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Modeling of Quaternary Adsorption System Applicability of Four Parameters Isotherm Models

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ABSTRACT

In this study activated carbon derived from oil-palm empty fruit bunch has been used as adsorbent for the removal of phenol, butanol, butan-2-ol and 2-methyl butan-2-ol, as organic contaminants from stock solution. The effect of adsorbent dosage on adsorption operation was carried out in order to determine the optimal adsorption condition. The experimental data were analyzed using four-parameter isotherm models (Fritz-Schluender and Baudu). However, all the parameters contained in those models, correlation coefficient (R^2) and average percentage error (APE) were determined. The regression analysis result obtained proven that equilibrium data for phenol and butan-2-ol fitted very well by the Baudu model while those of butanol and 2-methyl butan-2-ol were well fitted by the Fritz-Schluender model.

Keyword: activated carbon, adsorption, adsorbent, isotherm model, regression analysis.

INTRODUCTION

The presence of toxic organic contaminants in industrial wastewater has generated considerable concerns in recent years. Several organic compounds can enter the natural environment from industrial discharges, such substances have been found to be very toxic, persistent and bio accumulating [1]. In fact, they can provoke ecological damage as they enter the food chain. The removal of toxic organic compounds represents a problem, particularly when they are present at low concentrations [1-2].

A number of methods for the removal of organic contaminants from wastewater are available [3]. It is known that adsorption at a solid solution interface is one of the most efficient methods for the removal of organic contaminants from wastewater. The most common industrial adsorbents are activated carbon, silica gel and alumina. All these adsorbents are generally expensive, especially in developing countries of the world. As a result of this, there is need to create an avenue in which natural and low cost materials such as agricultural wastes and others from our environments are being converted into activated carbon, for removing organic solutes contained in wastewater. Adsorption on adsorbents derived from natural and low cost materials for removal of both organic and inorganic contaminants from waste water has been investigated extensively [4-11]. The characterizations of the adsorbents derived from these aforementioned materials have made them potential adsorbents for the adsorption process.

Agricultural wastes such as animal horn, animal hooves, walnut shell, palm kernel shell, cassava peeled, saw dust rice husk and so on constitute environmental pollution by producing offensive odour due to the decomposition of their organic contents. Several researchers have worked on the use of agricultural biomass for solutes removal from wastewater. These agricultural wastes include oil palm trunk [12], broad bean peels [13], rice straw-derived char [14], rice husk [15], pineapple stem [16], palm kernel fibre [17], the use of these wastes for the production of adsorbent shall not only aid in getting rid of them from the environment but shall provide an alternative to the use of expensive adsorbents such as zeolite, alumina and so on for the removal of contaminants from wastewater.

This present research work, most common four- parameters isotherm models were used for modeling the experimental equilibrium data for phenol, butanol, butan-2-ol and 2-methyl butan-2-ol onto activated carbon derived from oil-palm empty fruit bunch with the aim of estimating isotherm models parameters and also determine the goodness of fit based on correlation coefficient and average percentage error.

Modeling Equations

Temperature effects on adsorption are profound, and measurements are usually at a constant temperature. Graphs of data are called Isotherms. The results of adsorption experiments are most commonly presented in the form of adsorption isotherms, that is, function which connect the amount of adsorbate on the adsorbent, with its concentration at constant temperature. Various adsorption isotherms had been reported in literature to explain the wide variety of adsorption experimental results [17-19, 21]. The isotherm models are classified into 1, 2, 3, 4 and 5- parameter models. The parameters in adsorption models provide some information about adsorbent properties and adsorption mechanism [24]. In this present study, two most common four- parameter isotherm models were employed to describe the experimental results.

Fritz-Schluender Isotherm Model

This model is usually used when it is aimed to obtain a satisfactory fit of the adsorption data for organic liquids in aqueous mixtures. The isotherm contains more parameters than any other isotherms and is an empirical isotherm [24]. Fritz-Schluender model equation is given as follows:

$$q_e = \frac{AC_e^B}{1+CC_e^D} \quad (1)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l), A, B, C and D are fritz-Schluender parameters.

Baudu Isotherm Model

Baudu model equation is given as follows [25]:

$$q_e = \frac{ABC_e^{(1+C+D)}}{1+CC_e^{(1+C)}} \quad (2)$$

Where q_e is the adsorbed amount at equilibrium (mg/g), C_e the equilibrium concentration of the adsorbate (mg/l), A the Baudu maximum capacity (mg/g), B the equilibrium constant, and C and D are the Baudu model exponents.

