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Adsorption Equilibrium Characteristics of 2,4-Dichlorophenoxyacetic Acid and 2,4-Dinitrophenol on Granular Activated Carbons

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Abstract−Adsorption characteristics of 2,4-Dichlorophenoxyacetic acid (2,4-D) and 2,4-Dinitrophenol (2,4-DNP) onto granular activated carbon (GAC) were studied to obtain basic information on their removal from aqueous solution. Single component adsorption equilibria of 2,4-D and 2,4-DNP dissolved in water have been measured for three kinds of GACs (F400, SLS103, and WWL). In case of 2,4-D, the magnitude of adsorption capacity was in the order of F400> SLS103>WWL, and that for 2,4-DNP was SLS103>F400>WWL. The influence of temperature and initial pH of aqueous solution on adsorption has been discussed in detail by using the Sips equation.

Key words: Adsorption, GAC, 2,4-Dichlorophenoxyacetic Acid, 2,4-Dinitrophenol, Equilibrium

INTRODUCTION

Environmental contamination by toxic xenobiotic chemicals is a serious worldwide problem. These contaminants arise predominantly from agricultural and industrial sources [Vroumsia et al., 1999]. The widespread usage of pesticides has a potential negative impact on public health and the ecosystem. Some of the applied herbicides are continuously discharged into aquatic environments through the surface runoff, and such discharge can lead to contaminated aquatic environments which are hazardous to resident organisms [Wong, 2000].

Among the numerous agrochemicals in use today, the herbicide 2,4-dichlorophenoxy acetic acid (2,4-D), a member of the phenoxy herbicide group, has been widely applied to control broad leaf weeds [Mangat and Elefsiniotis, 1999]. 2,4-D is a regulated compound due to its toxicity; solids containing 2,4-D in excess of 1,000 ppm are classified as hazardous. 2,4-D is used as agricultural herbicides against broad leaf weeds in cereal crops as well as on pastures and lawns, in parks, and on golf courses. In commercial formulation processes involving phenoxyalkanoic acid herbicide, the level of 2,4-D in liquid and solid waste streams may be excessive and constitute a disposal problem. Disposal of unused 2,4-D and washing equipment may result in localized land pollution and also pollution of water supplies through direct contamination or leaching from soil [Oh and Kim, 1994].

2,4-Dinitrophenol (2,4-DNP) is used in the manufacture of dyes and wood preservatives and as a pesticide. It is also used as an indicator for the detection of potassium and ammonium ions. 2,4-DNP exists as yellowish crystals, is slightly soluble in water [The Merck Index, 1989], and is considered to be highly toxic to humans with a lethal oral dose of 14 to 43 mg/kg. The acute (short-term) effects of 2,4-DNP on humans through oral exposure are nausea, vomiting, sweating, dizziness, headaches, and loss of weight. Long-term oral exposure to 2,4-DNP could cause the formation of cataracts and skin lesions and affect the bone marrow, central nervous system (CNS) and cardiovascular system.

Various treatment techniques have been employed to treat the wastewater, including precipitation, adsorption, ion exchange and reverse osmosis [Chen and Wang, 2000]. Among them, adsorption onto solid adsorbents has great environmental significance, since it can effectively remove pollutants from both aqueous and gaseous streams [Lee and Moon, 2001; Kim et al., 2001; Markovska et al., 2001; Na et al., 2001]. In wastewater treatment, activated carbon is a powerful adsorbent because it has a large surface area and pore volume, which remove liquid-phase contaminants, including organic compounds, heavy metal ions and colors [Noll et al., 1992; Hsieh and Teng, 2000]. The characteristics, pH, and temperature of wastewater are likely to vary with time, so design of a suitable adsorption system is not that simple; this difficulty is compounded by the fact that the influence of these parameters on the adsorption of pollutants has not been extensively studied [Kim et al., 2001]. In order to design effective activated carbon adsorption units and to develop mathematical models that can accurately describe their operation, sufficient information on both the adsorption and the desorption of individual pollutants under different operating conditions is required [Khan et al., 1997].

The main purpose of this work is to select a proper adsorbent for elimination of 2,4-D and 2,4-DNP from its aqueous solution, and to study their adsorption characteristics experimentally as well as theoretically.

Equilibrium data are experimentally obtained and isotherm parameters are determined by employing typical single-component isotherm equations such as Langmuir, Freundlich, Sips, Redlich-Peterson, Radke-Prausnitz, Toth, Khan, and Fritz and Schlunder. Particularly, the effect of pH and temperature on adsorption equilibrium is extensively discussed.

THEORETICAL APPROACH

Adsorption mechanisms are so complicated that no simple theory can adequately explain adsorption characteristics. Many expres-

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Table 1. Various isotherm models for single component system

Isotherm	Model equations	Parameters
Langmuir	$q=\frac{q_m bC}{1+bC}$	q_m, b
Freundlich	$q=kC^{1/n}$	k, n
Sips	$q=\frac{q_m bC^{1/n}}{1+bC^{1/n}}$	q_m, b, n
Redlich-Peterson	$q=\frac{aC}{1+bC^{m}}$	a, b, m
Radke and Prausnitz	$q=\frac{q_m aC}{1+aC^{n}}$	q_m, a, n
Toth	$q=\frac{q_m a^{1/n}C}{(1+aC^{n})^{1/n}}$	q_m, a, n
Khan	$q=\frac{q_m aC}{(1+aC)^{n}}$	q_m, a, n
Fritz and Schlunder	$q=\frac{q_m a_1 C^{n_1}}{1+a_2 C^{n_2}}$	q_m, a_1, a_2, n_1, n_2

sions have been reported which describe the equilibrium relationship between the adsorbate and the adsorbent (activated carbon). Langmuir and Freundlich isotherms are the most commonly used, and sometimes piecewise equations are used for a selected range of concentration where implementation of only one expression fails badly [Khan et al., 1997].

Some of the well-known adsorption isotherms for single component systems are listed in Table 1.

1. Effect of Temperature

For useful description of adsorption equilibrium data for various temperatures, it is important to have the temperature-dependent form of an isotherm equation [Do, 1998]. The Sips equation of temperature dependency,

$$q=\frac{q_m bC^{1/n}}{1+bC^{1/n}} \tag{1}$$

for the affinity constant b and the exponent n may take the following form:

$$b=b_0\exp\left(\frac{-\Delta H\cdot Z}{R}\right) \tag{2}$$

$$Z=\frac{1}{T}-\frac{1}{T_m} \tag{3}$$

Here, b_0 is the adsorption affinity constant at mean temperature, T_m. The temperature dependency of the affinity constant b is taken from that of the Langmuir equation. Unlike ΔH in the Langmuir equation, where it is the isosteric heat, invariant with the surface loading, the parameter ΔH in the Sips equation is only the measure of the adsorption heat.

