

Adsorption Isotherm Modeling of Phenol Onto Natural soils – Applicability of Various Isotherm Models

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ABSTRACT: Liquid-phases adsorption equilibrium of phenol onto two naturally available soils namely Kalathur soil (Kr) and Adhanur soil (Ar) were studied. The experimental data were analyzed using fourteen isotherm models, ranging from single-parametric model to multi-parametric models (up to 5 parameters) of the system. Results show that in general the accuracy of models to fit experimental data improves with the degree of freedom. To understand the mechanism involved with different types of sorbate-sorbent system as well as to find out the best fitting isotherm model, the correlation coefficients, and average percentage error and student t-test were carried out. Temkin isotherm model, Langmuir-Freundlich isotherm model and Fritz-Schlunder model as well as Baudu model were found to be the best fit models amongst the two-parametric models, three parametric models and four parametric isotherms modeling, respectively. This study brings out the need of simultaneous solution of multi-parametric equations (using relevant softwares, MATLAB, in present case) than solution of their linearized forms, which is mostly followed by contemporary investigators.

Key words: Sorption, Wastewater, Multi- parametric, Correlation, t-test, MATLAB

INTRODUCTION

Traditionally the study of adsorption capacities of various adsorbents has mostly been based on study of 2-3 parametric models, (Sevil & Bilge, 2007). With better understanding the adsorption mechanisms and fast-computational facilities, of late there have been extensive attempts by various researchers in evaluating the characteristics of specific adsorbent-adsorbate systems and evaluating the degree of applicability of existing models for the specific systems concerned (Johnson & Arnold, 1995; Allen *et al.*, 2004; Kundu & Gupta, 2006; Ofomaja, 2009; Akhtar *et al.*, 2007; Tahir & Naseem, 2006; Oualid & Naffrechoux, 2007).

The applicability of isotherm models onto bentonite and activated carbon for removal of dyes, cationic dye and phenols from aqueous solution were studied using three well-known isotherms to model equilibrium data, revealing the significance of higher parametric-models over lower parametric-models. (Allen *et al.*, 2004; Tahir & Naseem, 2006; Maury & Mittal, 2006; Oualid & Naffrechoux, 2007). In fact, a minimum of three parametric models was recommended by several investigators, based on their independent study, to be used to fit a non-linear isotherm model (Alexander &

Erling, 1998; Oualid & Naffrechoux, 2007; Maury & Mittal, 2006; Malek & Farooq, 1996; Ting & Mittal, 1999). On contrary, Malek and Farooq (1996), used seven different parametric-isotherm models for hydro-carbon adsorption on activated carbon, found all the isotherm models performing reasonably well, with lower parametric model as the best, though. This finding was further supported by, Ting and Mittal (1999), on their study of adsorption of gold by solvents obtained from dead fungus.

The present research work, fourteen isotherm models were used for modeling the experimental equilibrium data for phenol adsorption onto naturally available soils with an objective of estimation of specific adsorption characteristics using various isotherm models (associated with a range of parameters) and evaluating their relative application with regards to the soil under consideration.

MATERIAL & METHODS

Two soil samples, namely, Kalathur(Kr) and Adhanur (Ar), were collected from Thanjavur districts of the state of Tamil Nadu (India) and were dried (at 105 °C in an electric oven for 2 hours), followed by crushing and sieving (100 - 635 SIEVE NO ASTM E11-

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87), to obtain the samples having an average diameter of 0.05mm. To remove organic matter, the samples were placed in a water bath at 80.0 °C and treated with increments of 5 mL of 30% H₂O₂. These soil samples were free of organic matter. This was indicated by the lack of effervescence. The sample, thus obtained was dried, desiccated and preserved in airtight containers, for subsequent analysis and experiments. Phenol (C₆H₅OH) of analytical reagent (AR grade; supplied by Ranbaxy Laboratories Ltd., India), was used for the preparation of synthetic adsorbate of concentration 100 mg/l. The required quantity of phenol accurately weighed and dissolved in distilled water to obtain stock solutions of 1 liter, which was prepared fresh every day (and stored in a brown color glass bottles to prevent photo-oxidation). For equilibrium study, batch experiments were conducted at room temperature (30±2°C) for an adsorption period of 24h (to attain the equilibrium condition) and the effect of adsorbent dosage on the uptake of phenol onto the soils studied. The adsorption equilibrium data of phenol were fitted to different isotherm models (one, two, three, four and five degree parameters), as described in the following paragraphs, to evaluate their suitability for the two soils studied.

