Original Research Article

APPLICATION OF NON-LINEAR REGRESSION ANALYSIS FOR THE ADSORPTION KINETICS AND EQUILIBRIUM ISOTHERM FOR PHENACETIN

Abstract

Activated carbon obtained from ayous sawdust, cucurbitaceae (egussi) peelings and the mixture of the two were studied for the adsorption of phenacetin. Characterisation of activated carbon by SEM and XRD analysis shows that the mixture of precursors combine the properties of activated carbon obtained separately. The well-known batch sorption models– Langmuir (one and two sites), Freudlich, Tempkin, Elovich, Langmuir-Freudlich, Redlich Peterson, Radke-Prausnitz, Fritz Shlunder)—were tested with experimental data for the adsorption of phenacetin to estimate adsorption equilibrium parameters—rate constants and adsorption capacities. The model with the best fit was identified from extensive statistical analysis of the results of nonlinear regression of the experimental data. Comparison of the statistical errors in parameter estimation between linear and non-linear isotherm models shows that transformation of non-linear isotherm equations to linear forms implicitly alter their error structure. The much smaller size of the various error indicators —Determination Coefficient, R^2; Sum of Square Errors, SSE; Chi Test, χ^2; Average Relative Errors, ARE—, calculated for the case of non linearization when compared to linearization, indicate the greater accuracy in the application of non linearization. The Langmuir model (one site) gave the best fit and thus the values of adsorption capacity for each activated carbon were calculated from it. Kinetic models show that weak and strong interactions are involved in the adsorption process and that the controlling mechanism may not be limited to intra particle diffusion. The lower value of the boundary layer thickness in the case of activated carbon obtained from the mixture, justified the higher adsorbed quantity of this activated carbon compared to those of activated carbon from each precursor.

Key words*: Activated carbon, mixture of precursor, non-linear kinetics, non-linear isotherms, SEM, XRD.*

1. Introduction

In recent years, the growth of the pharmaceutical industry and other chemical industries using feedstock of chemical nature has raised concerns about the rise in toxicity in our industrial effluents. Sometimes, these effluents flow into waterways, underground water sources, streams, etc. The treatment of water or industrial wastewater from this industry is thus an emergency for saving the natural environment [1-2].

Several separation industrial processes are available for purification of contaminants in liquid phase. Of the numerous techniques available, adsorption is one of the most widely applied techniques for the depollution of industrial effluents. Activated carbon has been the preferred material of choice in the process due to the abundance of harvestable biomass waste from which it can be sourced, and at little cost [3]. Sources include residues from agricultural and forestry activities which make these wastes available at little cost. For many sub Saharan

countries, such as Cameroon, their removal has a significant implication for urban sanitation as they are found in urban dumps.

Wastewater originating from pharmaceutical and animal feedstock industries often found their way into sources of surface water [4]. Of the drugs produced, phenacetin stands out as being highly toxic to the liver, and a consumer of it has a high potential for developing hepatitis and cancer [5]. Phenacetin is metabolized in the liver, mainly to paracetamol which is conjugated and excreted as glucuronide and sulphate. Phenacetin dominated the drug market during the first 50 years of the 20^{th} century. It was the most widely used and prescribed drug in most countries [6]. Because of the excessive use, phenacetin may end up in the environment through manufacturing waste, waste from animal excretion, runoff from animal feeding operations, or leaching from municipal landfills. It is obvious that with its frequent use it should be quite frequently present as a micro pollutant in our environment.

The modelling of adsorption is useful in providing the parameters for the design of adsorption systems. Several mechanisms have been presented to explain the uptake of solute in a solid–liquid adsorption system under isothermal conditions. Based on these mechanisms, several isotherm models have been developed. Among these isotherm models, we can cite those of two-parameters: Langmuir [7], Freundlich [8], Elovich [9], Temkin [10], those of three-parameters such as: Redlich-Peterson [11], Radke-Prausnitz [12], Langmuir-Freundlich [12] and those of four-parameters such as: Langmuir 2-sites [13] and Fritz-Schlunder [12]. Among the kinetic models we can cite, pseudo-first order [13], pseudo-second order [14], Elovich [15] and intra-particle diffusion [16].

The search for the adsorption isotherm model that best fits experimental data and kinetics is a widely used technique to evaluate the model parameters, and to determine the best-fit model. However, depending on the mathematical form of the isotherm or kinetic equation, linearization can modify the distribution of truncation errors, which may affect the accuracy of the best-fit equation [17]. The problems involved in the linearization of non-linear adsorption models such as the alteration of the error structures of such linearized equations can lead to inaccuracies in the choice of the best fitting equation. These issues have been discussed by Yuh-Shan Ho [18]. In his study of the sorption of cadmium on activated carbon, he used non-linear regression analysis to determine the best-fit model to the experimental results. He pointed out that it was not appropriate to use the correlation coefficient or the coefficient of determination of linear regression analysis, as it could falsify the choice of the best-fit adsorption model equation.

In yet another study, Hai Nguyen Tran *et al.* [19] undertook a critical review of what they characterise as mistakes and inconsistencies in publications reporting results of studies on adsorption of contaminants from aqueous solutions. On the aspects related to experimental data and model fitting, they found, in several published works, that the same isotherm or kinetic model could have more than one linear form that give different model constants [19], as a results of errors from researchers during linearization, thus leading to faulty parameter estimates. Furthermore, they found that in several instances, the Pseudo First Order (PFO) equation for sorbate uptake, in its linearized form, was only appropriate in the first 20-30 minutes of contact time and beyond that, failed to fit the experimental data. Several other studies have discussed the weaknesses of linearization of adsorption model equations [18-19-20].

In view of the above weaknesses, more and more researchers are resorting to the application of non-linear models as they are found to be best suitable to explain experimental data from adsorption studies because of the use of many error functions compared to linear models which use only determination coefficient [20-21-22-23]. Amongst the several error functions which are used to evaluate isotherm or kinetic data, the most used are: nonlinear Chi-square test (χ^2), the Sum of the Squares of the Errors (SSE), the Average Relative Error (ARE) and the coefficient of determination (R^2) [20-23-24]. The extra computational effort required, is compensated by appropriate choice of best-fit model equation and the accuracy of the parameter estimates, and theses have a serious implication for process design.

In this work, non-linear regression method using error analysis method was adopted to predict the optimum adsorption isotherm and also, to obtain the kinetic and isotherm parameters to enable us characterize the nature of the adsorption of phenacetin onto activated carbon. Non-linear kinetic and isotherm models mentioned above were applied to the adsorption data of phenacetin onto activated carbons. Furthermore, the characterizations of activated carbons had been done using SEM and XRD.

2. Materials and Methods

2.1 Adsorbents

10 g of ayous sawdust, *Cucurbitaceae* peelings (*egussi*) and mixture of the two biomass (in proportion ½:½) were weighed and added into beakers containing a solution of phosphoric acid (0.79 M). The mixtures were labelled as follows: BIM, consisting of activated carbon of ayous saw dust activated with 1 M phosphoric acid; PIM, *Cucurbitaceae* peelings derived carbon material activated with 1 M phosphoric acid and BPIM; a 1:1 mixture of the two materials the following. Each mixture, maintained at ambient temperature, was manually shaken for 2 hours, and then dried in an oven set at 105°C overnight. The reactor was loaded with 10 g of impregnated sample and then placed in a furnace. The furnace was heated at the rate of 5°C/min to the pre-determined or de sired activation temperature of 450°C. It was then held at this temperature for a period of 1 hour. After allowing to cool to ambient temperature, the samples were washed several times with distilled water. The washed samples were dried in the oven set at 105°C for 24 hours. The resulting products were crushed into powder and well - kept for further tests.

