

Adsorption of 2,4-dinitrophenol on activated carbon prepared from cotton cakes: non-linear isotherm modeling

ABSTRACT

In this research, cotton cake has been investigated as a cheap and available precursor used for the production of novel carbons using phosphoric acid and potassium hydroxide as chemical activating agents and 2:1; 1:1 impregnation ratio with various concentrations 0,5M; 1M; 1,5M. Carbonization was done at 450°C for one hour and allowed to cool. The KOH activated carbon gave high Iodine number values ranging between 447 and 590 mg/g. Thus, KOH is the activating agents agent activating in our study and the best will be used for the continuation of our work was characterized by Fourier transform-infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and proximate analysis (pHZCN, pH, Bulk density, moisture content, ash content, volatile matter, fixed carbon content and matter soluble in water). The experimental isotherms were analyzed using five two-parameter sorption isotherm models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Jovanovic), five three-parameter models (Redlich-Peterson, Sips, Khan, Hill and Toth) and three four-parameter models (Fritz-Schlunder, Baudu and Marczewski-Jaroniec). Three error analysis methods were used to evaluate the experimental data: correlation coefficient (R^2), Chi-square (χ^2), Average Relative Error (ARE), Sum of Absolute Errors (EABS) and Root mean square error (RMSE) values test to find the best fitting isotherm. In particular, Freundlich (two-parameter) and Toth (three-parameter) models described the adsorption isotherm data well.

Keywords: Adsorption, 2,4-Dinitrophenol, activated carbon, cotton cake, isotherms, Error functions.

1. INTRODUCTION

At present, the problems of pollution become alarming extensive more and more and this, following the spectacular rhythm of the industrial activities. Concerns intensify day by day, especially in terms of contamination of the drinking water resources. In the two last decades, several research tasks were devoted to the description of the principal pollutants being likely to increase the vulnerability of these resources. A report had just shown that the phenol and its derivatives represent the most dangerous pollutants on the matter. These residues come primarily from the rejections of pharmaceutical, polymeric, insecticidal industries. Among these compounds is 2,4-dinitrophenol, which is ranked by the US Environmental Protection Agency as being 121st out of the 275 most hazardous substances in terms of its toxicity [1]. Treatment of water contaminated by this class of compounds is generally a very difficult process. The presence of the nitro group in their structure provides them a strong chemical stability and resistance to microbial degradation [2]. Some physicochemical processes have been developed for the removal of phenolic compounds, including adsorption, extraction by chemical solvents, air stripping, freezing and crystallization, chemical oxidation, wet oxidation, and advanced oxidation processes [3], [4].

Adsorption onto activated carbon is often considered as the most economical and efficient process for the removal of 2,4-Dinitrophenol from dilute aqueous solutions because of its large surface area, controllable pore structure, high adsorption capacity, high purity, easy availability, thermal stability and functional groups. Some of the precursors for activated carbon such as bagasse Bagasse [5], Banana

Empty Fruit Bunch and Delonixregia Fruit Pod [6], *Fagopyrum esculentum* [7], coffee husks [8], rice husk [8], [9]. Plant *Manihot Esculenta* [10], pistachio-nut shell [11], Cola Nut Shells [12]. The advantage of using agricultural by-products as raw materials for manufacturing activated carbon is that these raw materials are renewable and potentially less expensive to produce.

Adsorption isotherm data modeling is a valuable tool for predicting and comparing adsorption performance of various adsorbents. There are two-, three-, and even four-parameter empirical isotherm models available for this purpose [13]. In recent years, the non-linear regression method has been proposed as a better way to find the best fitting of adsorption equilibrium. In the nonlinear regression method, the error distribution between the experimental data and the predicted isotherm must be minimized by an iterative procedure [14].

In this investigation, we are intended to examine nonlinear isotherms regressions method in more details and represent how to use these models to describe the adsorption 2,4-Dinitrophel by activated carbon obtain by cotton cakes was investigated.

2. Material and methods

2.1 Material

Coton cakes was collected from Zamay, Department of MayoTsanaga, far Nord region Cameroon, processed [6]. They were cut into small pieces of about 0.5 to 1 cm in size, dried in sunlight until all the moisture was evaporated.