ONEPARAMETER MODEL

Henry's Law model equation can be given as follows (Ruthven, 1984):

$$q_e = KC_e \quad (1)$$

Where q_e is the adsorbed amount (of adsorbent in adsorbate) at equilibrium with respect to the total adsorbents used in adsorption (mg/g), C_e is the concentration of adsorbate on adsorbent at equilibrium (mg/L) and K is the Henry's constant.

TWO-PARAMETER MODEL

Henry's Law (with constant) model equation can be given as follows:

$$q_e = KC_e + m \quad (2)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e is the adsorbed equilibrium concentration (mg/L) and K is the Henry's constant. (All the terms used have the same connotation as that in Mono-parametric model).

Modified Langmuir – 1 model equation can be given as follows (Yang &Doong, 1985)

$$q_e = \frac{bT^{-n}C_e}{1+bC_e} \quad (3)$$

Where q_e and C_e represent their usual connotations (as given above); T is the temperature (in Kelvin) and b is the constant related to the free energy of adsorption (expressed as, L/ mg).

Modified Langmuir – 2 model equation can be given as follows (Brien & Myers, 1984)

$$q_e = \frac{bC_e}{1+bC_e} \left(\frac{1+\sigma^2(1-bC_e)}{2(1+bC_e)^2} \right) \quad (4)$$

Where q_e and C_e represent their usual connotations (as given above) and σ is the isotherm constants related to the degree of sorption.

Dubinin-Radushkevich (D-R) isotherm (Akhtar et al, 2007) often used to estimate the characteristic porosity in addition to the apparent free energy of adsorption. Thus, for evaluating these parameters the Dubinin-Radushkevich isotherm is being used in the following form: (5)

$$q_e = K_{DR} \exp \left[b \left(RT \ln \left(1 + \frac{1}{C_e} \right) \right)^2 \right]$$

Where, q_e is the adsorbed amount at equilibrium (mg/g), C_e is the adsorbed equilibrium concentration (mg/l), K_{DR} relates to free energy of sorption, and b is the Dubinin-Radushkevich isotherm constants related to the degree of sorption.

Temkin isotherm (Aharoni & Tompkins, 1970) model considered that the effect of adsorbate interactions on adsorption isotherms and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm expressed in the following form:

$$Q_e = \frac{RT}{b} (\ln AC_e) \quad (6)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e is the adsorbed equilibrium concentration (mg/l), A and b are the isotherm constants.

THREEPARAMETER MODELS

Langmuir–Freundlich isotherm model equation can be given as follows (Sip, 2003)

$$q_e = \frac{q_{mLF}(K_{LF}C_e)^{mLF}}{1+(K_{LF}C_e)^{mLF}} \quad (7)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), q_{mLF} is the Langmuir-Freundlich maximum adsorption capacity (mg/g), C_e is the adsorbed equilibrium concentration (mg/L), K_{LF} is the equilibrium

constant for a heterogeneous solid and mLF Langmuir-Freundlich heterogeneity parameter lie between 0 and 1. The Langmuir-Freundlich isotherm model at low sorbate concentrations is effectively gets reduced to a Freundlich isotherm and thus does not follow Henry's law. At high sorbate concentrations, it behaves monolayer sorption and shows the Langmuir isotherm characteristics.

Fritz-Schlunder model equation given as follows (Mutassim & Bowen, 1992)

$$q_e = \frac{q_{mFS} K_{FS} C_e}{1 + q_{mFS} C_e^\alpha} \quad (8)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_{mFS} the Fritz-Schlunder maximum adsorption capacity (mg/g), K_{FS} the Fritz-Schlunder equilibrium constant (L/mg) and mFS is the Fritz-Schlunder model exponent.

Radke - Prausnitz model equation given as follows (Ramakrishna & Viraraghavan, 1997)

$$q_e = \frac{q_{mRP} K_{RP} C_e}{(1 + K_{RP} C_e)^{m_{RP}}} \quad (9)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), q_{mRP} is the Radke-Prausnitz maximum adsorption capacities (mg/g), C_e the adsorbate equilibrium concentration (mg/L), K_{RP} is the Radke-Prausnitz equilibrium constants and m_{RP} is the Radke-Prausnitz models exponents.

Toth has modified the Langmuir equation to reduce the error between experimental data and predicted values of equilibrium adsorption data. The application of his equation is best suited to multilayer adsorption similar to BET isotherms, which is a special type of Langmuir isotherm and has very restrictive validity. The Toth model (Toth, 2000) equation given as

$$q_e = \frac{q_{mT} C_e}{(1/K_T + C_e^{mT})^{1/mT}} \quad (10)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_{mT} the Toth maximum adsorption capacity (mg/g), K_T the Toth equilibrium constant, and mT is the Toth model exponent.