Scanning Electron Microscopy (SEM) and X ray diffraction have been done and the results are given by Figure 1 and 2 below. X rays diffraction data were collected on a STOE Stadi X-ray powder diffractometer with Cu $K_{\_1}$ radiation (= 1.54056 A°) in transmission geometry with an IP-PSD while SEM analysis was done using JSM-6010LA.

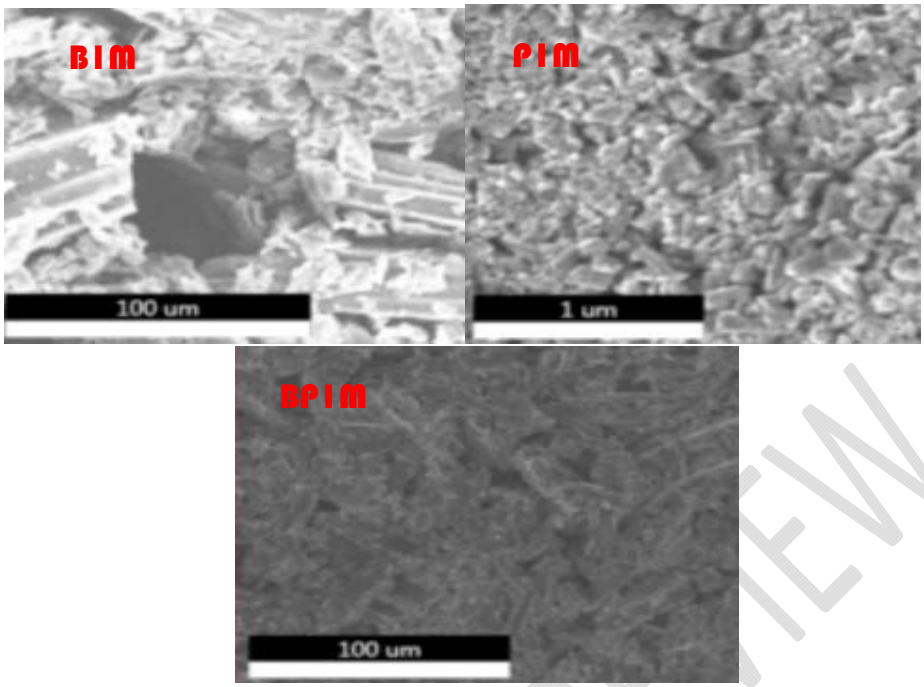


Figure 1: Electronic microscopy image of different activated carbon (B1M: activated carbon from ayous, P1M: activated carbon from egussi and BP1M: activated carbon from the mixture).

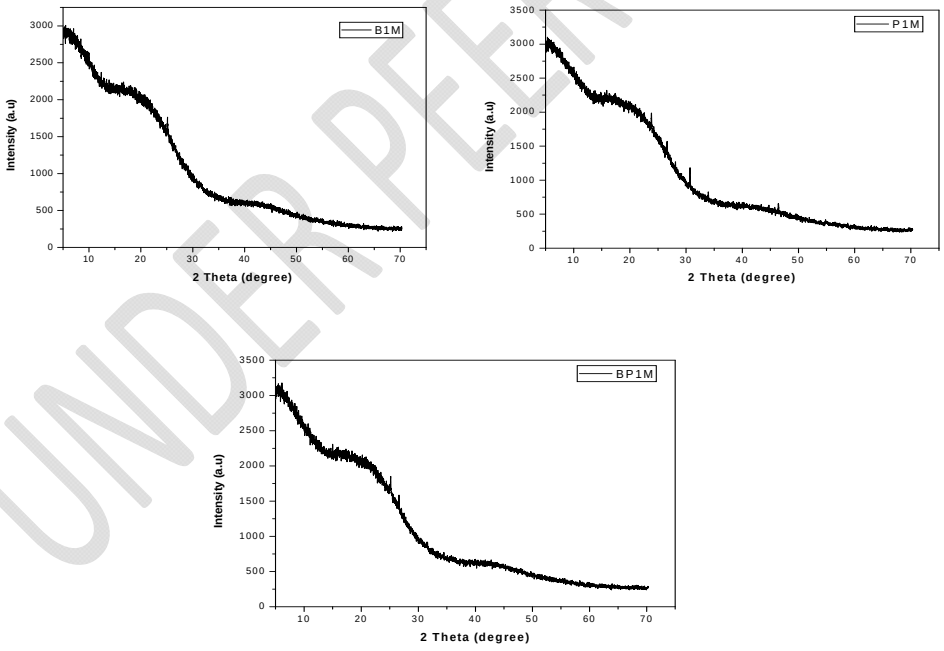


Figure 2: XRD spectrum of different activated carbon.

XRD analysis of activated obtained from mixture of precursor shows more crystallinities than B1M and less than P1M. This implies that the mixture of precursor combine the properties of activated carbon obtained from each precursor. This result is confirmed by the SEM analysis shown in Figure 1.

2.1. Adsorbate

The adsorbate used in this study is the phenacetin was provided by Aldrich Chemicals. The stock solution of phenacetin was prepared by dissolving 250 mg of phenacetin in 100 mL of hot distilled water (75 °C) and then completing to 500 mL with cold distilled water. The working phenacetin solution was prepared by diluting the stock solution with distilled water. Figure 1 below shows the 3D structure of phenacetin.

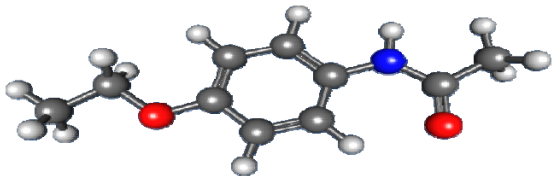


Figure 3: 3D structure of phenacetin.

2.2. Batch Adsorption

For batch adsorption experiments, 50 mg of activated was measured and mixed in 30 mL of phenacetin solution of a known initial phenacetin concentration, and at a pH of 2. The mixture was shaken at a speed of 200 RPM with a mechanical shaker. After two hours and thirty minutes, equilibrium is expected to have been attained. The solution and the activated carbon were separated by filtration, the remaining concentration of phenacetin in the filtrate was determined by using a JENWAY UV spectrophotometer.

2.3. Equilibrium isotherms

Nine different adsorption isotherm models were tested with experimental data for parameter estimation and evaluation of fit. The models include Langmuir, Frendlich, Elovich, Temkin, Redlich-Peterson, Langmuir-Freundlich, Radke-Prausnitz, Langmuir 2-sites and Fritz-Schlunder.

Langmuir isotherm: The Langmuir isotherm is often used for the equilibrium adsorption of solutes from solutions. It is expressed as [7]:

$$Q_e = \frac{Q_m K C_e}{1 + K_L C_e}$$

where, Qe is the adsorption capacity at the equilibrium concentration (mg/g); Ce is the equilibrium concentration of adsorbate in solution (mg/L), while Q_m is the maximum adsorption capacity (mg/g) and K_L is the Langmuir constant (L/mg).

Freundlich isotherm: The Freundlich isotherm is an empirical equation employed to describe the multilayer adsorption. This model predicts that the dye concentration on the adsorbent will increase with the increase of the adsorbate concentration in the solution. The model equation is given as [8]:

$$Q_e = K_f C_e^{1/n}$$

where, Qe is the adsorption capacity at the equilibrium concentration (mg/g); Ce is the equilibrium concentration of adsorbate in solution (mg/L), K_f (l/mg) is the Frendlich isotherm constant and 1/n is the heterogeneity factor which can vary between 0 and 1.

