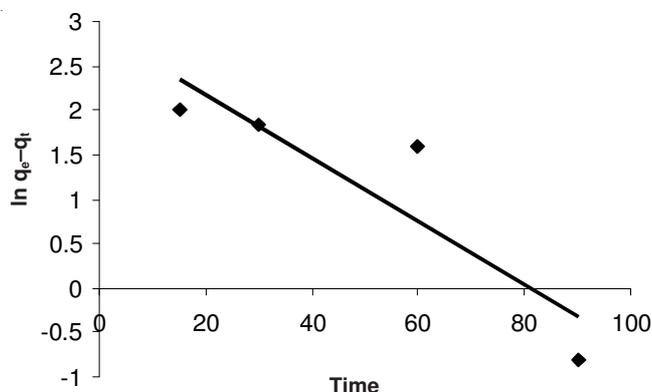


Fig. 6. Lagergreen model for a 2,4-dichlorophenoxy acetic acid of 100 ppm at 298 K

Time	q_t	q_e	$q_e - q_t$	$\ln q_e - q_t$
15	89.656		7.444	2.007
30	90.878		6.222	1.828
60	92.212	97.100	4.888	1.586
90	96.656		0.444	-0.811
120	97.100		0.000	-

Fig. 7 does not follow the adsorption kinetics of the first order. But when applied to the equation of the second order, it follow the kinetics of second order. The second adsorption kinetics of the 2,4-dichlorophenoxy acetic acid to α -alumina according to the following equation¹⁷:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (7)$$

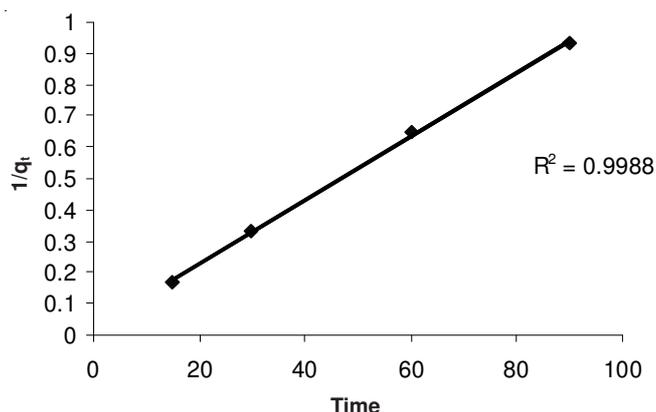


Fig. 7. t/q_t against time of the adsorption of 2,4-dichlorophenoxy acetic acid on to α -alumina of 100 ppm at 298 K

The value of rate constant for the pseudo second order reaction is calculated experimentally by plotting t/q_t against time of the adsorption of 2,4-dichlorophenoxy acetic acid on α -alumina clay according to equation 7, $K_{\text{ads}} (\text{min}^{-1} \text{ mg}^{-1} \text{ L}) = 0.04702$.

Morris -weber model: The kinetic model was used to estimate the rate limiting step of any adsorption process, the equation of this model could be expressed as follows¹⁸:

$$q_t = K_d \sqrt{t} \quad (8)$$

where q_t is the quantity of adsorbed material at any time (mg g^{-1}), K_d is the diffusion constant, \sqrt{t} is time of diffusion (min), the plotting of q_t against \sqrt{t} was accomplished at 298 K. Fig. 8 shows the plot of q_t against \sqrt{t} for 2,4-dichlorophenoxy acetic acid of 100 ppm at 298 K.

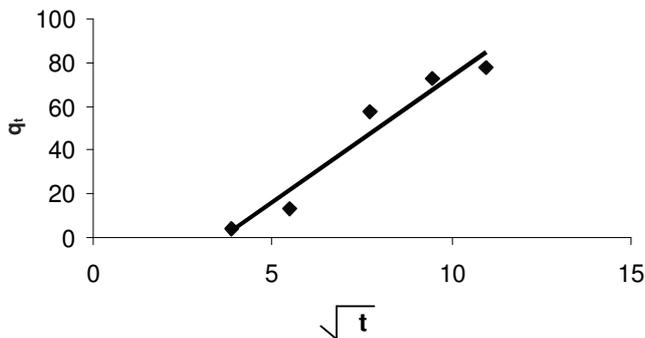


Fig. 8. Plot of q_t against \sqrt{t} for 2,4-dichlorophenoxy acetic acid of 100 ppm at 298 K

Reichenberg model: This kinetic model has been proposed to discuss the behaviour of many adsorption process in solution and Reichenberg had introduced following formula¹⁹:

$$F = (1 - 6/p^2) e^{-Bt} \quad (9)$$

$$B_t = -0.4977 - \ln(1 - F) \quad (10)$$

$$F = q_t/q_e \quad (11)$$

Plotting of time (min) against B_t revealed a linear relationship with relatively acceptable R^2 values.