The Jossens model (Akira *et al.*, 1984) described by distribution of energy (interactions adsorbate-adsorbent on adsorption sites). It considers that the activated carbon surface is heterogeneous, with

respect to the interactions, which it engages with the adsorbate

$$C_e = \frac{q_e}{H} \exp(F q_e^p) \quad (11)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L) and H, F, and p are the parameters of the equation of Jossens. H and F depend only on temperature. This equation can reduce to Henry's law at low capacities.

FOURPARAMETER MODELS

Fritz-Schlunder model equation can be given as follows (Fritz & Schluender, 1974)

$$q_e = \frac{A C_e^\alpha}{1 + B C_e^\beta} \quad (12)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), A and B are the Fritz-Schlunder parameters and α and β are the Fritz-Schlunder equation exponents.

Baudu model equation given as follows (Oualid & Emmanuel, 2007)

$$q_e = \frac{q_m b_0 C_e^{(1+x+y)}}{1 + b_0 C_e^{(1+x)}} \quad (13)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_m the Baudu maximum adsorption capacity (mg/g), b_0 the equilibrium constant, and x and y are the Baudu parameters.

FIVE-PARAMETER MODEL

Fritz-Schlunder model equation given as follows (Fritz & Schluender, 1974)

$$q_e = \frac{q_{mFSS} K_1 C_e^{m_1}}{1 + K_2 C_e^{m_2}} \quad (14)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), q_{mFSS} the Fritz-Schlunder maximum adsorption capacity (mg/g) and K_1 , K_2 , m_1 , and m_2 are the Fritz-Schlunder parameters.

RESULTS & DISCUSSION

The various isotherms obtained were analyzed by non-linear curve fitting (instead of linearization), using MATLAB-7 software. The criteria for selection of the

best isotherm model essentially based on correlation coefficient and the average percentage errors (APE). The correlation coefficient shows the fit between experimental data and isotherm model, while the average percentage errors (APE) were calculated using equation (15) indicating the fit between the experimental data and calculated data used for plotting isotherm curves

$$APE = \frac{\sum_{i=1}^N |(q_e)_{\text{experimental}} - (q_e)_{\text{calculated}}|}{(q_e)_{\text{experimental}}} \times 100$$

One parameter model (i.e., Henry’s law) is applied to the experimental data obtained from the adsorption of phenol onto naturally available soils. As indicated in Fig. 1 and 2, this model failed in predicting the equilibrium isotherm model. The linear relation between Q and Ce, was slightly improved by introducing Henry’s law in the intercept model. In fact, the addition of a constant term in the model found to render better characteristics of the equilibrium isotherm curve, especially at higher effluent concentrations. As indicated by Fig. 1 and 2, the adsorption of phenol by two naturally soils (Kalathur and Adhanur soils), was quite evident of the improvement in the predictability of the values by Henry’s law with intercept over that without intercept (Table 1). The present study supports the failure of the Henry’s law at initial concentration of phenol and improvement in plot characteristics by introducing the intercept in Henry’s model, which confirms with the findings (Maurya & Mittal, 2006; Faust & Aly, 1987).

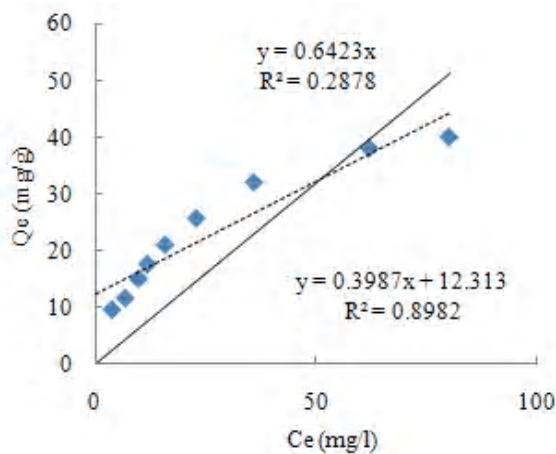


Fig. 1. Henry’s Law one degree of freedom isotherm model fits (for Kalathur soil)

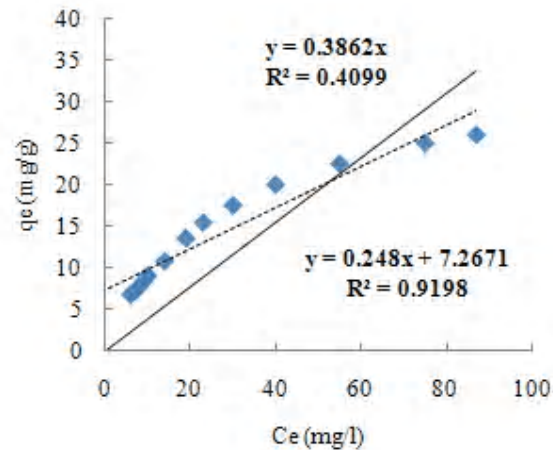


Fig. 2. Henry’s Law one degree of freedom isotherm model fits (for Adhanur soil)