This temperature-dependent form of the Sips equation can be used to fit adsorption equilibrium data of various temperatures to obtain the parameter b_0, q_m, and ΔH .

2. Effect of Initial pH

The surface heterogeneity and chemical nature of the adsorbent surface are important factors for the determination of the influence of pH on the adsorption of single systems. In general, high pH depresses the equilibrium amount adsorbed, but neutral salt addition to the solution increases adsorption. Each experimental isotherm was plotted in terms of the Sips equation to obtain the pH-dependent parameters, q_m and b. The pH dependency of these parameters was assumed to obey the following empirical expression.

The Sips equation of pH dependency

$$q=\frac{q_m bC^{1/n}}{1+bC^{1/n}} \tag{1}$$

for the maximum adsorption amount q_m, the affinity constant b, and the exponent n may take the following form:

$$q_m=q_{m0}\exp(\alpha\cdot Z) \tag{4}$$

$$b=b_0\exp(-\beta\cdot Z) \tag{5}$$

$$Z=\frac{1}{pH}-\frac{1}{pH_m} \tag{6}$$

Here, b_0 is the adsorption affinity constant at mean pH, pH_m, α, and β are parameters of the Sips equation of pH dependency.

EXPERIMENTAL

1. Adsorbents and Adsorbates

The adsorbents used in this study were granular activated carbon (GAC) F400, SLS103 and WWL manufactured by Calgon, Samchully and Union Carbon Co., respectively. GAC was sieved into a narrow range of particle sizes (0.055-0.065 cm in diameter), and washed with distilled water several times to remove impurities. The GACs were then stored in a sealed bottle with a silica gel to prevent the readsorption of moisture. The structural characterization of the GACs was measured by a static volumetric adsorption analyzer (Micrometrics ASAP 2000) using nitrogen adsorption at 77 K.

The adsorbates investigated were 2,4-D and 2,4-DNP. The purities of each adsorbate as follows: 2,4-D, 99.0% (Acros Co.); 2,4-DNP, special grade (Yakuri Co.). All chemicals were used as received without further treatment. The solution pH was adjusted to 3.5, 7.0, 10.0 using NaOH or HCl. The solution pH, however, was not controlled during the adsorption process. The physical properties of 2,4-D and 2,4-DNP are shown in Table 2.

2. Isotherm Test

Adsorption isotherms were determined by contacting a volume

Table 2. Properties of adsorbates used in this study [Hornsby et al., 1996; Buckingham, 1988]

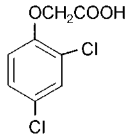
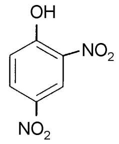
Compound	Structure	Mw	Water solubility (mg/*l*)	pKa (at 298.15 K)
2,4-D		221.04	1,072 (298.15 K)	2.8
2,4-DNP		184.11	<1,000 (292.65 K)	4.0

Table 3. Properties of adsorbents

Physical properties	Unit	F400	SLS103	WWL
Type	-	Coal-based	Coconut-based	Coal-based
Particle diameter	mm	0.37-0.54	0.37-0.54	0.37-0.54
Particle density	kg/m^3	682	880	707
Particle porosity	-	0.62	0.47	0.57
BET surface area	m^2/g	800	1040	670
Micropore area	m^2/g	490	930	360
Average pore diameter	Å	19.02	15.11	15.44

of solution with a carefully weighed amount of GAC in a conical flask. The amounts of carbon were varied (0.001-0.25 g), and the volume of the solution was 200 ml in single solute test. The flasks were shaken for 7 days to provide enough time and contact for equilibrium between the solid and liquid phase. Prior to analysis of the sample taken from the flask, it was filtered to remove suspended carbon particles. Concentrations of the solution of 2,4-D and 2,4-DNP were determined with UV spectrophotometer (Shimadzu 1601) at λ=284 nm and 325 nm, respectively. The amounts of 2,4-D and 2,4-DNP adsorbed onto the GAC at equilibrium were calculated from the following mass balance equation:

$$q=(C_i-C)\frac{V}{W} \tag{3}$$

Here q is the equilibrium amount adsorbed on the adsorbent (mol/kg), C_i is the initial concentration of bulk fluid (mol/m^3), C is the equilibrium concentration of the solution (mol/m^3), V is the volume of solution (m^3), and W is the weight of adsorbent (kg).

RESULTS AND DISCUSSION

Adsorption isotherms are very important in the design of an adsorption-based process for wastewater treatment. In this study, seven isotherm models - Langmuir, Freundlich, Sips, Redlich-Peterson [Ko, 2001], Radke-Prausnitz [Radke and Prausnitz, 1972], Toth [Toth, 1983], Khan [Moon et al., 1989; Khan et al., 1997], and Fritz and Schlunder [Khan et al., 1997] - were used to correlate our experimental equilibrium data. The Langmuir and Freundlich equations have two parameters; the Sips, Redlich-Peterson, Radke-Prausnitz, Toth, and Khan equations have three parameters; and the Fritz and

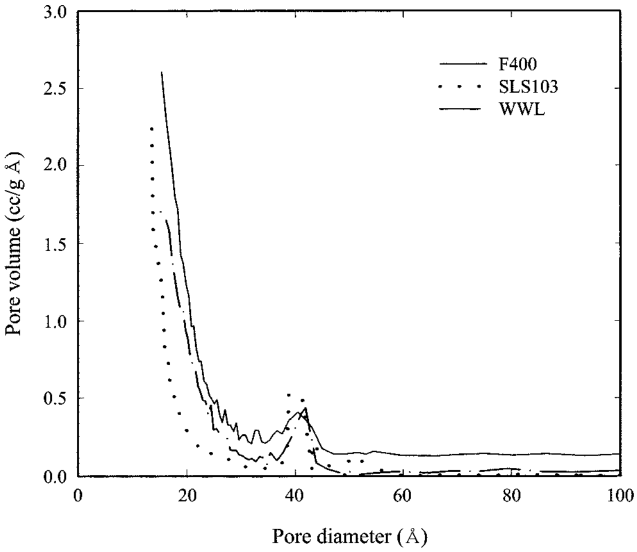


Fig. 1. Pore size distribution of three different adsorbents calculated from desorption experiments of N_2.