Elovich isotherm: The Elovich isotherm is an equation employed to describe monolayer adsorption. This model predicts that chemical bond is formed between adsorbent and adsorbate. The model equation is given as [9]:

$$\frac{Q_e}{Q_m} = K_E C_e \exp\left(-\frac{Q_e}{Q_m}\right)$$

where, Qe is the adsorption capacity at the equilibrium concentration (mg/g); Ce is the equilibrium concentration of adsorbate in solution (mg/L), while Q_m is the maximum adsorption capacity (mg/g) and K_E is Elovich constant.

Temkin isotherm: The Temkin isotherm assumes that the decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. It is expressed by following equation [10]:

$$Q_e = \frac{RT}{b} \ln(K_T C_e)$$

where, b = RT/B is related to heat of adsorption (J/mol), R is the gas constant (8.314 J. $mol^{-1}.K^{-1}$), T is the absolute temperature (K) and K_T is the Temkin equilibrium constant (L/g) corresponding to the maximum binding energy.

Redlich-Peterson isotherm: The Redlisch-Peterson is an empirical isotherm which incorporates three parameters. It may be used to represent adsorption equilibrium over a wide concentration range. It combines some elements from both the Langmuir and Frendlich equation, and consequently, it can be employed either in heterogeneous or homogenous systems [11]. It can be described as follow:

$$Q_e = \frac{A_{RP} C_e}{1 + B_{RP} C_e^{\beta}}$$

where, A_{RP} (L/g) and B_{RP} (L/mg) are Redlisch–Peterson isotherm constants, β is an exponent which lies between 0 and 1.

Langmuir-Freundlich isotherm: The Langmuir-Freundlich isotherm includes the knowledge of adsorption on heterogeneous surfaces. It describes the distribution of adsorption energy onto heterogeneous surface of the adsorbent [12]. It can be described as follow:

$$Q_e = \frac{Q_m K_{LF} C_e^{\beta}}{1 + K_{LF} C_e^{\beta}}$$

where, Qe is the adsorption capacity at the equilibrium concentration (mg/g); Ce is the equilibrium concentration of adsorbate in solution (mg/L), while Qm is the maximum adsorption capacity (mg/g), K_{LF} is the Langmuir-Freundlich constant (L/mg) and β is the heterogeneous parameter and it lies between 0 and 1.

Radke-Prausnitz isotherm: The Radke-Prausnitz isotherm model has several important properties which makes it more preferred in most adsorption systems at low adsorbate concentration [12]. It can be described as follow:

$$Q_e = \frac{Q_m K_{RaP} C_e}{(1 + K_{RaP} C_e)^{\beta}}$$

where, Qe is the adsorption capacity at the equilibrium concentration (mg/g); Ce is the equilibrium concentration of adsorbate in solution (mg/L), while Qm is the maximum adsorption capacity (mg/g), K_{RaP} is the Radke-Prausnitz constant and β is the model exponent.

Langmuir 2-sites: The Langmuir 2-sites isotherm is another form of Langmuir isotherm. It supposes that adsorbents have two types of adsorption sites designated A and B [12]. It can be described as follow:

$$Q_e = Q_m \left(\frac{f_A K_{LA} C_e}{1+K_{LA} C_e} + \frac{f_B K_{LB} C_e}{1+K_{LB} C_e}\right)$$

where, Qe is the adsorption capacity at the equilibrium concentration (mg/g); Ce is the equilibrium concentration of adsorbate in solution (mg/L), while Qm is the maximum adsorption capacity (mg/g), f_A, f_B, K_{LA} and K_{LB} are Langmuir 2-sites parameters.

Fritz-Schlunder isotherm: Fritz and Schlunder developed a five-parameter empirical model that is capable of simulating the model variations more precisely for application over a wide range of equilibrium data [12]. It can be described as follow:

$$Q_e = \frac{Q_m A_{FS} C_e^{\alpha}}{1+B_{FS} C_e^{\beta}}$$

where, Ce is the equilibrium concentration of adsorbate in solution (mg/L), Qm is the maximum adsorption capacity (mg/g), A_{FS}, B_{FS}, α and β are Fritz-Schlunder parameters.

2.4. Kinetic models

Four different kinetic models were considered for this study: pseudo-first order, pseudo-second order, Elovich and intra particle diffusion.

Pseudo-first order model: The pseudo-first-order kinetic model describes an adsorption process base on multilayer adsorption. Lagergren's first-order rate equation is called pseudo-first-order in order to distinguish kinetic equations based on the adsorption capacity of solids from those based on the concentration of a solution. Their equation is generally expressed as [14-19]:

$$Q_t = Q_e [1 - \exp(-K_1 t)]$$

where, Q_e and Q_t are the adsorption capacity at equilibrium and at time t, respectively (in mg/g) and K_1 is the rate constant for the pseudo-first order adsorption (L/mg.min).

Pseudo-second order model: The pseudo-second order kinetic model was initially proposed as a second order rate equation for the removal of heavy metals from water using natural zeolites and it was based on the strong bond between adsorbent and adsorbate [16-19].

$$Q_t = \frac{Q_e^2 K_2 t}{1+K_2 Q_e t}$$

where, Q_e and Q_t are the adsorption capacity at equilibrium and at time t, respectively (in mg/g) and K_2 is the rate constant for the pseudo-first order adsorption (L/mg.min).

Elovich model: The Elovich empirical equation model was firstly for the adsorption of carbon monoxide onto manganese dioxide. However, this equation is now generally known as

the Elovich equation and has been extensively applied to chemisorption data. This equation can be expressed mathematically as follows [13-19]:

$$Q_t = \frac{1}{\beta}\ln(1 + \alpha\beta t)$$

where, Q_t are the adsorption capacity at time t, α (mg/g.min) represent the initial rate of adsorption and β (mg/g.min) the desorption rate constant.

Intra-particular diffusion model: The intra-particle diffusion model developed by Weber and Morris is presented as follows [19-20]:

$$Q_t = K_{id}t^{1/2} + C$$

where, K_{id}(mg/g.min$^{-1/2}$) is the rate constant of the intra-particle diffusion model and C(mg/g) is a constant associated with the thickness of the boundary layer, where a higher value of C corresponds to a greater effect on the limiting boundary layer.

2.5. Error functions

In this work, four different error functions were examined by minimizing the respective error function across the concentration and time range studied, using the "SOLVER ADD-IN" with Microsoft's spread sheet. The error functions are divided in two: quantitative and qualitative [26]. The quantitative error functions are studied well in detail in the following paragraph.

The Sum of the Squares of the Errors (SSE): At higher end of the liquid-phase concentration and time ranges, the magnitude and squares of the errors tend to increase. This illustrates a better fit for the isotherm and kinetic parameters derivation [27]. This error function can be represented by the equation:

$$SSE = \sum_{i=1}^{n}(Q_{e,cal} - Q_{e,exp})_i^2 \quad \text{..... (1)}$$

where $Q_{e,calc}$ is the theoretical adsorbed solid phase concentrations of adsorbate on adsorbent, that have been calculated from one of the isotherm equations, n the number of experimental points and $Q_{e,exp}$ is the experimental adsorbed solid phase concentrations of adsorbate on sorbent.