TWO-PARAMETER MODEL

Modified Langmuir-1, Modified Langmuir-2, Temkin and Dubinin-Rdushkevich isotherms were modified by rearranging the constants without changing the degree of freedom with regards to the original second-degree isotherm models (namely Langmuir and Freundlich)(Yang & Doong, 1985). The present paper focused more on Modified Langmuir-1, Modified Langmuir-2, Temkin and Dubinin-Rdushkevich models instead of regular (namely, the Langmuir, Freundlich, Sip and Redlich–Peterson) isotherm models, which were already studied by the authors with confirmation of isotherm models fairly obeying by both the soils, yet the best models explaining the adsorption were found to be the Sip and Redlich–Peterson isotherm models (Subramanyam & Das, 2009). Model fits for the two-parameter isotherms along with experimental data are presented in Fig. 03 and Fig. 04, respectively. The values of model constants along with corresponding correlation coefficient, average percentage error and t-test values of paired student’s t-test (95% confidence interval) for all sorbent-sorbate system studied are presented in Table 1. In fact the Modified Langmuir model-1 was explained to account for temperature variability of the system, whereas Modified Langmuir model-2, introduced by Brien and Myers (1984) was meant to account for heterogeneity of the adsorbent used. On study, for both the soils, the modified Langmuir -2 was found to fail in t-test (95% confidence interval) in addition to high average percent error (31.276 and 40.15 for Kr and Ar soil respectively) and poor correlation coefficients ($r^2 = 0.231$ and 0.356 for Kr and Ar soil respectively). However, Modified Langmuir -1 isotherm model was found to obey the experimental data fairly well i.e., $r^2 = 0.9952$, APE = 1.204 and $t > 0.05$ for 95% confidence interval for Kr soil & $r^2 = 0.998$, APE = 0.836 and $t > 0.05$

Table 1. Isotherm parameters (one and two parameters) average percentage error, correlation coefficients and t-values

Isotherm model	Degree of Freedom	Constants	Kalathur soil				Adhanur soil			
			Parameter values	Average percent error	R ²	t	Parameter values	Average percent error	R ²	t
Henry's Law	1	K	0.287		0.642		0.386		0.409	
Henry's Law with linear intercept	2	K	0.398		0.898		0.248		0.919	
		m	12.31				7.267			
Modified Langmuir-1	2	b	0.04333	1.204123	0.9952	0.764	0.03529	0.835598	0.998	
		n	-0.6909				-0.6186		0.68	
Modified Langmuir 2	2	b	0.2619	31.27598	0.2311	0.041	0.187	40.14976	0.3566	
		σ^2	0.0425				0.0552		0.012	
Dubinin-Radushkevich	2	b	15.6	13.009	0.815	0.435	13.93	3.821196	0.8269	
		K _{DR}	35.97				21.73			
Temkin	2	b	0.2262	0.574123	0.9821	1	0.3325	0.588056	0.9929	
		A	0.4483				0.3429		1	

for 95% confidence interval for Ar soil. In this case, the value of exponent 'n' was found to be negative; this indicates that phenol adsorption could be an endothermic reaction (which means, it is likely to favor the adsorption at higher temperature). This finding was quite akin to finding by Singh and Rawat (Binay & Narendra, 2004) based on their studies of sorption of phenol by fly ash and impregnated fly ash, who reported the increase in sorption of phenol by fly ash with increasing temperature (in the range of 30^o – 50^o C).

Application of Dubinin–Radushkevich isotherm, which was mostly used for gas phase adsorption on activated carbon [9], was also found applicable to the liquid-solid phase adsorption, of late (Maury & Mittal, 2006). In the present study, when Dubinin-Rdushkevich model applied to study the adsorption of phenol, the model found to fit experimental data (for two soils) fairly well, though not adequate, as shown in Fig. 3

and Fig. 04. [$r^2 = 0.815$, APE = 13 and $t > 0.05$ for 95% confidence interval for Kr soil and $r^2 = 0.827$, APE = 3.83 and $t > 0.05$ for 95% confidence interval for Kr soil].