Determination of Solute Adsorbed and Adsorption Percentage

The amount of adsorbates (mg/g) adsorbed onto activated carbon at equilibrium, q_e (mg/g) was determined by the equation reported by Vanderborght and Van Grieken**.** [23].

$$q_e = \frac{V(C_i - C_e)}{W} \quad (3)$$

The adsorption efficiency (%) was calculated from the following equation

$$\text{Adsorption } \% = \frac{C_i - C_e}{C_i} x100\% \quad (4)$$

and the effect of adsorbent dosage on the uptake of these four organic components onto activated carbon was studied (Olateju et. al., 2014) . The equilibrium data of phenol, butan-2-ol, butanol and 2-methylbutane were fitted to two different 4-parameter isotherm models

RESULTS AND DISCUSSION

Table 1: Concentration and Absorbance Data

Phenol		Butanol		Butan-2-ol		2-Methylbutan-2-ol	
Conc. (g/*l*)	Absorbance	Conc. (g/*l*)	Absorbance	Conc. (g./*l*)	Absorbance	Conc. (g/*l*)	Absorbance
0.407	0.091	0.405	0.111	0.403	0.097	0.402	0.098
0.646	0.101	0.648	0.115	0.645	0.112	0.644	0.116
0.856	0.120	0.810	0.128	0.807	0.117	0.805	0.119
1.080	0.126	1.080	0.133	1.080	0.124	1.080	0.131
1.291	0.138	1.296	0.136	1.291	0.137	1.290	0.140

Table 2: Quaternary Adsorption Data from an Aqueous System

Mass (g)	Phenol (g/*l*)	Butanol (g/*l*)	Butan-2-ol (g/*l*)	2-Methylbutan-2-ol (g/*l*)
0.10	1.08000	0.96026	1.08000	1.00445
0.50	1.03704	0.86093	1.02644	0.93764
0.75	1.01852	0.82781	1.00240	0.91537
1.00	1.00000	0.79470	0.97837	0.89310
1.50	0.96296	0.72848	0.93029	0.84855

Source: [26].

Table 2 depicts the concentration of each of the adsorbate in an aqueous system for specific masses of activated carbon. Different mass of granulated activated carbon were used to determine the adsorptive capacity in quaternary adsorption system. According to the results, it was observed that, there was progressive decrease in the concentrations of the contaminants, thus corresponding decrease in the quantities of adsorbates per specific weights of the adsorbent. More so, the adsorption efficiency increases and adsorbed amount at equilibrium (q_e) decreases with increasing of adsorbent dosage. Increase in adsorption efficiency is due to availability of more adsorption sites, which results from increasing of adsorbent dosage. The decrease in the adsorbed amount at equilibrium (q_e) is as a result of unsaturation of some adsorption sites in the high adsorbent dosages. A similar observation was also reported by Behnajady *et al*. [20].

Isotherm Model Analysis

These isotherm models (Fritz-Schluender and Baudu) are non-linear types; all the parameters contained in those models were evaluated by trial and error method using Excel Solver. The determined adsorption model parameters, correlation coefficient (R^2), average percentage error (APE) are reported in Table 1. In this study, the goodness of fit was based on correlation coefficient (R^2) and average percentage error (APE). The average percentage error was calculated using equation (7). According to subramanyam and Ashutosh (2014), the correlation coefficient indicates the fit between experimental data and predicted values.

$$APE = \frac{100\%}{N}\sum_{i=1}^{N}\frac{q_e - q_p}{q_e} \quad (5)$$

The Baudu model seemed to fit well for both phenol and butan-2-ol adsorption onto activated carbon (figure 1 and 3 and Table 1). Meanwhile, the Fritz-Schluender was found to be the best fit model for both butanol and 2-methyl butan-2-ol adsorption onto activated carbon (figure 2 and 4 and table 1). For phenol and butan-2-ol, the values of correlation coefficient (R^2) were almost equal (for both Fritz-Schluender and Baudu isotherm models), whereas average percentage error was found to vary with the models, such as 0.15864 and 0.13822 for phenol and butan-2-ol respectively (in case of Baudu isotherm). For butanol and 2-methyl butan-2-ol, the values of correlation coefficient for butanol was greater than that of 2-methyl butan-2-ol (for both Fritz-Schluender and Baudu isotherms). Also, average percentage errors for both butanol and 2-methyl butan-2-ol were greater than one (for both Fritz-Schluender and Baudu models). Thus, the studies indicate that Baudu isotherm was seemingly a better isotherm model for both phenol and butan-2-ol adsorption onto activated carbon, whereas equilibrium data of butanol and 2-methyl butan-2-ol adsorption onto activated carbon fitted very well by the Fritz-Schluender isotherm model.

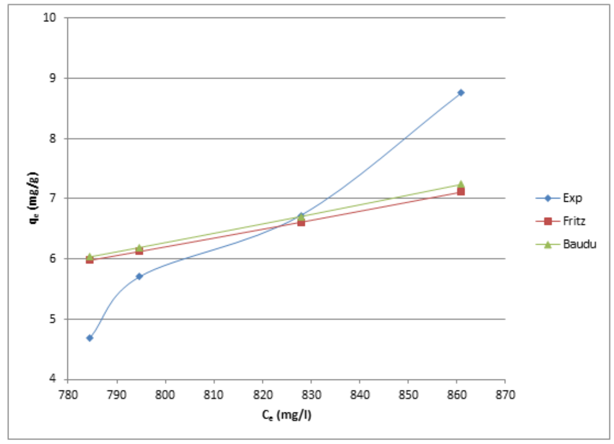

Fig. 2: Butanol Adsorption (Four parameter-isotherm models)