Nonlinear chi-square test: This statistical tool is necessary for the best fit of an adsorption system. It is obtained by judging the sum of squares difference between the experimental and calculated data, with each squared difference is divided by its corresponding value [26-27]. The value of chi-square is calculated by using this equation:

$$\chi^2 = \sum_{i=1}^{n}\frac{(Q_{e,cal} - Q_{e,exp})_i^2}{Q_{e,exp}} \quad \text{..... (2)}$$

The average relative error (ARE): Developed by Kapoor and Yang, this error function attempts to minimize the fractional error distribution across the entire concentration or time range. It can be expressed by [26-27]:

$$ARE = \frac{100}{n}\sum_{i=1}^{n}\left|\frac{Q_{e,cal} - Q_{e,exp}}{Q_{e,exp}}\right|_i \quad \text{..... (3)}$$

Coefficient of determination: The coefficient of determination is used to evaluate the comparison of kinetic and isotherm models with experimental data [26-27]. It is given as:

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(Q_{e,cal} - Q_{e,exp})^2}{\sum_{i=1}^{n}[Q_{e,cal} - moy(Q_{e,exp})]^2} \quad \text{..... (4)}$$

The qualitative error function is the residual plot. This important criterion allows access to the adequateness of a regression model [27]. The residual plot with a clean pattern indicates that the isotherm or kinetic model has fixed model errors and is not adequate while a uniform distribution of residual indicates the adequacy of the model. The residue is calculated using the following formula:

$$Residue = Q_{t,exp} - Q_{t,cal} \quad \text{..... (5)}$$

where $Q_{t,exp}$ is the i[th] experimental adsorbed quantity and $Q_{t,cal}$ is the i[th] theoretical adsorbed quantity

2.6. CALCULATION PROCEDURE APPLYING NON-LINEAR REGRESSION PROCEDURE *CASE FOR LANGMUIR ISOTHERM*

To execute non-linear regression analysis in the case of Langmuir isotherm, the following procedure was formulated:

- We input in the spreadsheet, the equilibrium concentration and the experimental adsorbed quantities. We also input different set of the model constants and the Langmuir model equation was used to calculate the theoretical adsorbed quantities. For each set of model constants input, equation (1) was used to calculate the sum of squares of the errors. The values obtained were calculated using Solver. The final model parameter estimates were those that minimize the sum of square error.

- The function errors given by the other Isotherm Model equations (2), (3) and (4) were also calculated after estimating the set of model parameters which minimize the sum of square of the errors.

The same procedure was followed for all the models used in this work. In the case of kinetic studies, we introduce in the spreadsheet the agitation time and the adsorbed quantities.

3 Results and Discussion

The result obtained by the application of non-linear regression analysis on kinetic and equilibrium data are presented below.

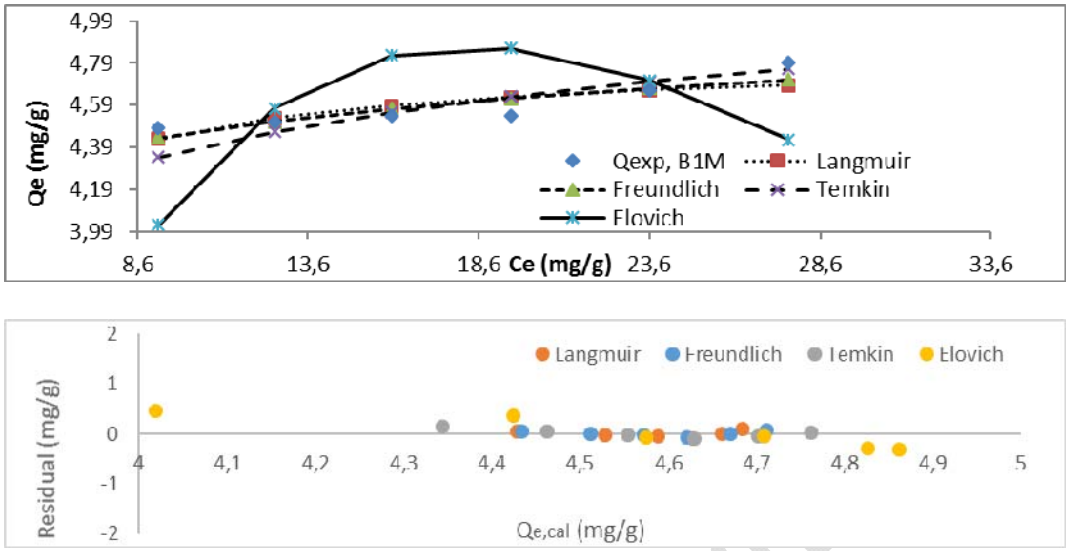
2.7. Isotherm study

In general, the adsorption isotherm indicates the distribution of molecules are distributed between the liquid and solid phase when the adsorption processes attains equilibrium. It is employed to establish the maximum capacity of adsorption of adsorbate on adsorbents, which, in this case is expressed in terms of quantity of phenacetin adsorbed per unit of mass of adsorbent used.

3.1.1. Isotherm with two parameters

The non-linear plots of those isotherms are given on Figure 4 to 6 bellow.

Models	Adsorbents	Parameters		R^2	Errors		
					SSE	χ^2	ARE
Langmuir	B1M	K_L (L/mg)	1.22	0.456	0.024	0.0002	1.133
		Q_m (mg/g)	4.82				
	P1M	K_L (L/mg)	0.64	0.990	0.009	0.00005	0.298
		Q_m (mg/g)	5.33				
	BP1M	K_L (L/mg)	0.59	0.931	0.64	0.0065	2.349
		Q_m (mg/g)	15.43				
Freundlich	B1M	K_F (mg/L)	3.92	0.694	0.016	0.0034	0.902
		1/n	0.055				
	P1M	K_F (mg/L)	4.08	0.980	0.004	0.0007	0.363
		1/n	0.099				
	BP1M	K_F (mg/L)	8.33	0.984	0.144	0.0012	1.057
		1/n	0.19				
Temkin	B1M	K_T (L/mg)	6511.18	0.739	0.031	0.0070	1.306
		b	9837.92				
	P1M	K_T (L/mg)	4128.39	0.977	0.005	0.001	0.449
		b	660.74				
	BP1M	K_T (L/mg)	1039.68	0.976	0.222	0.019	1.281
		b	24.35				
Elovich	B1M	K_E	0.039	-0.081	0.537	0.122	6.626
		Q_m	18.39				
	P1M	K_E	0.058	0.544	0.296	0.058	3.661
		Q_m	16.26				
	BP1M	K_E	0.348	0.646	6.730	0.613	7.787
		Q_m	10.51				



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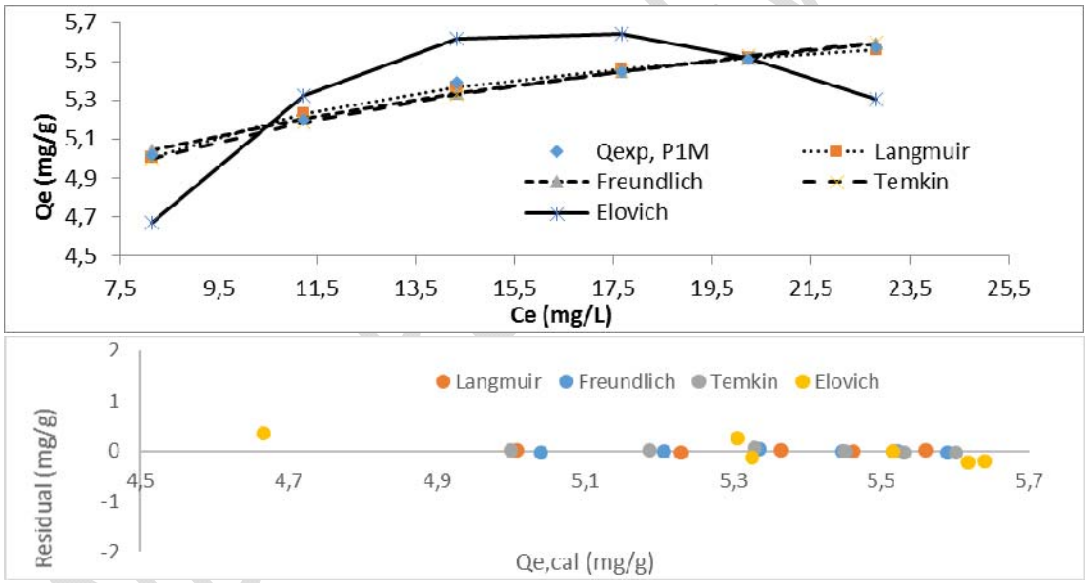
320 **Figure 4**: Non-linear isotherm and residual plot for two parameters in the case of B1M.