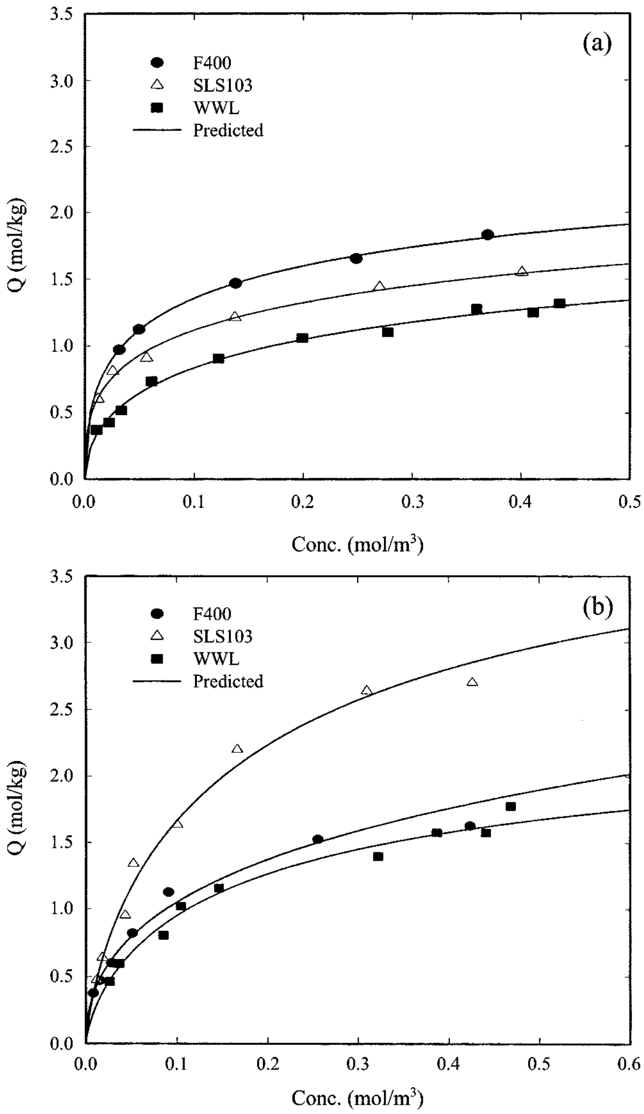


Fig. 2. Adsorption equilibrium of 2,4-D (a) and 2,4-DNP (b) onto three different adsorbents at initial pH of 3.5 and 298.15 K.

Schlunder equation has five parameters. To find the isotherm parameters for each adsorption, the linear least square method and the pattern search algorithm (NMEAD) were used. The value of the mean percentage error has been used as a test criterion for the fit of the correlations. The mean percent deviation between experimental and predicted values is as follows:

$$\mathrm{Error}(\%)=\frac{100}{N}\sum_{k=1}^{N}\left[\frac{|q_{exp,k}-q_{cal,k}|}{q_{exp,k}}\right] \tag{8}$$

1. Effect of Adsorbents

The surface chemistry of activated carbon and the chemical characteristics of adsorbate such as polarity, ionic nature, functional groups, and solubility in water determine the nature of bonding mechanisms as well as the extent and strength of adsorption. A variety of physicochemical forces, such as van der Waals, H-binding, dipole-dipole interactions, ion exchange, covalent bonding, cation bridging, and water bridging, can be responsible for the adsorption of organic compounds on activated carbon [Zumriye and Julide, 2001].

The physical properties of the GACs are listed in Table 3. As shown there, the average pore diameter of F400 is 19.02 Å, while those of SLS103 and WWL are 15.11 Å and 15.44 Å, respectively. Fig. 1 shows the pore size distribution of three different adsorbents measured by desorption isotherms. According to the pore size distribution analysis, SLS103 has a somewhat broader distribution compared to those for F400 and WWL. Such a difference can affect the adsorption characteristics.

The adsorption isotherms of 2,4-D and 2,4-DNP onto three different adsorbents are shown in Fig. 2. As illustrated in these figures, in case of 2,4-D, the magnitude of adsorption capacity was in the order of F400>SLS103>WWL, and that for 2,4-DNP is SLS103 >F400>WWL. This result may come from the effect of the pore size distribution and the surface area, and surface properties. The estimated values of parameters for adsorption isotherms onto three different adsorbents are listed in Tables 4, 5 and 6, respectively.

2. Effect of Temperature

The present experimental data are analyzed to study the effect

Table 4. Adsorption equilibrium constants of 2,4-D and 2,4-DNP onto F400 for different initial pHs at 298.15 K

Isotherm	Parameters	pH3.5		pH7.0		pH10.0	
		2,4-D	2,4-DNP	2,4-D	2,4-DNP	2,4-D	2,4-DNP
Langmuir	q_m	1.857	1.809	0.615	0.532	0.503	0.501
	b	33.86	20.54	40.69	385.1	83.83	124.3
	Error (%)	3.111	9.786	2.937	4.844	2.710	3.432
Freundlich	k	2.369	2.542	0.771	0.754	0.598	0.697
	n	3.974	2.541	4.451	5.872	6.819	5.218
	Error (%)	1.354	5.725	2.335	5.001	2.011	2.985
Sips	q_m	3.025	6.995	0.747	0.583	0.629	0.583
	b	2.361	0.514	7.324	32.38	6.584	15.76
	n	2.164	2.163	1.623	1.616	2.156	1.619
	Error (%)	1.020	4.593	1.701	2.403	0.270	1.511
Redlich-Peterson	a	197.3	57.03	56.84	332.5	82.63	122.1
	b	87.23	27.42	78.96	517.1	147.2	198.5
	m	0.808	0.826	0.854	0.912	0.915	0.887
	Error (%)	0.561	6.843	1.623	2.086	0.515	1.146
Radke-Prausnitz	q_m	2.262	2.080	0.720	0.643	0.561	0.615
	a	87.20	27.42	78.96	517.1	147.2	199.3
	n	0.808	0.826	0.854	0.912	0.914	0.887
	Error (%)	0.560	6.843	1.623	2.086	0.515	1.140
Toth	q_m	5.694	2.613	1.052	0.688	0.646	0.717
	a	4.714	6.011	7.178	21.52	14.94	13.10
	n	0.202	0.507	0.314	0.374	0.388	0.357
	Error (%)	0.709	5.809	1.805	2.614	0.336	1.471
Khan	q_m	0.798	0.900	0.335	0.349	0.348	0.307
	a	170.9	54.90	133.1	830.7	203.2	332.0
	n	0.798	0.793	0.844	0.909	0.910	0.879
	Error (%)	0.515	7.435	1.574	2.019	0.539	1.077
Fritz-Schlunder	q_m	2.278	2.469	1.428	8.203	1.627	535.3
	a_1	1.181	1.758	0.647	25.30	0.469	751.2
	a_2	1.270	0.163	1.981	785.3	2.773	834.9
	n_1	0.287	0.527	0.274	0.958	0.212	2.112
	n_2	0.272	7.915	0.276	0.866	0.281	1.989
	Error (%)	0.906	3.379	2.049	2.031	0.195	1.003

Table 5. Adsorption equilibrium constants of 2,4-D and 2,4-DNP onto SLS103 for different initial pHs at 298.15 K