2.1.1 Preparation of Activated Carbon

Preparation of activated carbon from Cotton cakes was carried out by chemical activation process with H_3PO_4 and KOH activating agent at different concentration (0.5M; 1M and 1.5M). 120 grams of different material were inserted into each of five flasks, and activating agent solutions whose impregnation ratios were 1/1, and 2/1, (w/w) were added to these flasks in order to activate the carbons. The mixture was allowed for 30 minutes for activation to take place before being dried in an oven set at 105°C for 48 hours. The samples impregnated were carbonized for 1hour at 450°C, at a heating rate of 5°C/min. After impregnation and carbonization, the pyrolysis carbons based KOH were leached with 1% HCl (v/v) for 2-3 hours and together with those from H_3PO_4 , were washed several times with distilled water until a neutral pH for the two carbon based H_3PO_4 and KOH was achieved. Later, the carbon paste was dried in an oven at 110°C for at least 24 hours which were later converted to powder activated carbon of particles of size lower than 100 μm and pestle before application. The prepared activated carbon was characterized by the adsorption capacity towards iodine using the standard test method for the determination of iodine number of activated carbon (ASTM) for KOH and H_3PO_4 activation.

2.1.2 Characterization of Activated Carbons

The activated carbons were characterized by, Fourier transform-infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and proximate analysis (pH_{PZC} , pH, Bulk density, moisture content, ash content, volatile mater, fix carbon content and matter soluble in water).

2.1.3 Batch equilibrium experiments and analytical method

68 Stock solution of 2,4-dinitrophenol at the concentration of 500 mg/L was prepared by dissolving 0.125
 69 g of sodium 2,4-Dinitrophenol in 0.5 L of distilled water. Experimental solutions at desired
 70 concentrations were obtained by dilution of the stock solution with distilled water pre-adjusted to pH 2.
 71 The initial concentrations of the experimental solutions of 2,4-Dinitrophenol were determined as 20,
 72 25, 30, 35, 40, 45 and 50 mg/L. 30 mL of the experimental solutions were placed in bottles and then
 73 0.05 g prepared activated carbon was added to each bottle. After agitation for about about 2 hours,
 74 the solution was filtered, and the filtrate analyzed to obtain the residual concentration 2,4-
 75 Dinitrophenol by using the UV/Vis spectrophotometer at λ_{max} value of 320 nm.

76 2.2 Modelling Theoretical Background

77 Table 1 summarizes the non-linear forms of the two, three and four parameter isotherms models used
 78 in this study.

79 **Table 1:** Non-linear forms of the two, three and four parameter isotherms

Parameter	isotherms	Non-linear forms	Reference
Two	Langmuir	$Q_e = \frac{Q_m K C_e}{1 + K C_e}$	[15]
	Freundlich	$Q_e = K_f C_e^{1/n}$	[15]
	Dubinin- Radushkevich	$Q_e = Q_m \exp(-K \epsilon^2);$ $\epsilon = RT \ln(1 + 1/C_e);$	[16]
	Temkin	$Q_e = Q_m \frac{RT}{\Delta Q} \ln(AC_e)$	[17]
	Jovanovic	$q_e = q_m (1 - e^{-k_j C_e})$	[18]
Three	Redlich-Peterson	$q_e = \frac{AC_e}{1 + BC_e^\beta}$	[19]
	Sips	$q_e = \frac{K_s C_e^\beta}{1 + a_s C_e^\beta}$	[19]
	Toth	$\frac{q_e}{q_m} = \frac{K_t C_e}{[1 + (K_t C_e)^n]^{1/n}}$	[19]
	Hill	$q_e = \frac{q_{sH} C_e^{nH}}{K_D + C_e^{nH}}$	[19]
	Kahn	$Q_e = \frac{Q_{max} b_k C_e}{(1 + b_k C_e) a_k}$	[19]
Four	Fritz-Schlunder	$q_e = \frac{q_{mFS} K_{FS} C_e}{1 + q_{mFS} C_e^{K_{FS}}}$	[20]
	Baudu	$q_e = \frac{q_m b_0 C_e^{1+x+y}}{1 + b_0 C_e^{1+x+y}}$	[21]
	Marczewski-Jaroniec	$q_e = q_{MMJ} \left(\frac{(K_{MJ} C_e)^{n_{MJ}}}{1 + (K_{MJ} C_e)^{n_{MJ}}} \right)^{M_{MJ}/n_{MJ}}$	[19]

80 2.3 Error functions analysis

81 In general, **plus values** of errors function are low it means more there is an agreement between the
 82 experimental and calculate data and more the model converges and becomes favourable, their
 83 functions are listed in table 2 below