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324 **Figure 5**: Non-linear isotherm and residual plot for two parameters in the case of P1M.

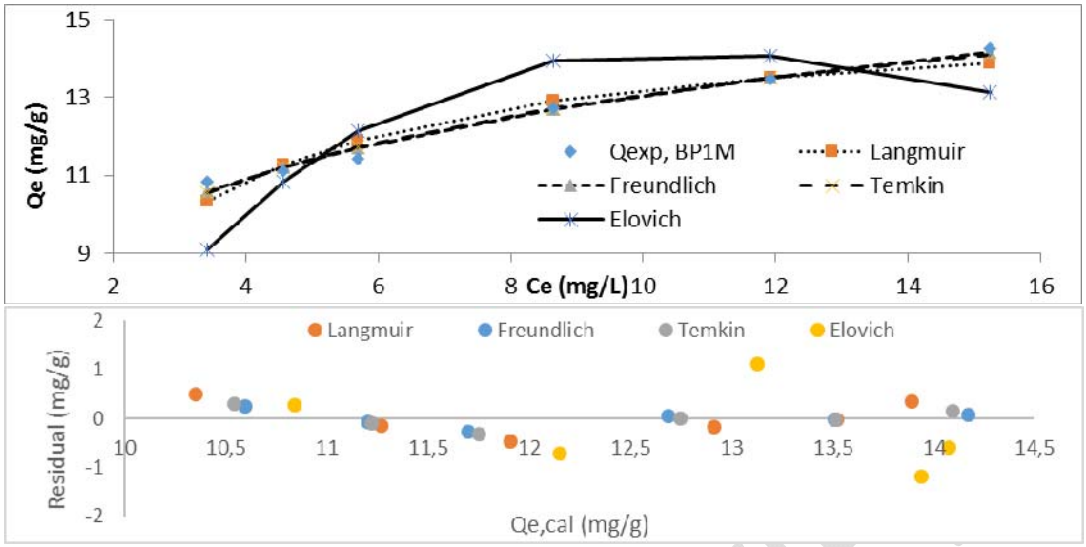


Figure 6: Non-linear isotherm and residual plot for two parameters in the case of BP1M.

Table 1 shows isotherm with two parameters obtained by using non-linear equations.

Table 1: Value of parameters and error analysis for two parameters isotherms models.

The coefficient of determination and the other errors present on Table 1 and particularly the residual plot show that non-linear Elovich is not adequate to describe phenacetin adsorption on different activated carbons. For Langmuir, Freundlich and Temkin isotherm, the residual plot shows that those models are adequate for adsorption description. In the case of Elovich model, the asymmetry in residual distribution around the zero axis suggest that one of the basic hypothesis of the model is not able to describe the adsorption process. The small error values and coefficient of determination near 1 suggest that in the case of P1M and BP1M, Langmuir, Freundlich and Temkin models are adequate. The small quantities adsorbed by B1M imply that the adsorption sites of B1M have high energy than those of P1M and BP1M [28]. Freundlich isotherm suggests that P1M and BP1M have heterogeneous surfaces with a non-uniform distribution of adsorption energy on the surface. The values of 1/n high in BP1M than P1M suggest that adsorption site in BP1M is more dense [29]. This shows that the mixture of precursor in activated carbon preparation can increase the adsorption sites density.

2.7.1. Isotherm with more than two parameters

The non-linear plots of those isotherms are given on figure 7 to 9 below.

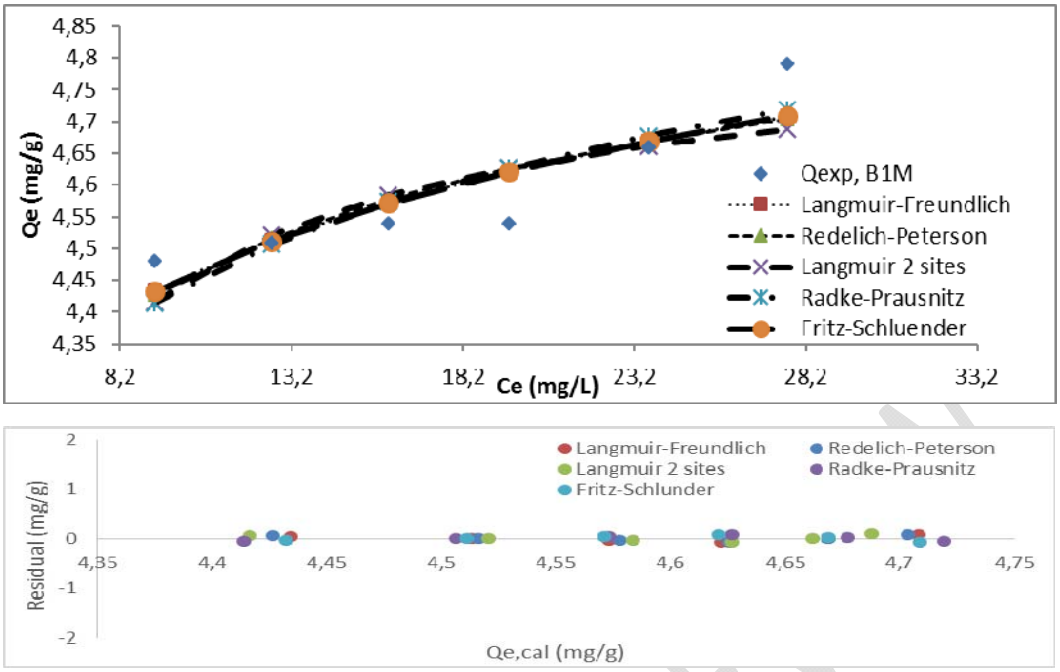


Figure 7: Non-linear isotherm and residual plot for more than two parameters in the case of B1M.