Isotherm	Parameters	pH3.5		pH7.0		pH10.0	
		2,4-D	2,4-DNP	2,4-D	2,4-DNP	2,4-D	2,4-DNP
Langmuir	q_m	1.384	3.247	0.646	0.569	0.631	0.552
	b	61.79	12.24	38.32	68.73	24.28	69.44
	Error (%)	8.451	7.462	3.935	1.021	2.261	1.536
Freundlich	k	2.011	4.823	0.898	0.713	0.761	0.656
	n	3.798	2.011	3.558	5.416	3.836	6.224
	Error (%)	2.990	8.980	3.428	2.570	2.203	1.775
Sips	q_m	3.458	4.466	1.393	0.584	0.753	0.643
	b	1.137	3.355	1.345	42.59	6.515	9.700
	n	2.664	1.332	2.447	1.123	1.464	1.786
	Error (%)	2.434	5.077	3.685	0.802	1.163	0.667
Redlich-Peterson	a	547.3	42.17	66.08	50.11	28.64	65.28
	b	279.3	12.18	80.19	82.37	40.21	107.9
	m	0.762	0.932	0.801	0.949	0.851	0.921
	Error (%)	2.602	7.401	3.436	0.894	1.075	0.665
Radke-Prausnitz	q_m	1.959	3.463	0.824	0.608	0.712	0.605
	a	279.3	12.18	80.19	82.37	40.21	107.9
	n	0.762	0.932	0.801	0.949	0.851	0.921
	Error (%)	2.602	7.401	3.436	0.894	1.075	0.665
Toth	q_m	37.09	3.730	2.047	0.602	0.951	0.661
	a	3.513	7.392	4.520	33.96	6.645	16.74
	n	0.085	0.789	0.213	0.755	0.415	0.475
	Error (%)	2.609	6.682	3.625	0.968	1.191	0.665
Khan	q_m	0.392	2.757	0.279	0.464	0.353	0.396
	a	755.4	14.48	167.3	102.2	66.75	144.7
	n	0.757	0.923	0.789	0.941	0.834	0.915
	Error (%)	2.584	7.900	3.356	0.872	1.038	0.664
Fritz-Schlunder	q_m	1.209	42.97	58.47	90.17	8.678	1.198
	a_1	1.791	0.271	128.3	43.19	60.67	0.764
	a_2	0.035	1.868	342.5	208.5	122.8	3.267
	n_1	0.282	0.723	1.773	1.706	1.544	0.249
	n_2	5.187	1.425	1.563	1.640	1.374	0.346
	Error (%)	2.514	5.181	3.301	0.783	1.000	0.727

of temperature on the adsorption isotherms of 2,4-D and 2,4-DNP. In Figs. 3 and 4, the equilibrium data for 2,4-D and 2,4-DNP are plotted with generalized Sips equation (a) and Sips equation of temperature dependency (b). The parameters of each isotherm were obtained by least square fitting with experimental data. These parameters and the average percent differences between measured and calculated values are given in Table 7. The accuracy of the values is dependent on the degree of fitness, which can be judged by comparing average percentage error. The values of heat of adsorption, ΔH, for different adsorbates and F400 systems, have been plotted in Fig. 5. The value of heat of adsorption for 2,4-D was 1.450×10^4 J/mol and that for 2,4-DNP was 1.001×10^4 J/mol. So that the adsorption capacity of 2,4-D is greater than 2,4-DNP.

In all cases there is a substantial effect of temperature on the adsorption isotherm, and it becomes more linear as temperature increases. So we may conclude that physical adsorption is dominant for these adsorption systems.

3. Effect of Initial pH

All of the constant pH adsorption isotherms show type I adsorption isotherm behavior, with saturation capacities depending on pH. Figs. 6, 7 and 8 show that the experimental equilibrium adsorption isotherms obtained at different initial pH for the adsorption of 2,4-D onto F400, SLS103, and WWL, respectively. As shown in those figures, the adsorption amounts decreased with increasing initial pH of the solution, for pH range of 3.0-10.0. In general, the influence of pH is attributed to the electrostatic interaction between the adsorbent surface and the adsorbate molecule or ion. This suggests that effective separation could be achieved by the adjustment of pH. Figs. 9, 10 and 11 also show the experimental equilibrium adsorption isotherms obtained at different initial pH for the adsorption of 2,4-DNP onto F400, SLS103, and WWL, respectively. As shown in those Figures, the GACs has a higher adsorption equilibrium capacity at lower pH. And also, the experimental data are well represented by the Sips equation (a) and Sips equation of pH dependency (b). A Sips model and that with pH dependent parameters were fitted with experimental equilibrium data successfully for all of the pH

Table 6. Adsorption equilibrium constants of 2,4-D and 2,4-DNP onto WWL for different initial pHs at 298.15 K

Isotherm	Parameters	pH3.5		pH7.0		pH10.0	
		2,4-D	2,4-DNP	2,4-D	2,4-DNP	2,4-D	2,4-DNP
Langmuir	q_m	1.431	1.770	0.571	1.182	2.183	0.542
	b	17.95	13.45	6.502	1.696	0.405	8.234
	Error (%)	7.660	5.560	1.828	5.690	3.701	7.139
Freundlich	k	1.802	2.394	0.696	1.009	0.698	0.589
	n	2.836	2.346	1.994	1.273	1.104	2.714
	Error (%)	4.797	5.679	1.693	5.638	3.943	7.531
Sips	q_m	2.460	2.593	1.012	1.144	1.453	0.463
	b	1.738	3.000	1.405	1.803	0.686	22.96
	n	1.900	1.402	1.423	0.992	0.958	0.786
	Error (%)	4.375	4.537	1.094	5.873	3.805	6.930
Redlich-Peterson	a	82.99	42.53	8.814	2.401	0.925	8.898
	b	49.43	18.95	12.65	1.974	0.541	15.80
	m	0.744	0.733	0.626	0.739	0.964	0.806
	Error (%)	4.855	4.630	1.229	6.826	4.184	7.511
Radke-Prausnitz	q_m	1.679	2.244	0.697	1.216	1.711	0.563
	a	49.43	18.95	12.65	1.974	0.541	15.80
	n	0.744	0.733	0.626	0.739	0.964	0.806
	Error (%)	4.855	4.629	1.229	6.826	4.184	7.511
Toth	q_m	4.180	5.005	5.736	2.158	1.723	0.931
	a	3.514	2.845	1.521	1.086	0.537	3.652
	n	0.260	0.343	0.230	0.655	0.993	0.420
	Error (%)	4.536	4.735	1.266	6.802	4.168	7.621
Khan	q_m	0.413	0.653	0.138	0.357	0.627	0.257
	a	146.5	49.87	41.37	6.367	1.490	28.05
	n	0.719	0.691	0.579	0.506	0.454	0.773
	Error (%)	5.030	4.558	1.196	6.813	4.241	7.455
Fritz-Schlunder	q_m	0.620	20.62	0.665	6.063	2.136	9.479
	a_1	4.498	45.96	3.154	10.84	9.905	20.55
	a_2	6.287	114.1	23.91	34.59	22.37	55.25
	n_1	0.460	1.599	0.785	1.773	1.824	1.686
	n_2	0.288	1.282	0.363	1.222	1.122	1.466
	Error (%)	4.284	4.487	1.244	6.184	3.831	7.338