84
 85

86 **Table 2:** Error functions and their equations

Error function	Abbreviation	formula	Reference
Residual Root Mean Square Error	RMSE	$\sqrt{\frac{1}{n-2} \sum_{i=1}^n (q_{e,exp} - q_{e,calc})^2}$	[22]
Hybrid fractional error function	HYBRID	$\frac{100}{n-p} \sum_{i=1}^n \frac{(q_{e,i,means} - q_{e,i,calc})^2}{q_{e,i,means}}$	[21]
Average relative error	ARE	$\frac{100}{n-p} \sum_{i=1}^n \frac{(q_{e,i,calc} - q_{e,i,means})}{q_{e,i,means}}$	[23]
Nonlinear Chi-Square Test	χ^2	$\sum_{i=1}^n \frac{(q_{ecal} - q_{emeas})^2}{q_{emeas}}$	[24]
Sum of Absolute Errors	EABS	$\sum_{i=1}^p (q_{e,i,means} - q_{e,i,calc})$	[19]
coefficient of determination	R^2	$\frac{\sum_{i=1}^n (q_{ecal} - q_{mexp})^2}{\sum_{i=1}^n (q_{ecal} - q_{mexp})^2 + (q_{ecal} - q_{meas})^2}$	[19]

87

88 3 Results and discussion

89 3.1 Characterization of Activated Carbons

90

- Burn off and yield

91 The progress of the activation may be followed by the yield, the extent of "burn-off. The extent of
 92 burn-off of the carbon material is taken as a measure of the degree of activation. The burn-off of
 93 materials increases linearly with the total porous volume which is directly related to the yield due to
 94 the reactions of activation of various biomasses used. Table 3 below contains the burn-off and the
 95 yield for various carbons.

96 **Table 3:** Burn-off and yield of the chemical activation of the activated carbon by phosphoric acid and
 97 potassium hydroxide
 98

Activating agent	Impregnation ratio	Concentration activating agent (M)	Y(%)	B(%)
KOH	1:1	0.5	37.43	62.57
		1.0	36.41	63.59
		1.5	36.30	63.70
	2:1	0.5	36.14	63.86
		1.0	35.90	64.10
		1.5	34.41	65.59
H ₃ PO ₄	1:1	0.5	43.56	56.44
		1.0	43.76	56.24
		1.5	42.68	57.37
	2:1	0.5	44.54	55.46
		1.0	42.67	57.33
		1.5	42.31	57.69

It is deduced from this table that the yield obtained by the process of activation from carbons obtained of the cotton cake varies between 34-45% which indicates that activation results from a reaction from KOH and H_3PO_4 with the precursor which limits the burn-off of volatile matter. In this concern, table 3 below shows that the burn-off increases with decreasing the yield, depending on the raw material. The values of burn-off ranges from 57 to 66 % which indicates that these carbons have a structure of micro and mesopores [25].

- **Iodine number**

In order to gain further knowledge of the porous structure of activated carbon, iodine adsorption from liquid phase was adopted by other researchers in the characterization of activated carbons. The adsorption of aqueous iodine is considered a simple and quick test for evaluating the surface area of activated carbons associated with pores larger than 1 nm [26]. Iodine number is an indication of the adsorption capacity in microspores; therefore it is often employed to examine the adsorption capacity of the activated carbons by researchers. Table 4 exhibits the iodine number of different activation carbons.

Table 4: Iodine number of activation carbons

activating agent	Impregnation ratios	Concentration activating agent (M)	Iodine number
KOH	1:1	0.5	494.91
		1.0	504.43
		1.5	523.46
	2:1	0.5	513.95
		1.0	523.46
		1.5	542.5
H_3PO_4	1:1	0.5	237.93
		1.0	295.05
		1.5	228.42
	2:1	0.5	352.15
		1.0	361.66
		1.5	276.01

The results obtained by successive variation of the concentration of activating agents and the impregnation ratio on the production of activated carbons show that: in the case of KOH, the iodine number increases with an increase in concentration. For H_3PO_4 , a maximum is reached which is of the order of 1M. These results confirm that chemical activation involves not only the creation of new pores, but also the widening of the pores available. Moreover, the type of activating agent used in the preparation of the activated carbon has an influence on the effectiveness of these carbons.