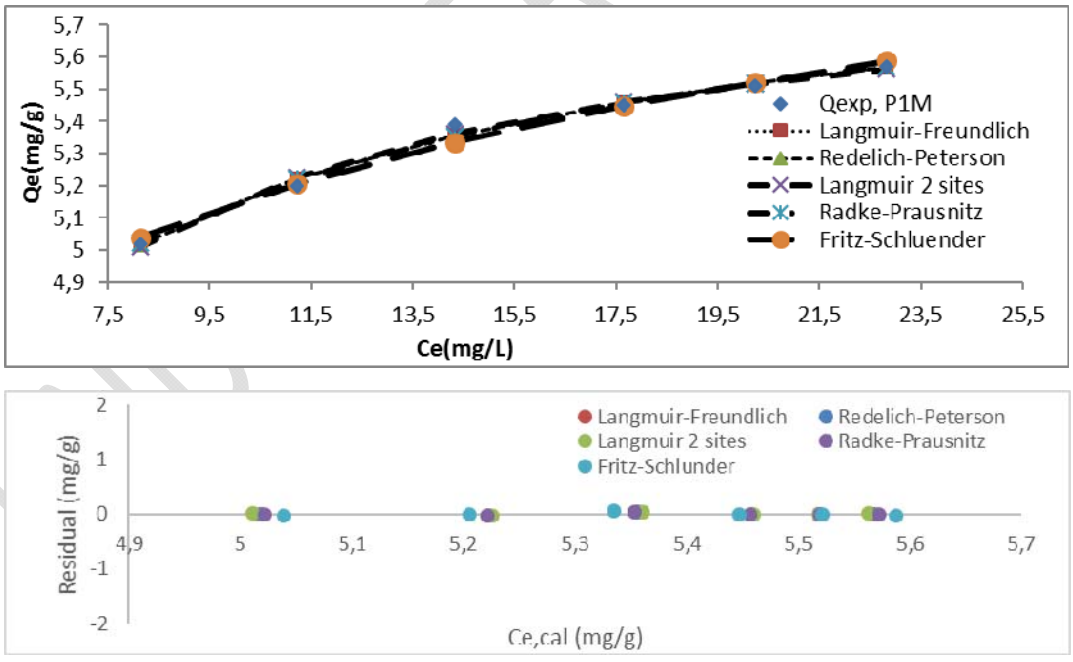
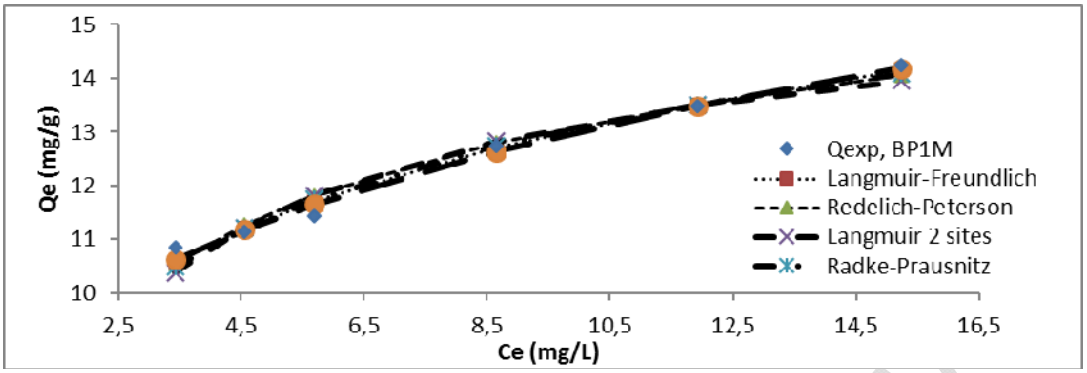


Figure 8: Non-linear isotherm and residual plot for more than two parameters in the case of P1M.



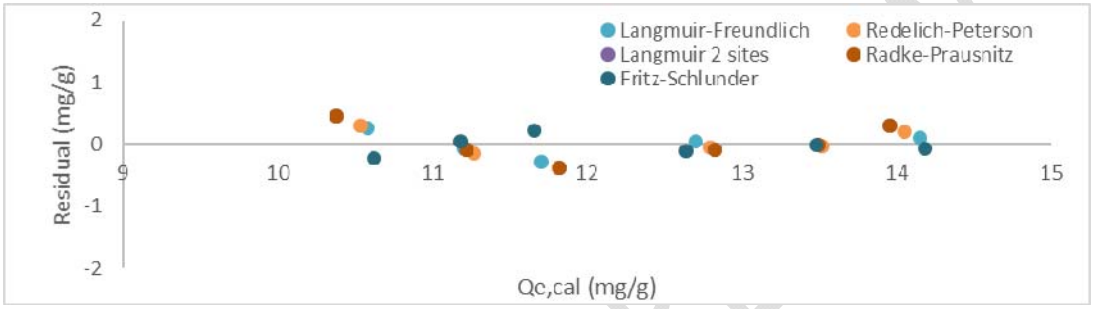


Figure 9: Non-linear isotherm and residual plot for more than two parameters in the case of BP1M.

Table 2 shows isotherm models with three parameters obtained by using non-linear equations

Table 2: Value of parameters and error analysis for three parameters isotherm models.

Models	Activated carbon	Parameters		R^2	Errors		
					SSE	χ^2	ARE
Langmuir-Freundlich	B1M	Q_m (mg/g)	7.87	0.675	0.0167	0.0036	0.922
		K_{LF} ($L^{\beta}.mg^{-\beta}$)	0.75				
		β	0.12				
	P1M	Q_m (mg/g)	6.18	0.991	0.0017	0.0003	0.235
		K_{LF} ($L^{\beta}.mg^{-\beta}$)	0.93				
		β	0.72				
	BP1M	Q_m (mg/g)	61.51	0.983	0.1604	0.0141	1.104
		K_{LF} ($L^{\beta}.mg^{-\beta}$)	0.0004				
		β	0.24				
Redelich-Peterson	B1M	A_{RP} ($L.mg^2/g$)	13.20	0.635	0.0192	0.0041	1.008
		B_{RP}	3.09				
		β	0.96				
	P1M	A_{RP} ($L.mg^2/g$)	5.46	0.991	0.0017	0.0003	0.240
		B_{RP}	1.02				
		β	0.97				
	BP1M	A_{RP} ($L.mg^2/g$)	19.59	0.966	0.3053	0.0263	1.585
		B_{RP}	1.79				
		β	0.88				
		Q_m (mg/g)	3.72				

	B1M	K_{RaP} (L/mg)	5.22	0.713	0.0183	0.0039	1.007
		β	0.95				
		Q_m (mg/g)	5.008				
Radke-Prausnitz	P1M	K_{RaP} (L/mg)	1.18	0.991	0.0019	0.0003	0.239
		β	0.95				
		Q_m (mg/g)	8.70				
	BP1M	K_{RaP} (L/mg)	2.22	0.973	0.2558	0.0226	1.323
		β	0.85				

The residual plot shows that three parameter models are adequate for adsorption description. The symmetry in residual distribution around the zero axis suggests that the basic hypothesis of those models are followed by the adsorption process. The low value of the error functions particularly ARE indicate that adsorption process follow the models. Langmuir-Freundlich model confirms that adsorption surface is heterogeneous with distribution of adsorption energy between the surfaces [30]. It also suppose that if adsorption surface is homogeneous, adsorption is due to adsorbent-adsorbate interactions. Redelich-Peterson isotherm is based ideal multi-layer adsorption layer [26]. Radke-Prausnitz model present the same conclusion and those of Langmuir-Freundlich and Redelich-Peterson but have the advantage to be adequate on a large concentration range [32]. The value of heterogeneous parameter β of Langmuir-Freundlich model range between 0 and 1 confirms the heterogeneous nature of the adsorption surface. The heterogeneous parameter of both Radke-Prausnitz and Redelich-Peterson less than 1 suggests that this two models cannot be reduce to Langmuir model and conduct to non-homogeneous adsorbent surface.

Table 3 shows isotherm parameters with more than three parameters obtained by using non-linear equations.

Table 3: Value of parameters and error analysis for four and five parameters isotherm models.