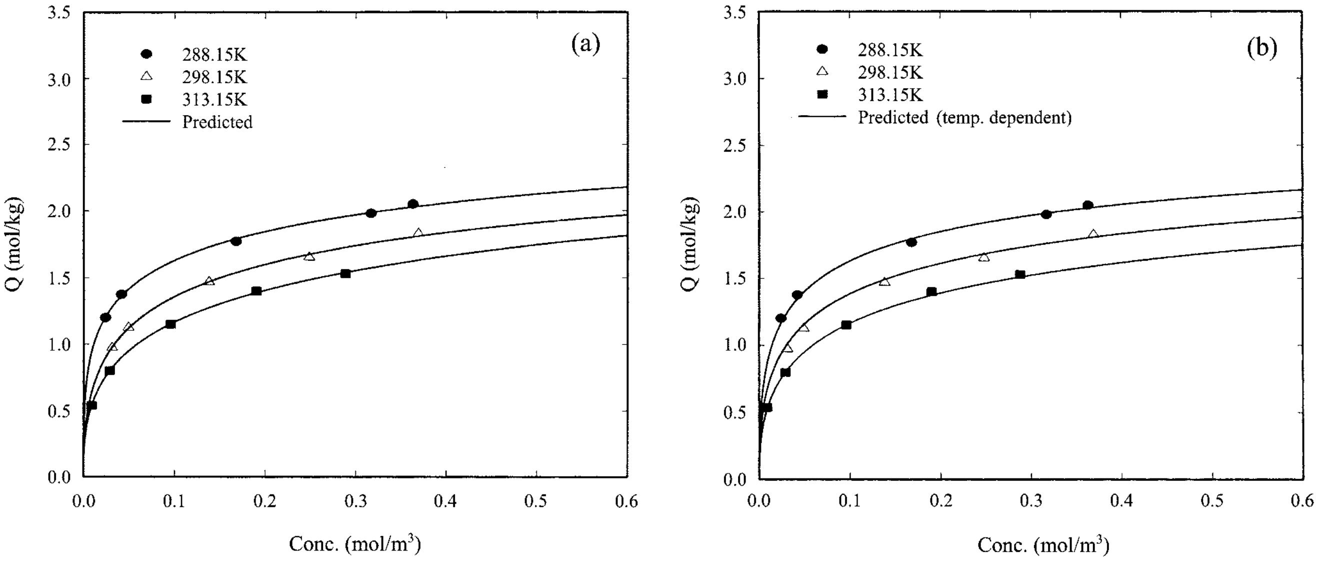


Fig. 3. Experimental data and predicted adsorption isotherm for 2,4-D - F400 system for different temperatures at initial pH of 3.5 (a: Sips Eq., b: Temperature dependent Sips Eq.).

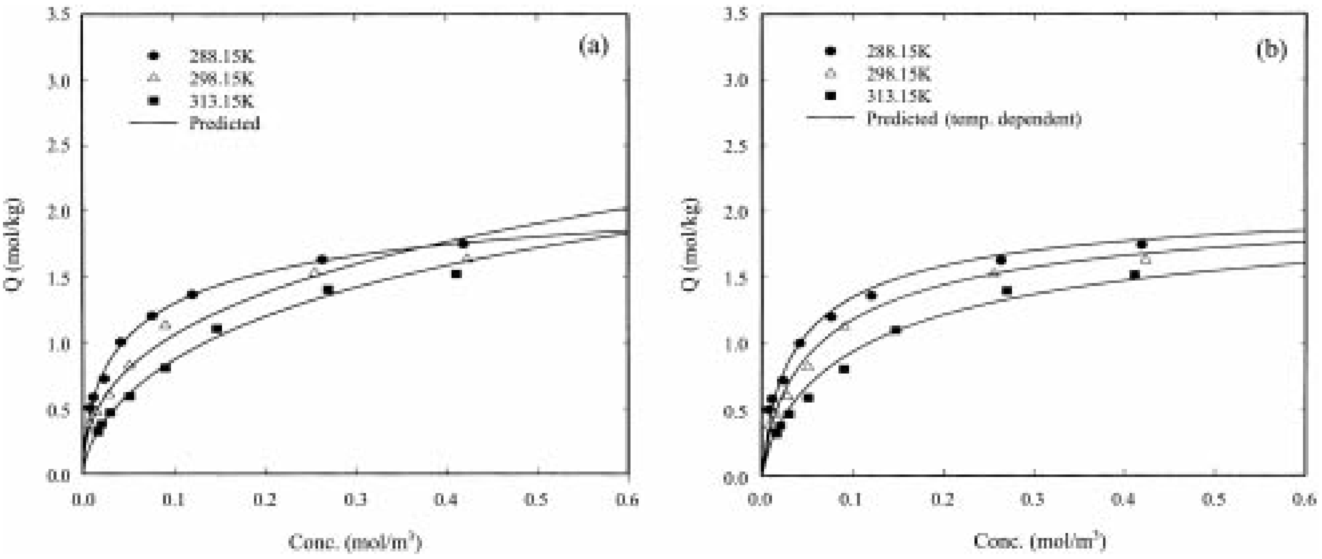


Fig. 4. Experimental data and predicted adsorption isotherm for 2,4-DNP - F400 system for different temperatures at initial pH of 3.5 (a: Sips Eq., b: Temperature dependent Sips Eq.).