The Temkin isotherm model, also widely used in gas phase adsorption (with its application, rather limited to liquid-solid adsorption equilibrium) assumes adsorption to be characterized by a uniform distribution of binding energies up to some maximum value (Maurya & Mittal, 2006; Malek & Farooq, 1996). In the present study, the experimental data for phenol onto two soils, analyzed by non-linear regression analysis to fit the Temkin isotherm model are presented in Fig. 3 and Fig. 4. The parameters of Temkin model (Table 1) as well as the higher values of the correlation coefficient i.e., $r^2 = 0.9821$ and $r^2 = 0.993$ for Kr and Ar soil, lower average percentage error i.e., APE = 0.574 and 0.588 for Kr and Ar soil and better t-test values at 95 % confidence

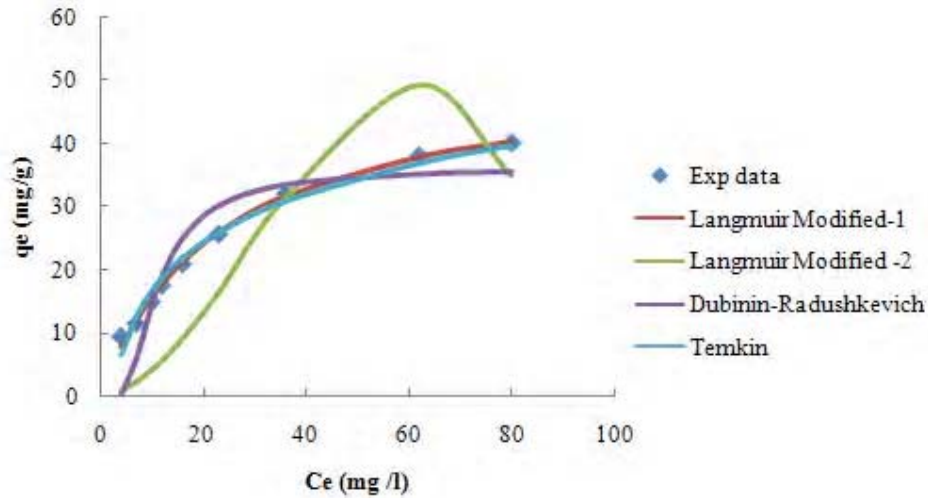


Fig. 3. For Kalathur soil (Two-parameter isotherm models)

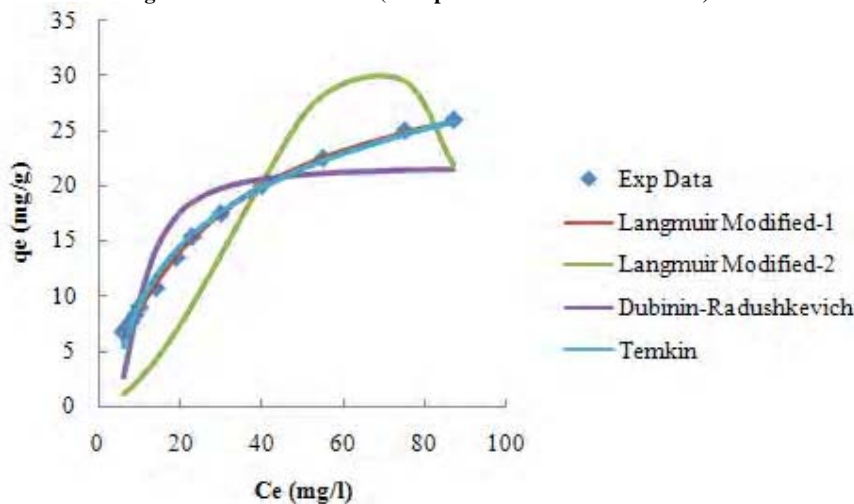


Fig. 4. For Adhanur soil (Two-parameter isotherm models)

interval for (Kr and Ar soil) indicate adequate match of the data with the model.

THREE PARAMETER MODELS

The experimental adsorption data of phenol adsorption onto two soils was also analyzed using the well-known three-parameter isotherm models (namely, Langmuir-Freundlich, Redlich-Peterson, Sip, Fritz-Schlunder, and Radke - Prausnitz, Toth and Jossens model). The model seemed to fit well for both soils studied (Fig. 5 and 6; Table 2). The Langmuir-Freundlich isotherm model includes the characteristics of Langmuir and Freundlich isotherm and provide a better fit i.e., $r^2=0.996$, APE=0.50 and $t > 0.05$ for 95% confidence interval for Kr Soil and $r^2=0.998$, APE=0.155 and $t > 0.05$ for 95% confidence interval for Ar Soil. However, the Toth isotherm equation was not less

satisfactory, compared to Langmuir-Freundlich equation with regard t-test values (95% confidence interval). Radke – Prausnitz, Jossens and Fritz-Schlunder isotherm models were also found similar to the Langmuir-Freundlich and Toth isotherm models, showing good fits, yet with no significant improvement in the model’s data fitting. However, based on the t-test ($t > 0.05$ for 95% confidence level), it was observed that the isotherms for all the systems were significantly correlated regarding the three-parameter models. These models can be presented in the following orders of fitness (1) based on correlation coefficient and average percent error: Jossens > Langmuir-Freundlich > Toth > Radke-Prausnitz > Fritz-Schlunder and (2) based on maximum adsorption equilibrium capacity: Toth > Langmuir-Freundlich > Radke-Prausnitz > Fritz-Schlunder.