Models	**Activated carbon**	**Parameters**		**R^2**	**Errors**		
					SSE	**χ^2**	**ARE**
		K_{LA} (L/mg)	0.0017				
		f_A	0.059				
	B1M	K_{LB} (L/mg)	1.18	0.527	0.0240	0.0052	1.117
		f_B	0.95				
		Q_m (mg/g)	5.05				
		K_{LA} (L/mg)	0.12				
		f_A	0.10				
Langmuir 2 sites	P1M	K_{LB} (L/mg)	0.86	0.991	0.0017	0.0003	0.276
		f_B	0.89				
		Q_m (mg/g)	6.02				
		K_{LA} (L/mg)	0.82				
		f_A	0.86				
	BP1M	K_{LB} (L/mg)	0.066	0.951	0.4643	0.0406	1.873
		f_B	0.22				
		Q_m (mg/g)	15.30				
		A_{FS} $(mg/g)^2$	4.82				
	B1M	B_{FS} (mg/g)	0.242	0.688	0.0164	0.0035	0.906
		α	0.035				

		β	-0.13				
Fritz-Schlunder	P1M	A_{FS} (mg/g)²	6.35	0.981	0.0039	0.0007	0.348
		B_{FS} (mg/g)	0.569				
		α	0.069				
		β	-0.10				
	BP1M	A_{FS} (mg/g)²	5.67	0.987	0.1156	0.0101	0.961
		B_{FS} (mg/g)	-0.35				
		α	0.262				
		β	-0.24				

Table 3 shows small error values and residual plot shows error distribution around the zero axis. This confirms the hypothesis given by the other models which is heterogeneous adsorption surface. The Langmuir 2 sites adsorption model confirms the presence of more than one type of adsorption site.

Comparison between the error functions of non-linear and linear isotherm models

In order to confirm the fact that non-linear is better than linear, the error given by the equation (2), (3) and (4) were calculated and the results are presented in table 4 below. This table shows the error of non-linear models and those for linear isotherm models with two parameters since it is not possible to linearize the models with more than two parameters.

Table 4: Non-linear and linear isotherms with two parameters error functions

Models	Activated carbons	Linear isotherm errors				Non-linear isotherm errors			
		R^2	SSE	χ^2	ARE	R^2	SSE	χ^2	ARE
Langmuir	B1M	0.645	0.032	0.007	0.052	0.456	0.024	0.0002	1.133
	P1M	0.990	0.002	0.0003	0.002	0.990	0.009	0.00005	0.298
	BP1M	0.935	0.748	0.068	0.197	0.931	0.64	0.0065	2.349
Freundlich	B1M	0.677	0.0163	0.0035	0.025	0.694	0.016	0.0034	0.902
	P1M	0.081	7.134	1.091	8126.	0.980	0.004	0.0007	0.363
	BP1M	0.101	53.160	5.489	10.548	0.984	0.144	0.0012	1.057
Temkin	B1M	4.18×10^{-6}	4842044.46	1175.05	7671887.85	0.739	0.031	0.007	1.306
	P1M	4.90×10^{-5}	445999.96	305.20	517508.90	0.977	0.005	0.001	0.449
	BP1M	0.003	32210.62	35.52	7014.32	0.976	0.222	0.019	1.281
Elovich	B1M	0.002	5.782	0.886	9.209	-0.081	0.537	0.122	6.626
	P1M	0.232	0.629	0.261	0.725	0.544	0.296	0.058	3.661
	BP1M	0.647	4.621	0.020	1.193	0.646	6.730	0.613	7.787

In general, Table 4 shows that, non-linear isotherm models with two parameters have good R^2, SSE, ARE and χ^2 than linear isotherm. This allows us to confirm the fact that non-linear form of equation describes well the adsorption process than linear models. The less value of χ^2 in the non-linear compare to those of linear confirms that linearization modified the distribution of error between the experimental and predicted value. However, this table also confirms that transformations of non-linear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares.

2.8. Kinetic studies

To simulate the adsorption kinetics, commonly used models such as: pseudo-first and second-order, Elovich equation and the intra-particle diffusion equations, were applied for phenacetin-activated carbon interactions. The results are shown in Figures 10 to 12.

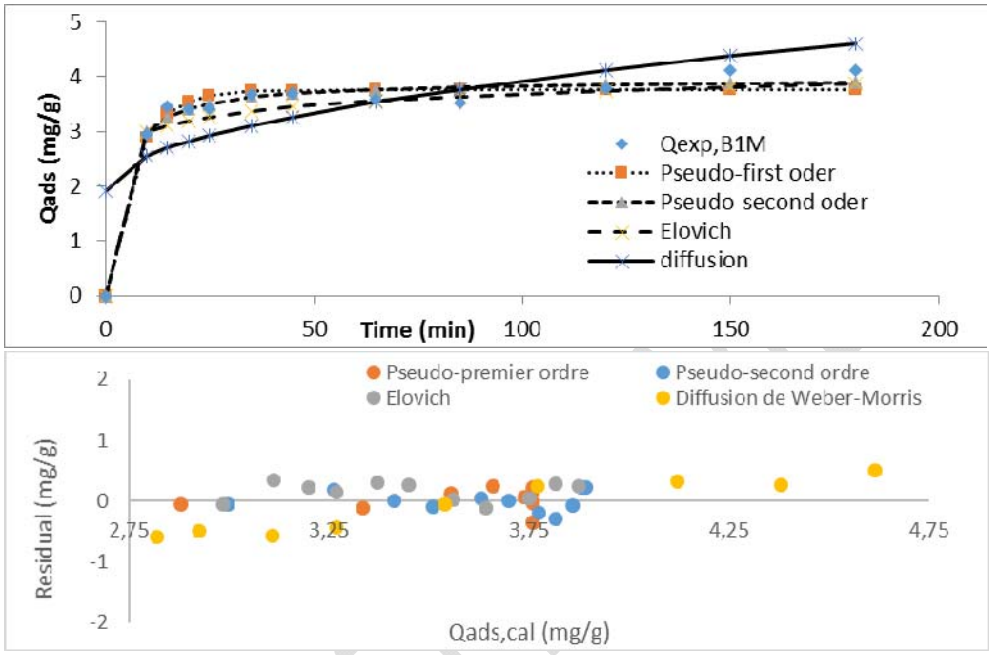


Figure 10: Non-linear kinetic models and residual plot in the case of B1M.

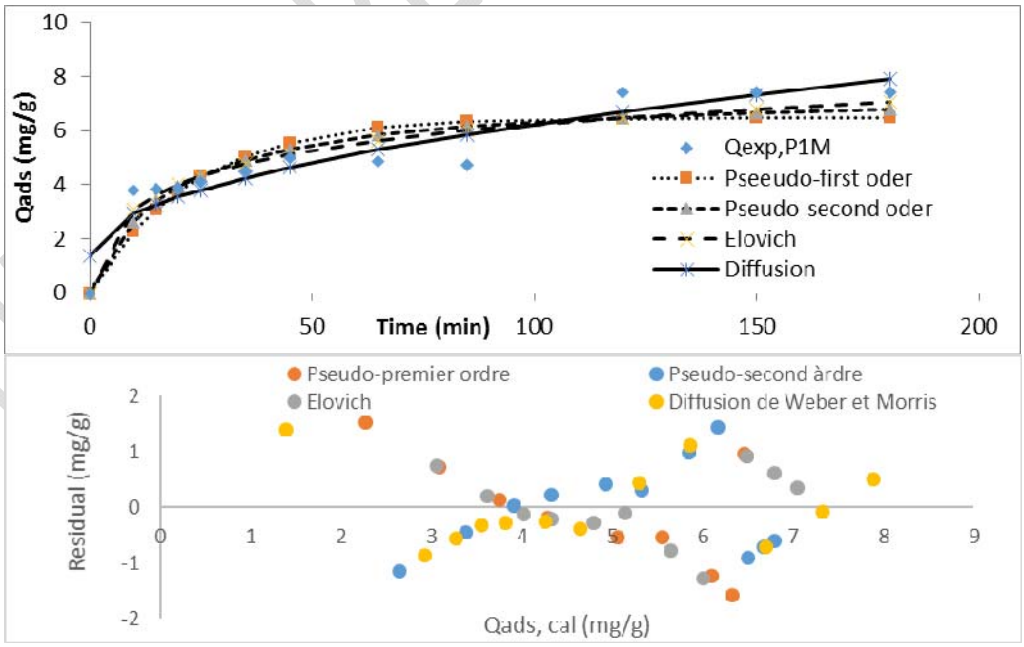


Figure 11: Non-linear kinetic models and residual plot in the case of P1M.