Table 4 shows that the activated carbon by KOH gave high Iodine number value ranging between 442 and 543 mg/g. These high values of the iodine number are due to the presence of a high microporosity what could be explained by reactivity of the KOH. This microporosity is very low for the activated carbons prepared from H_3PO_4 with iodine numbers ranging between 228 and 320 mg/g. During the process of activation and carbonization, oxygen of the KOH could stabilize the carbon atoms crystallites. The potassium metal, obtained at the reaction temperature, can intercalate and

force separately the separate lamellae of crystallite. The removal of potassium salts of the internal volume of carbon by washing creates microporosity in the activated carbon [27].

Generally, the higher the iodine number, the greater the sorption capacity. ASTM D 4607 describes the procedure of determining the iodine number. The iodine number recommended as a minimum by the American Water Works Association for a carbon to be used in removing low molecular weight compounds is 500. Thus, KOH is the best agent activating in our study and the best will be used for the continuation of our work, following the example dressed activated carbon from:

- ✓ Cotton cakes to the Impregnation ratios 1:1 with the concentration 1.5 M (CCK1)
- ✓ Cotton cakes to the Impregnation ratios 2:1 with the concentration 1 M (CCK2)
- ✓ Cotton cakes to the Impregnation ratios 2:1 with the concentration 1.5 M (CCK3)

• The proximate analysis

The proximate analysis was performed according to the ASTM methods. The proximate analysis for the determination of the pH, pH_{PZC} , Bulk density, matter soluble in water, volatile matter, ash content, moisture content and fixed carbon content was examined and shown in table 5 below.

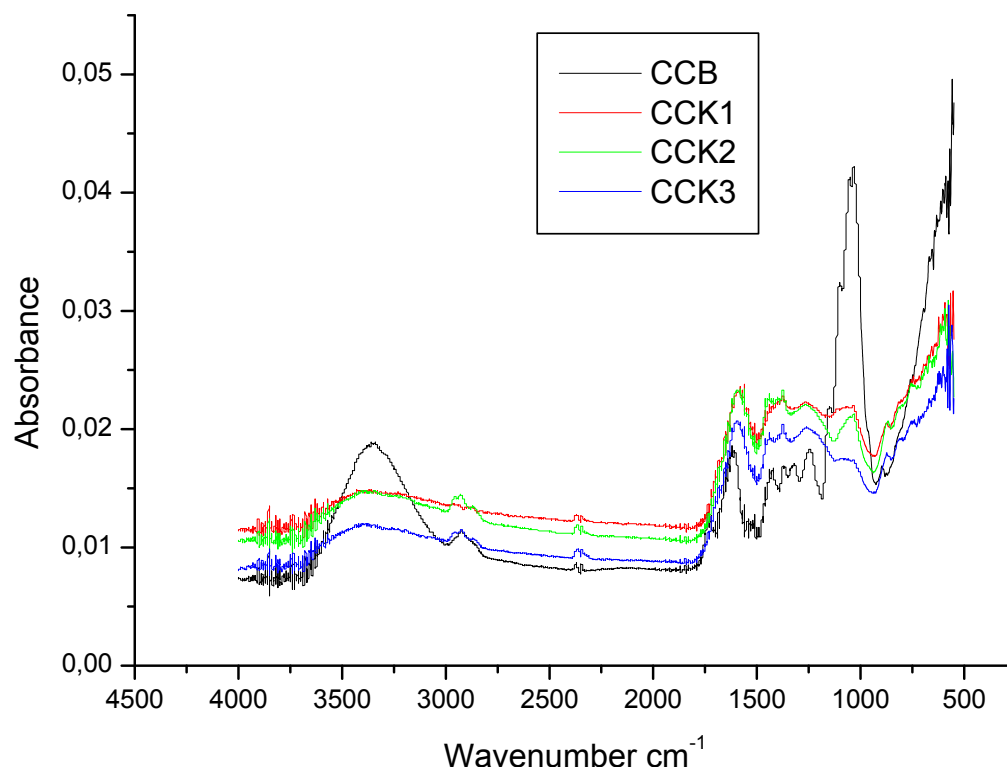
Table 5: The proximate analysis composition of CCK1, CCK2 and CCK3

Charbons actifs	CCK1	CCK2	CCK3
pH_{PZC}	6.55	6.58	6.47
pH	6.80	6.78	6.95
Bulk density (kg/m^3)	464.80	592.80	522.00
moisture content (%)	4.00	1.94	5.00
ash content (%)	16.20	11.00	8.20
volatile matter (%)	24.40	29.80	28.40
fixed carbon content (%)	55.40	57.26	58.40
matter soluble in water	0.35	0.30	0.28