Fig. 9 shows the variation of B_t with time for 2,4-dichlorophenoxy acetic acid of 100 ppm at 298 K. According to this model, it characterized the rate determining mechanisms which was diffusion process for 2,4-dichlorophenoxy acetic acid ions from the bulk solution to the adsorbent surface and adsorption occurred.

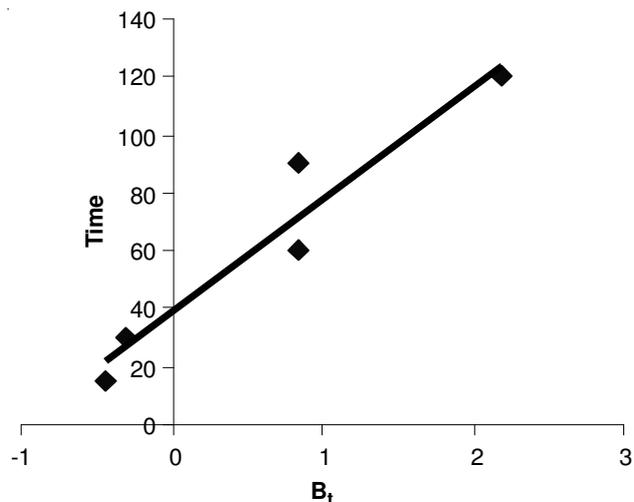


Fig. 9. Variation of B_t with time for 2,4-dichlorophenoxy acetic acid of 100 ppm at 298 K

REFERENCES

1. S. Hiradate, A. Furubayashi, N. Uchida and Y. Fujii, *J. Environ. Qual.*, **36**, 101 (2007).
2. B.V. Kavanagh, A.M. Posner and J.P. Quirk, *J. Colloid Interf. Sci.*, **61**, 545 (1977).
3. W.C. Koskinen and S.S. Harper, *The Retention Process-Pesticides in the Soil Environment: Processes, Impacts and Modeling*, SSSA, Madison, WI (1990).
4. G.V. Bhaskar and S.M. Bhamidimarri, *J. Chem. Technol. Biotechnol.*, **53**, 297 (2007).
5. G.S. Alexandre and C. Airoldi, *Anal. Chim. Acta*, **432**, 201 (2001).
6. I.S. Ahmed Farag, M.F. Kotkata, M.M. Selim, I.K. Battisha and M.M. El-Rafaay, *Egypt. J. Solids*, **27**, 233 (2004).
7. W.L. Moore, *Physical Chemistry*, Prentice-Hall, INC:495, edn. 4 (1972).
8. A. Hussien and H. Falah, *Thermodynamic of Liquids and Solution*, AL-Qadisiyah University (1993).
9. Metcalf & Eddy Inc., *Wastewater Engineering Treatment, Disposal, Reuse*, McGraw-Hill, edn. 3 (1991).
10. V.P. Vinod and T.S. Anirudhan, *J. Chem. Technol. Biotechnol.*, **77**, 92 (2001).
11. S.J. Kim, T.Y. Kim, S.J. Kim and S.Y. Cho, *Korean J. Chem. Eng.*, **19**, 1050 (2002).
12. W.H. Johns and T.R. Bates, *J. Pharm. Sci.*, **61**, 730 (1972).
13. J.J. Kipling, *Adsorption from Solution of Non-Electrolytes*, Academic Press, London, pp. 101-257 (1965).
14. R.W. Gaik Wad, *J. Environ. Agric. Food Chem.*, **3**, 702 (2004).
15. M.J. Horsfall, A.A. Abia and A.I. Spiff, *J. Biotechnol.*, **2**, 360 (2003).
16. M.H. Entizaei and T.R. Bastami, *J. Hazard. Mater. B*, **137**, 959 (2006).
17. M.J. Horsfall and A.I. Spiff, *Electron. J. Biotechnol.*, **8**, 163 (2005).
18. Y.S. McKay and G. Ho, *Water Res.*, **34**, 735 (2000).
19. W.S. Wan Ngah, M.A.K.M. Hanafiah, S.S. Yong, *Colloids Surf. B*, **65**, 18 (2008).