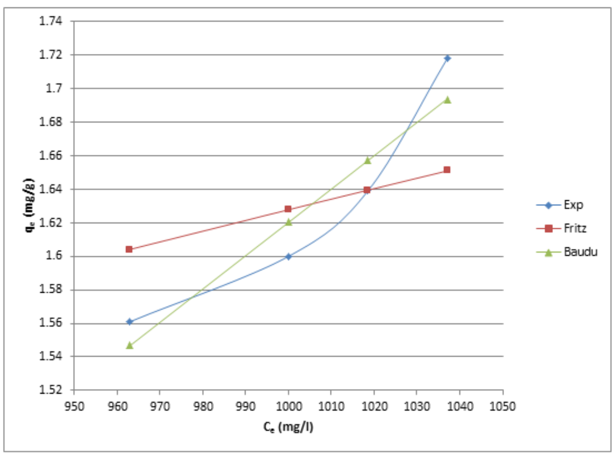

Fig. 1: Phenol Adsorption (Four parameter–isotherm models).

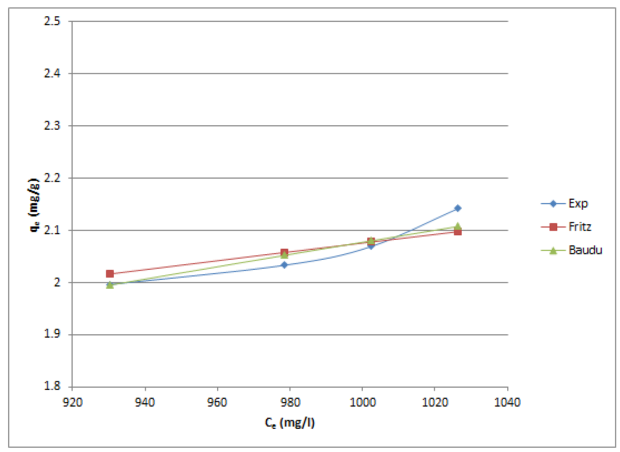

Fig.3: Butan-2-ol Adsorption (Four parameter-isotherm models).

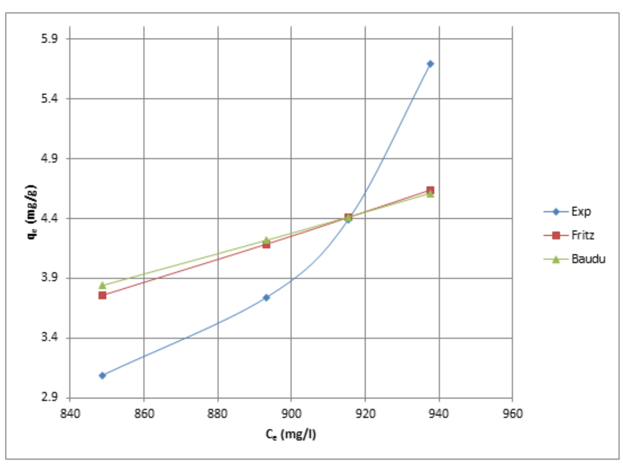

Fig.4: 2-Methyl butan-2-ol Adsorption (Four parameter-isotherm models).

Table 1: Isotherm parameters (Four parameters), average percentage error (APE) and correlation coefficient (R2).

			Phenol			Butanol			Butan-2-ol			2-MB	
Isotherm model	Constants	Parameter Values	APE	R^2	Parameter Values	APE	R^2	Parameter Values	APE	R^2	Parameter Values	APE	R^2
Fritz-Schluender	J	0.133793			8.53E-05			0.218357			1.126E-05		
	K	0.388593	0.15864	0.9395	1.867652	3.59237	0.9872	0.517732	0.13822	0.9406	2.1127376	3.86472	0.9482
	L	0.203923			2.633235			0.92428 0.158382			3.6215478		
	M	0.000000			0.000000						0.00000		
Baudu	q_m	0.017203	0.01399	0.9419	1.66E-05			0.044025			1.99E-05		
	b_o	0.001102			0.039558	4.90986	0.9872	0.195144	0.048869	0.9414	0.03845	4.65282	0.9468
	x	1.25E-08			3.4E-12			0.286478			3.26E-12		
	y	0.751477			1.92611			0.558026			1.808912		

2-MB: 2-methyl butan-2-ol; APE: Average percentage error; R2: correlation coefficient.

CONCLUSION

In this work activated carbon derived from oil-palm empty fruit bunch was used as an adsorbent for removal of phenol, butanol, butan-2-ol and 2-methyl butan-2-ol from aqueous solution. Experimental data obtained indicate that adsorbent dosage is a very important factor in the adsorption process. The adsorption efficiency increases and adsorbed amount at equilibrium (q_e) decreases with increasing of adsorbent dosages. A comprehensive isotherm analysis for the quaternary adsorption system was carried out using Baudu and Fritz-Schluender isotherm models. However, from non-linear analysis result obtained indicated that Baudu was seemingly a better isotherm model for both phenol and butan-2-ol adsorption onto activated carbon, whereas equilibrium data of butanol and 2-methyl butan-2-ol adsorption onto activated carbon fitted well by the Fritz- Schluender isotherm model.

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