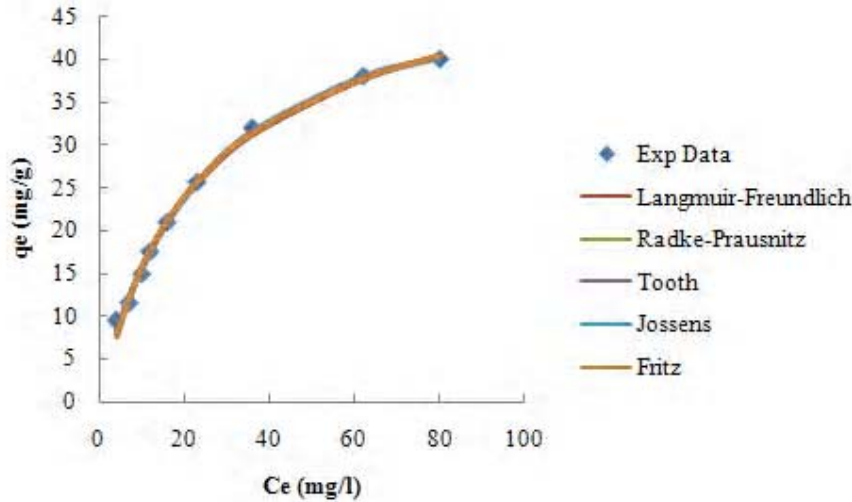


Fig. 5. For Kalathur soil (Three-parameter isotherm models)

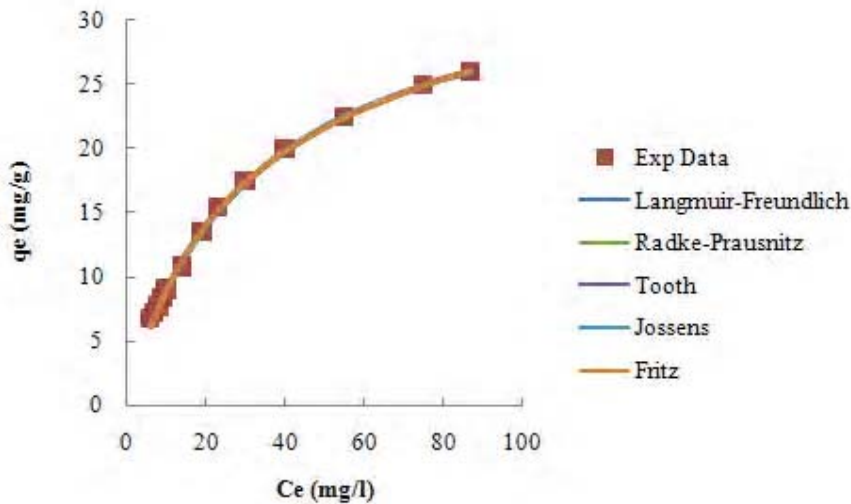


Fig. 6 . For Adhanur soil (Three-parameter isotherm models)

Table 2. Isotherm parameters (three parameters) average percentage error, correlation coefficients and t-values

Isotherm model	Degree of Freedom	Constants	Kalathur soil				Adhanur soil			
			Parameter values	Average percent error	R ²	t	Parameter values	Average percent error	R ²	t
Langmuir-Freundlich	3	q _{mLF}	55.71	0.502493	0.9958	0.901	37.83	0.155025	0.9988	0.937
		K _{LF}	0.03635				0.02785			
		mLF	0.9165				0.9044			
Fritz-Schlunder	3	q _{mFS}	43.79				22.9			
		K _{FS}	0.05369	0.928541	0.9953	0.819	0.05849	0.277059	0.9986	0.886
		mFS	0.9634				0.9138			
Radke-Prasnitz	3	q _{MIRP}	48.93				25.73			
		K _{RP}	0.04652	1.092868	0.9953	0.663	0.05	1.530964	0.9985	0.862
		mRP	0.9717				0.8679			
Toth	3	q _{mt}	56.08				39.51			
		K _T	0.06649	0.719655	0.9955	0.863	0.06771	0.21387	0.9987	0.913
		mT	0.8718				0.809			
Jossens	3	F	-0.3022				-0.3221			
		H	0.2853	0.610338	0.9968	0.867	0.173	0.141336	0.999	0.938
		p	0.4248				0.3991			