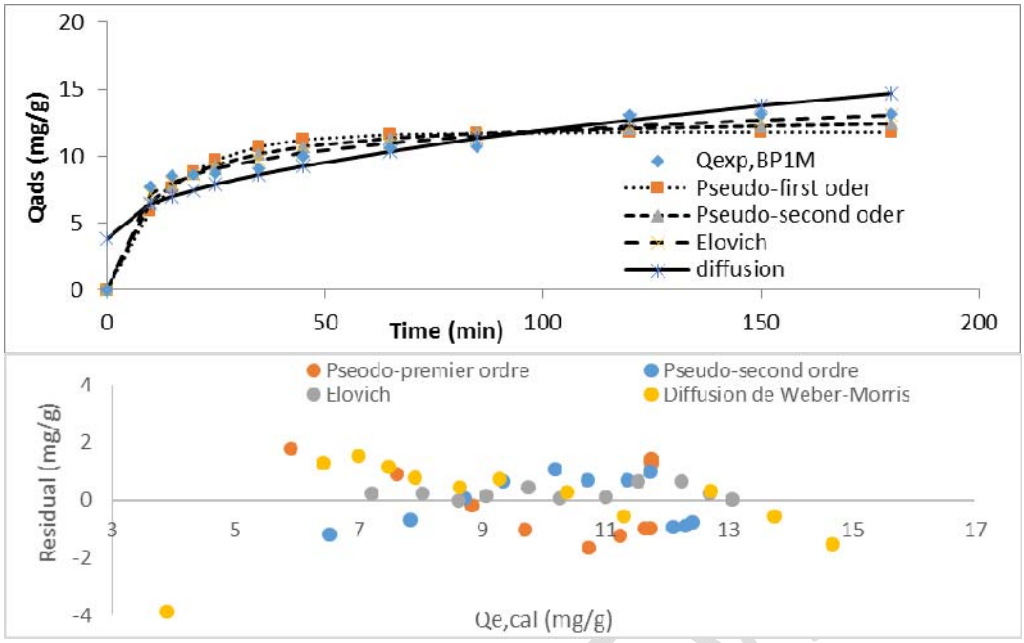


Figure 12: Non-linear kinetics models and residual plot in the case of BP1M.

Table 5 below shows kinetic parameters obtained by using non-linear equations.

Table 5: Value of parameters and error analysis in the case of kinetic models.

Models	Activated carbon	Parameters		R^2	Errors		
					SSE	χ^2	ARE
Pseudo-first oder	B1M	K_1 (min^{-1})	0.14	0.966	0.4304	0.1159	4.403
		Q_e (mg/g)	3.76				
	P1M	K_1 (min^{-1})	0.04	0.782	10.1307	2.3676	16.948
		Q_e (mg/g)	6.49				
	BP1M	K_1 (min^{-1})	0.06	0.875	16.9449	1.7969	11.640
		Q_e (mg/g)	11.75				
Pseudo-second oder	B1M	K_2 (min^{-1})	0.07	0.978	0.2738	0.0734	3.481
		Q_e (mg/g)	3.96				
	P1M	K_2 (min^{-1})	0.007	0.852	6.5510	1.3764	13.099
		Q_e (mg/g)	7.49				
	BP1M	K_2 (min^{-1})	0.007	0.943	7.6817	0.7905	7.829
		Q_e (mg/g)	13.11				
Elovich	B1M	α (mg/g.min)	521.6	0.547	0.5057	0.1479	5.036
		β (mg/g.min)	3.26				
	P1M	α (mg/g.min)	1.26	0.783	4.3172	0.8049	10.046
		β (mg/g.min)	0.72				
	BP1M	α (mg/g.min)	7.15	0.940	2.7904	0.2693	4.370
		β (mg/g.min)	0.49				
Intraparticular diffusion	B1M	K_{id} $(mg/g.min)^{1/2}$	0.20	0.146	6.0186	2.6741	3.326
		C	1.92				
	P1M	K_{id} $(mg/g.min)^{1/2}$	0.48	0.864	5.5964	2.2001	12.328
		C	1.39				
	BP1M	K_{id} $(mg/g.min)^{1/2}$	0.80	0.782	24.8123	5.0261	11.828
		C	3.87				

Pseudo-first order is based on a multi-layer adsorption on adsorbent surface. This type of adsorption is based on weak interaction between adosrbate and adsorbent such as Van der Waals forces. The residual plot and the different errors in the case of pseudo-first order show that this model does not adequately describe the phenacetin adsorption process but the proximity between the experimental adsorbed quantity and the predicted one allow us to say that adsorption of phenacetin do not follow ideal multi-layer adsorption. This conclusion is same as the one obtained in linear plot [25]. The pseudo-second order is based on π-π interaction between adsorbent and adsorbate [19]. This interaction implies mono-layer adsorption and in the case of phenacetin adsorption, the proximity between the experimental and predicted adsorbed quantity and the low error values in the case of pseudo-second order allow us to say that π-π interactions are the major bonds formed in phenacetin adsorption. The residual plot in the case of pseudo-second order shows asymmetry of the distribution of the residuals about zero and suggests a problem with the model i.e the absence of a parameter in model definition [33]. The value of 1/β of Elovich model suggests that adsorption sites of BP1M are greater than those of B1M and P1M [34]. Weber and Morris intra-particular diffusion model shows that diffusion of phenacatin molecule is not rate limiting step. The increase of the thickness of the boundary layer by the mixture of precursor can be observed in table 10. This increase is responsible for the high adsorbed quantities obtained in the case of BP1M [35]. The residual plot shows that kinetic models are more appropriate in the case of B1M and the asymmetry in residual distribution around the zero axis suggests the absence of one of important variable in models definition or a systematic error in data collection.

3. Conclusion

The non-linear kinetic and equilibrium isotherm models were applied to the adsorption of phenacetin onto activated carbon obtained from ayous sawdust and cucurbitaceae peelings. SEM and XRD analysis show that the mixture of precursor combines the properties of activated carbon obtained from each precursor. Non-linear equilibrium isotherm models show that phenacetin adsorption is done on heterogeneous surface and do not form ideal monolayer. Comparison between linear and non-linear isotherm models with two parameters shows that transformations of non-linear isotherm equations to linear forms implicitly alter their error structure. Non-linear kinetic models show that more than one process is responsible for the adsorption of phenacetin and the mixture of the precursor increase the boundary layer. Residual plots show that equilibrium isotherm models are appropriate to study the adsorption of phenacetin while one of the important variable do not consider in kinetic models or an

existence of a systematic error in kinetic data collection. This study confirms that mixture of precursor is one of the new ways to prepare activated carbon.

4. References

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