Table 7. Adsorption equilibrium constants of 2,4-D and 2,4-DNP onto F400 for different temperature at initial pH of 3.5

Isotherm	Parameters	288.15 K		298.15 K		313.15 K	
		2,4-D	2,4-DNP	2,4-D	2,4-DNP	2,4-D	2,4-DNP
Langmuir	q_m	2.047	1.511	1.857	2.308	1.396	1.857
	b	56.14	57.57	33.86	26.51	67.36	10.57
	Error (%)	3.566	8.405	3.111	6.785	8.712	7.362
Freundlich	k	2.485	2.554	2.369	4.068	2.292	2.609
	n	5.223	3.077	3.974	2.374	3.306	2.011
	Error (%)	0.839	5.838	1.354	3.815	1.968	4.071
Sips	q_m	3.498	2.349	3.025	3.781	3.688	3.887
	b	1.979	5.021	2.361	2.924	1.196	1.223
	n	2.811	1.629	2.164	1.644	2.426	1.584
	Error (%)	0.760	2.225	1.020	0.388	0.349	2.950
Redlich-Peterson	a	629.5	117.1	197.3	133.0	290.1	26.82
	b	259.0	55.20	87.23	40.97	136.5	12.32
	m	0.835	0.832	0.808	0.741	0.756	0.793
	Error (%)	0.631	3.049	0.561	1.171	0.774	4.841
Radke-Prausnitz	q_m	2.430	2.121	2.262	3.242	2.126	2.177
	a	259.0	55.20	87.20	40.57	136.5	12.32
	n	0.835	0.832	0.808	0.742	0.756	0.793
	Error (%)	0.631	3.049	0.560	1.142	0.774	4.841
Toth	q_m	12.74	2.708	5.694	5.414	7.544	2.708
	a	5.386	7.166	4.714	4.163	3.890	7.166
	n	0.102	0.426	0.202	0.349	0.174	0.426
	Error (%)	0.743	2.479	0.709	0.700	0.592	2.479
Khan	q_m	0.863	0.861	0.798	0.765	0.449	0.863
	a	465.5	114.6	170.9	134.1	433.2	27.26
	n	0.832	0.810	0.798	0.703	0.743	0.730
	Error (%)	0.602	3.261	0.515	1.405	0.868	5.232
Fritz-Schlunder	q_m	1.509	1.378	2.278	2.672	1.672	23.46
	a_1	1.734	3.241	1.181	2.224	1.602	1.285
	a_2	1.867	4.634	1.270	1.730	0.238	76.68
	n_1	0.205	0.453	0.287	0.505	0.338	0.981
	n_2	0.081	0.508	0.272	0.971	2.080	0.596
	Error (%)	0.802	1.836	0.906	0.603	0.384	3.751

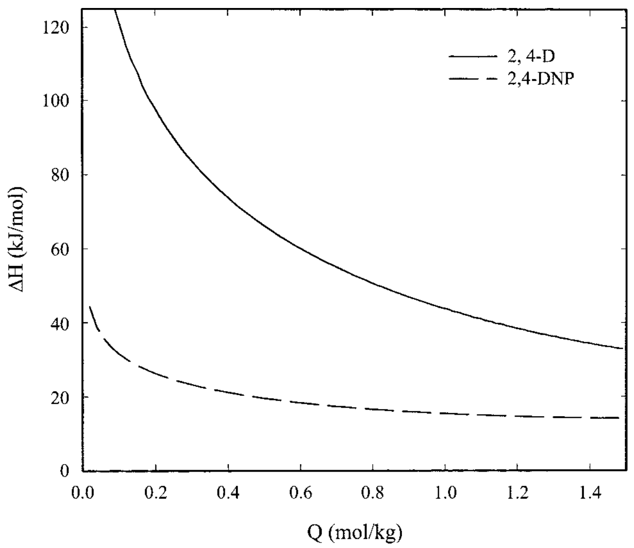


Fig. 5. Heat of adsorption for 2,4-D and 2,4-DNP onto F400.

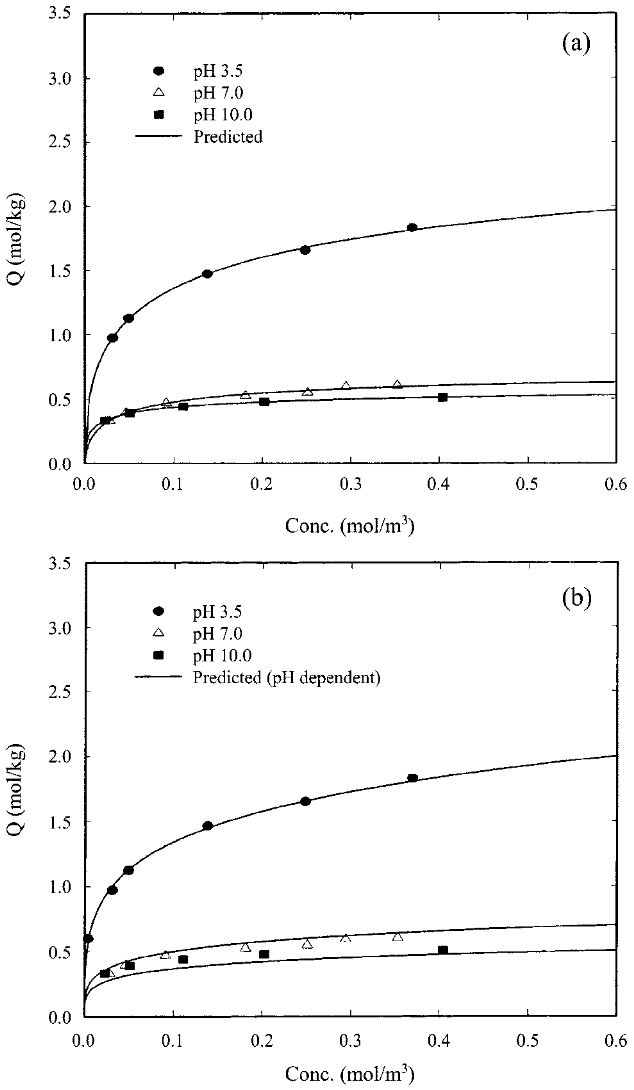


Fig. 6. Experimental data and predicted adsorption isotherm for 2,4-D - F400 system for different initial pH at 298.15 K (a: Sips Eq., b: pH dependent Sips Eq.).