FOUR-PARAMETER MODELS

The experimental equilibrium data were also analyzed using four-parametric models - Fritz-Schlunder, and Baudu model. These models, with parameters obtained using non-linear curve fitting analysis, was found to fit experimental data better than lower parameter models for both soil-types (Fig. 7 and 8, Table 3). For Kr soil, the values of correlation coefficient ($r^2=0.998$), average percentage error (APE=0.18) and t-test value (0.995, 95% confidence interval) were almost equal. For Ar soil, the values of correlation coefficients was greater than 0.95 (for both Fritz-Schlunder and Baudu isotherms), whereas average percentage error was found to vary with the models, such as 0.061 (in case of Baudu isotherm) and 1.36 (in case of Fritz isotherm). Thus, the studies indicate that Baudu isotherm was seemingly a better isotherm model

than Fritz isotherm model, which were further supported by t-test values, as well (0.52 and 0.92, respectively).

FIVE-PARAMETER MODELS

When the experimental equilibrium data was analyzed using a five-parameter model, namely, Fritz-Schlunder model (a model with higher complexities, and necessitate nonlinear regression techniques for its solution). Although, several researchers had indicated its poor performance in aqueous phase adsorption (Brien & Myers, 1984), yet in the present studies, Fritz-Schlunder isotherm model was found to provide a good fit for both the soils are presented in Fig. 9 and Fig. 10 (Table 3). Probably, the increased number of parameters was able to simulate the model more accurately, better than two, three and four parameters.

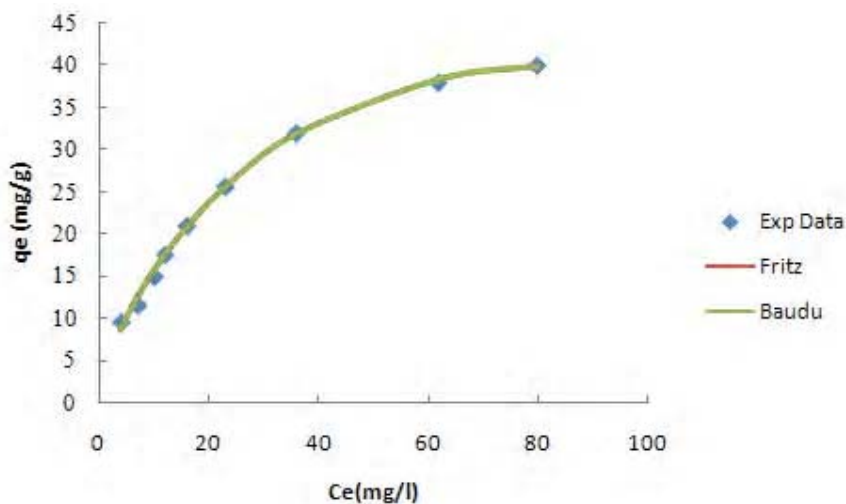


Fig.7. For Kalathur soil (Four-parameter isotherm models)

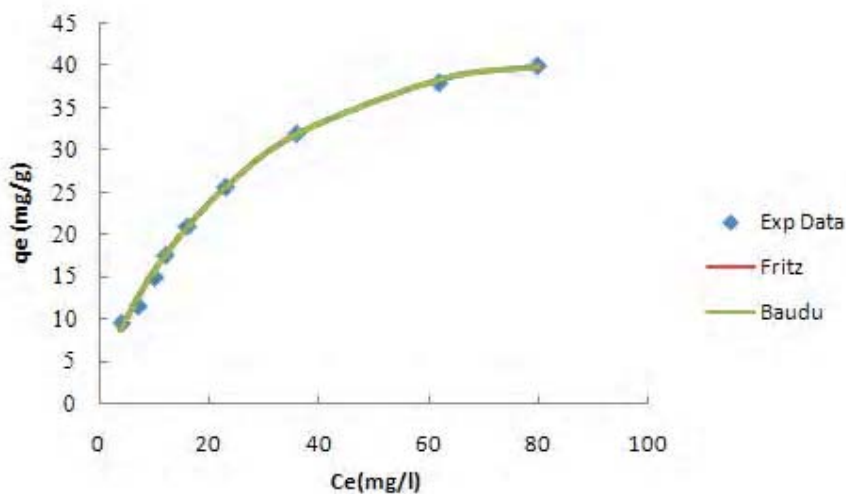


Fig. 8. For Adhanur soil (Four-parameter isotherm models)