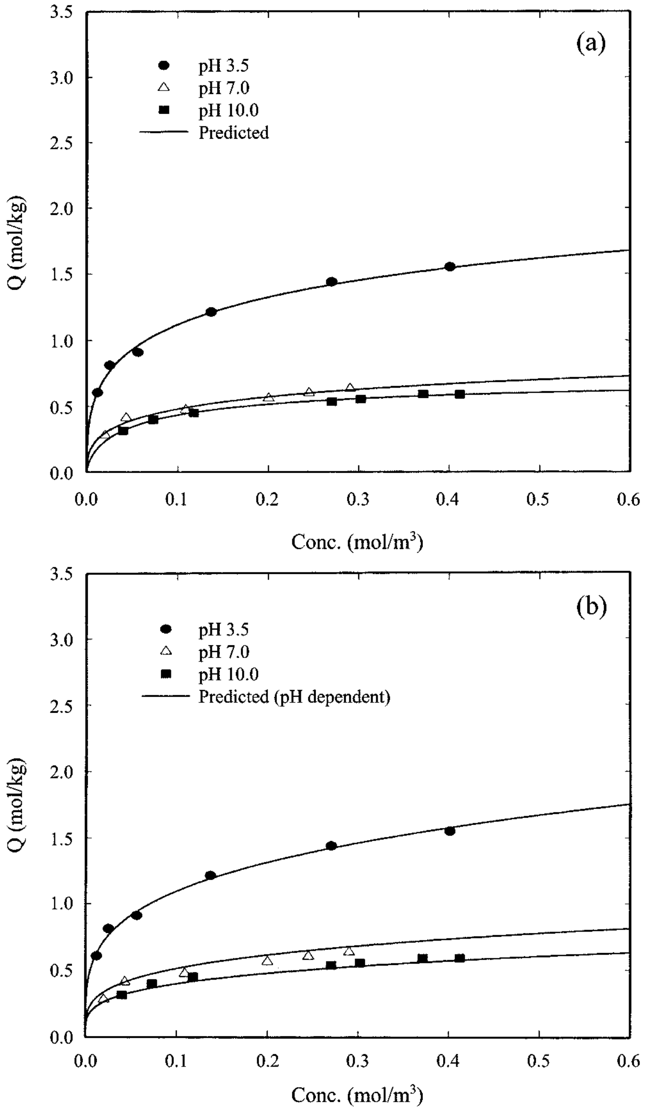


Fig. 7. Experimental data and predicted adsorption isotherm for 2,4-D - SLS103 system for different initial pH at 298.15 K (a: Sips Eq., b: pH dependent Sips Eq.).

conditions. The calculated parameters of Sips equation of pH dependency listed in Table 8. Compared with those in Table 4, the error percent differences between Sips equation and Sips equation of pH dependency are not very large. So, we could correlate single component isotherm data by the modified Sips equation. The choice of the pH dependent function is arbitrary.

CONCLUSION

This study presents the adsorption characteristics of 2,4-D and 2,4-DNP onto three kinds of GACs, F400, SLS103, and WWL. The adsorption of 2,4-D and 2,4-DNP onto GACs-F400, SLS103, and WWL - was favorable, and single adsorption equilibrium data were fitted by the several proposed isotherms. Among these isotherms for single species, Sips isotherm was used to fit experimental equilibrium data. The affinity of 2,4-D onto GACs was in the following order: F400>SLS103>WWL, and that for 2,4-DNP is

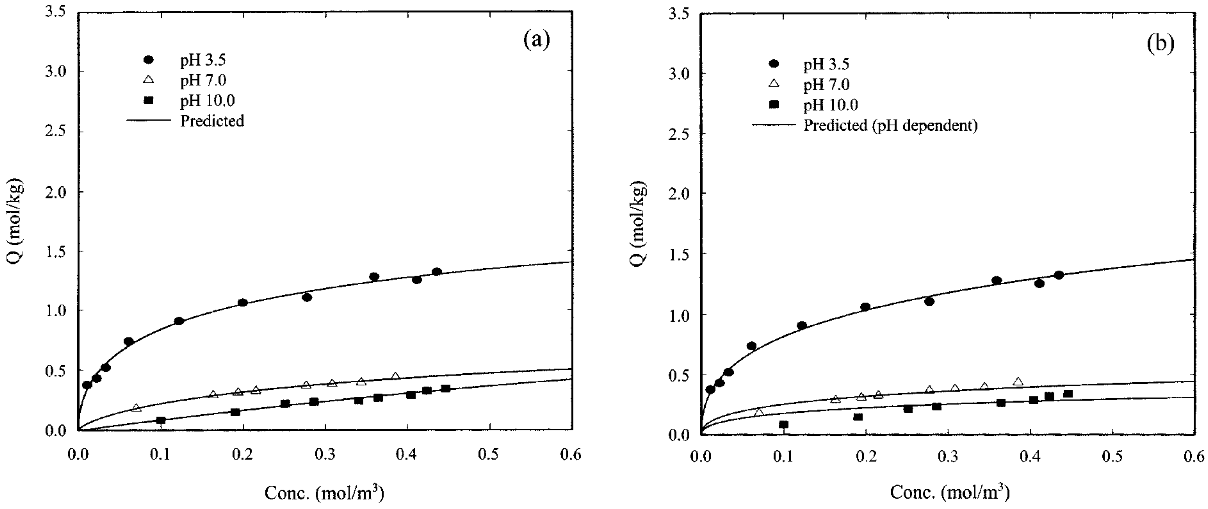


Fig. 8. Experimental data and predicted adsorption isotherm for 2,4-D - WWL system for different initial pH at 298.15 K (a: Sips Eq., b: pH dependent Sips Eq.).

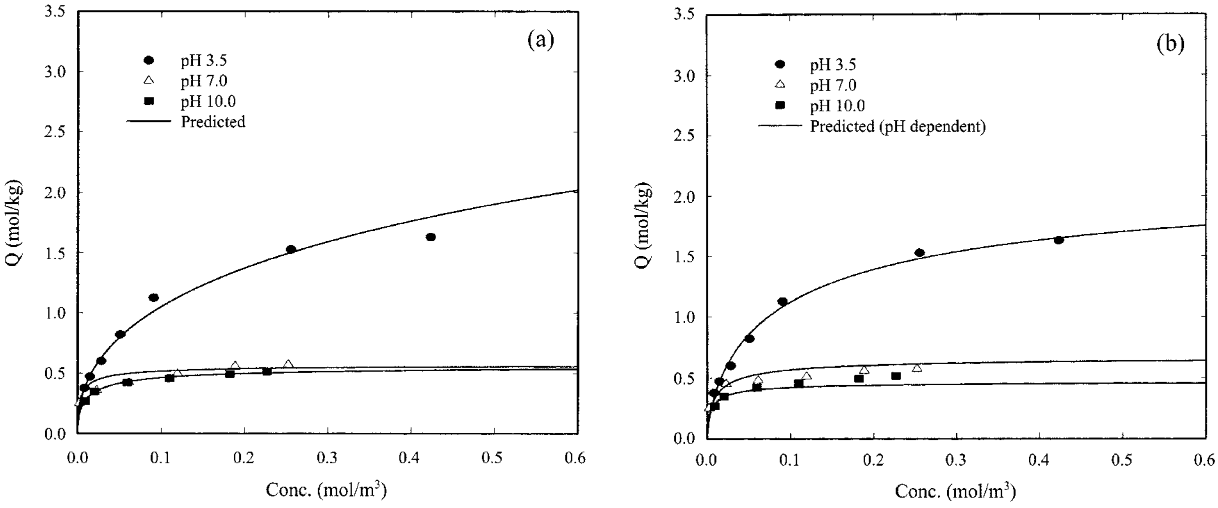


Fig. 9. Experimental data and predicted adsorption isotherm for 2,4-DNP - F400 system for different initial pH at 298.15 K (a: Sips Eq., b: pH dependent Sips Eq.).

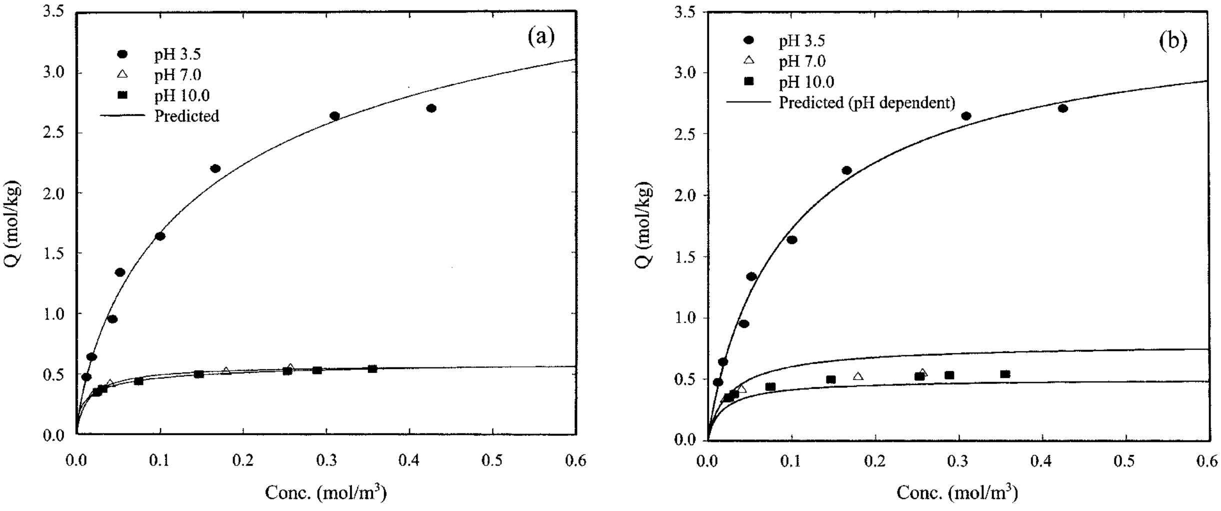


Fig. 10. Experimental data and predicted adsorption isotherm for 2,4-DNP - SLS103 system for different initial pH at 298.15 K (a: Sips Eq., b: pH dependent Sips Eq.).

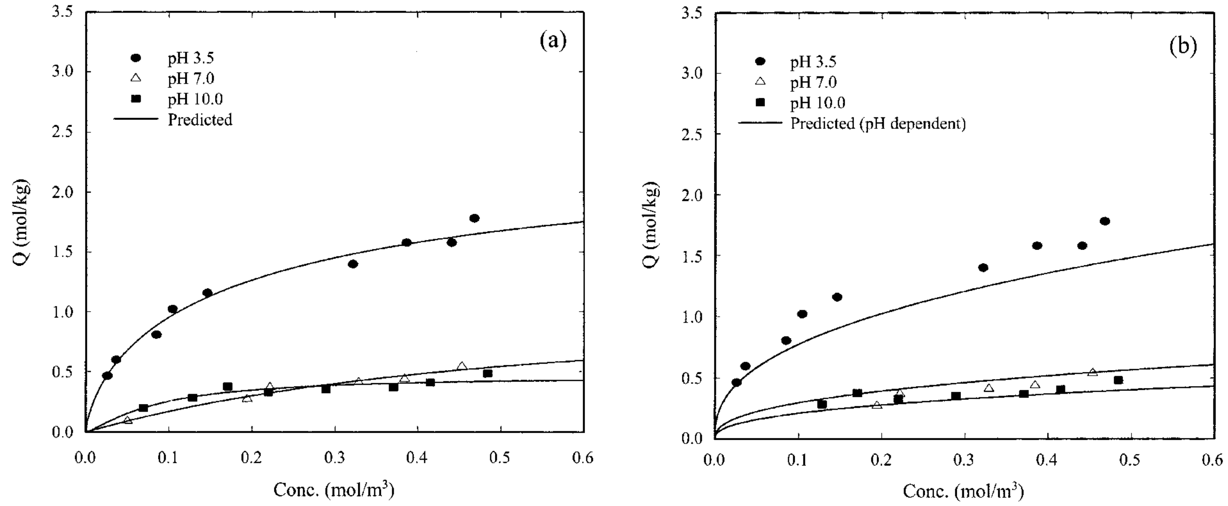


Fig. 11. Experimental data and predicted adsorption isotherm for 2,4-DNP - WWL system for different initial pH at 298.15 K (a: Sips Eq., b: pH dependent Sips Eq.).

Table 8. The calculated parameters of the Sips equation of pH dependency

Adsorbates	Parameters	2,4-D	2,4-DNP
F400	q_{m0}	1.558	0.699
	α	9.219	8.494
	b	1.012	23.34
	β	3.221	11.52
	n	3.192	1.456
	Error (%)	7.931	8.237
SLS103	q_{m0}	34.30	0.823
	α	11.45	10.49
	b	0.028	23.95
	β	6.081	8.424
	n	3.779	1.122
	Error (%)	5.002	11.59
WWL	q_{m0}	1.182	340.3
	α	8.476	24.10
	b	0.795	0.002
	β	0.340	16.29
	n	2.230	2.489
	Error (%)	8.861	11.43

SLS103>F400>WWL. The present experimental data have been used to analyze the effect of temperature on the adsorption isotherms of 2,4-D and 2,4-DNP. The equilibrium data for 2,4-D and 2,4-DNP could be represented with the Sips equation and the Sips equation of temperature dependency. Also, experimental equilibrium adsorption data are obtained with the different initial pHs, and are correlated with the pH dependent Sips isotherm. A Sips model with pH dependent parameters was fitted successfully with experimental data for all of the initial pHs studied. Adsorption capacities of 2,4-D and 2,4-DNP were decreased with increasing pH, for the pH range of 3.0-10.0, for three different adsorbents.

ACKNOWLEDGEMENT

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NOMENCLATURE

a : isotherm parameter
b : isotherm parameter
b_0 : temperature dependent parameter pH dependent parameter
C : equilibrium concentration of the solution [mol/m^3]
C_i : initial concentration of bulk fluid [mol/m^3]
ΔH : heat of adsorption [J/mol]
k : isotherm parameter
n : empirical pressure for the adsorbed phase
q : equilibrium amount adsorbed on the adsorbent [mol/kg]
q_m : fixed number of surface sites, i.e. maxium adsorption capacity of adsorbent [mol/kg]
R : gas constant (=8.314 J/mol·K)
T : temperature [K]
V : volume of solution
W : weight of adsorbent [kg]

Greek Letters

α : equilibrium constant of Sip equation of pH dependency
β : equilibrium constant of Sip equation of pH dependency

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