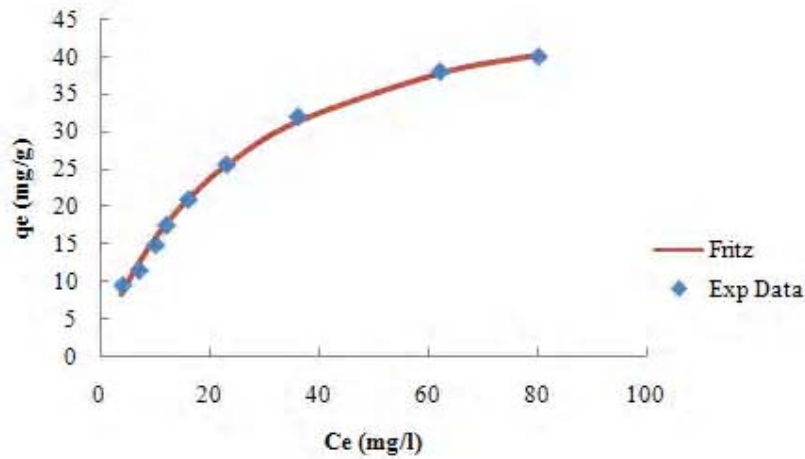


Fig. 9. For Kalathur soil (Five-parameter isotherm models)

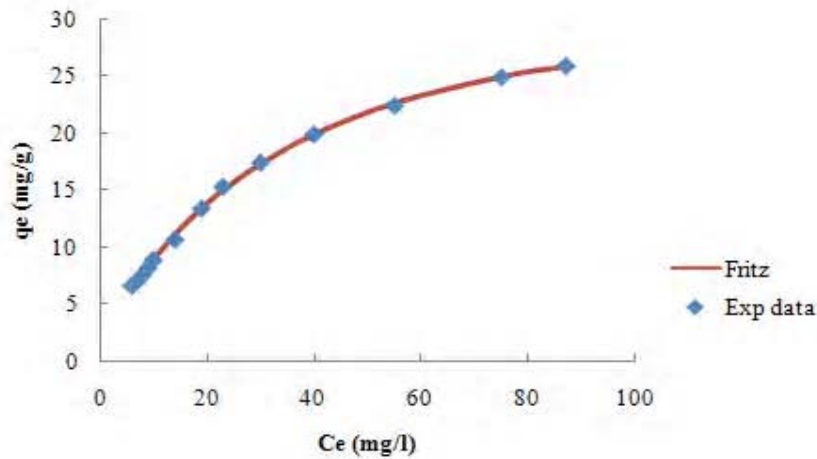


Fig.10.For Adhanur soil (Five-parameter isotherm models)

Table 3. Isotherm parameters (four and five parameters) average percentage error, correlation coefficients and t-values

Isotherm model	Degree of Freedom	Constants	Kalathur soil				Adhanur soil			
			Parameter values	Average percent error	R ²	t	Parameter values	Average percent error	R ²	t
Fritz-Schlunder	4	A	3.5				2.73			
		B	0.000555	0.180569	0.998	0.95	0.000457	1.358441	0.986	0.521
		α	0.658				0.547			
		β	1.58				1.32			
Baund	4	q _m	3.495				1.97			
		b ₀	1801	0.180569	0.9979	0.95	1645	0.061063	0.9976	0.92
		x	-2.582				-2.45			
		y	0.6583				0.85			
Fritz-Schlunder	5	q _{mFSS}	14.54				9.883			
		K1	0.2404				0.1808			
		K2	0.0005551	0.180569	0.9979	0.95	0.004462	0.1282	0.9991	0.981
		m1	0.6583				0.7302			
		m2	1.582				0.7302			

CONCLUSION

The study of adsorption equilibrium data for phenol on two types of adsorbent, i.e., Kalathur and Adhanur soil using 14 well-known isotherm models indicated that higher parametric models seemed to be better options for their modeling in comparison to lower parametric models. Out of all isotherm models studied, most of the isotherm models could predict the adsorption equilibrium well (Except Henry's, Modified Langmuir-2 and D-R isotherm models), yet with a varying degree of correlation, average percentage error and student t-test. As reported in various literatures, and quoted in preceding paragraphs, which report varying degree of obedience to different models, specific to each adsorbent-adsorbate system. However, for a complex heterogeneous mass like soils, the study of higher-parameter models using non-linear analysis seems to be more preferable than lower-parameter and linear (ized) models.

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