The values of pH and pH_{PZC} that all the seven adsorbents less than 7, this result shows that these adsorbents have more acid groups on their surfaces. This result is according to Ahmedna *et al.*, (2000) [28] and Okieimen *et al.*, (2007) [29]. The bulk density of the prepared carbon is in the range between 464 and 618 (table 3). The American Water Works Association (AWWA) has set a lower limit on the bulk density at 250 kg/m^3 for activated carbons to be of practical use [30]. The moisture content of the carbons should be less than 5 %. All the activated carbons studied had the moisture content less than 5 %. These results are in agreement with the set standards by American Water Works Association (AWWA). The low value of Matter soluble in water was less than 0.5% indicating that all carbons studied is almost insoluble in water and hence can be used for water analysis. This table shows us respectively that the ash content, volatile matter and fixed carbon content for these carbons between 8 and 17%; 25 and 32; 55 and 59. One has low values of ash content and high value of fixed carbons. The ash content decreases while the volatile matter rates increase for these carbons. These results show which these materials are employed as a good precursor to produce activated carbon [31]. From the data it was clear that all the carbons have a good percentage of fixed carbon.

159 • **Fourier Transform Infra-red spectroscopy (FTIR)**

160 The FTIR Analysis result depicts the absorbance spectra of the cotton cake and activated carbons
 161 powder show that from figures 1 ~~below~~.



162 **Figure 1:** Fourier transform infrared spectra of cotton cake and cotton cake based activated carbon
 163
 164 The FTIR Analysis result depicts the absorbance spectra of the cotton cakes powder. From figure 1,
 165 CCB spectra's vibrations implies the presence of either a free O-H or alcohol at the broad band with
 166 wave numbers between 3200 cm^{-1} to 3400 cm^{-1} . A vibration band at 3317 cm^{-1} was attributed to the
 167 presence of acetylenic stretching. The region between 2920 and 2550 cm^{-1} is assigned to C-H
 168 stretching vibrations. Also, 1605 cm^{-1} adsorption bands were attributed to quinonic, a
 169 monosubstituted alkene and carboxylate structures mean while the adsorption band of 1728 cm^{-1} was
 170 attributed to a carboxylic tautomeric structure (C=O). The bands located at 1100 and 1120 cm^{-1} are
 171 related to C-O stretching vibrations in alcohols and phenols [32]. Halogeno-alkanes could also be
 172 allocated at vibrations between 500 cm^{-1} and 800 cm^{-1} .
 173 This behavior suggests that the activated carbon is mainly an aromatic polymer of activated carbon.
 174 The most important bands and peaks appearing on the spectrum of CCK1 are the same presented on
 175 CCK2 and CCK3 but with low intensities of peaks O-H and C-H and that can be explained by the
 176 carbonization which is at the origin of the atoms of C, O, H, in the form of CO_2 , H_2O , aldehyde [33].
 177 This comparison shows us an increase in the intensity of the peaks C-H and C=C of spectrum CCK1,
 178 CCK2 and CCK3 because of the elimination of the volatile mater by the carbonization process.

• SEM analysis

The surface morphology of the activated carbons was studied by SEM techniques. The surface structures of the activated carbons have burnt out pores with tunnel or honeycomb-like structures as shown in figure 3 below:

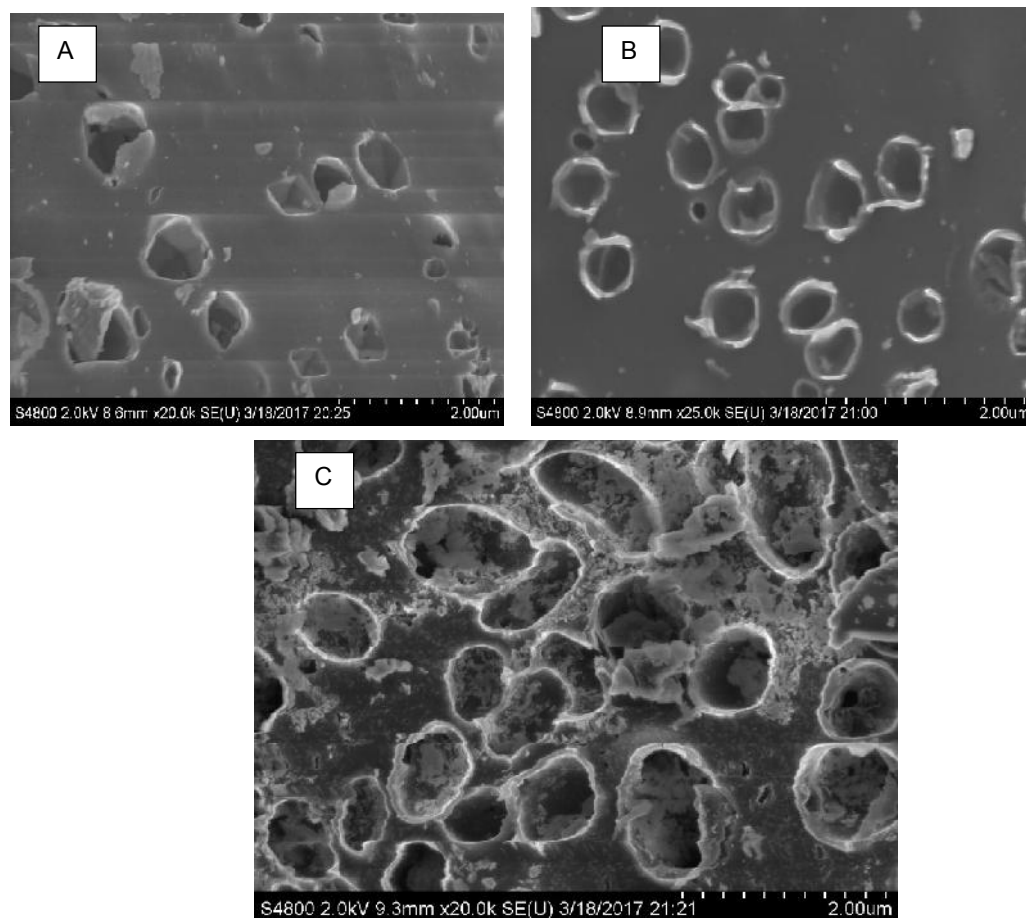


Figure 3: SEM micrographs of activated carbon of samples: A) CCK1; B) CCK2 and C) CCK3

Figure 3 show that the adsorbent have rough texture with heterogeneous surface and a variety of randomly distributed pore size. The surface of the activated carbons changed with, impregnation ratios and concentration of activating agents. The SEM photographs for samples are characterized by a smooth surface with many orderly pores developed. This is as a result of lack of impurities such as tar that could clog up the pores and inhibit good pore structure development [34]. The development of large macropores on the particle surface can be appreciated when going from the carbonized raw material to the activated carbons CCK1, CCK2 and sample CCK3. However, the pores are not-uniform. During carbonization process, pores are developed in the carbon and promote the diffusion of KOH molecules into these pores and thereby increase the KOH-carbon reactions which would then create more pores in the activated carbon [27]. The external surface of the activated carbon is full of cavities with well-developed porous structure. The external surface shows a rough area having

different pore diameters distributed over the surface of activated carbon. It seems that formation of cavity resulted from the removal of major components of raw materials and potassium hydroxide.

- **The Boehm's titration results**

Table 6 lists the amount of surface functional groups of activated carbon impregnated with KOH. A large amount of acidic groups were detected on the adsorbents CCK1 and CCK2 such as carboxyl, phenolic, lactonic, and on the adsorbents CCK3 such as carboxyl carboxyl which was consistent with the results of FTIR, pH and pH_{pzc} . The amount of acid groups was higher than the alkaline groups. The acid groups are beneficial for the ion exchange and electrostatic adsorption [12].

Table 6: Total acid and basic groups on surface of activated carbon

Samples	CCK1	CCK2	CCK3
Carboxylic groups (meq/g)	0.45	0.35	0.75
Lactonic groups (meq/g)	0.20	0.15	0.00
Phenolic groups (meq/g)	0.00	0.35	0.00
Total Acid group (meq g ⁻¹)	0.65	0.85	0.75
Total basic group (meq g ⁻¹)	0.45	0.45	0.55

3.2 Adsorption Isotherm Modelling onto CCK1, CCK2 and CCK3

In Non-linear regression method, the abilities of the widely used isotherms to model the equilibrium data were examined by a trial-and-error procedure using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. The R^2 value is used to minimize the error distribution between the experimental equilibrium data and the predicted isotherms. To avoid such errors, we use the non-linear analysis as an adequate method. It is an interesting way for describing adsorption isotherms used for many applications such as wastewater treatment from industry. Figure 4 to 12 below shows the fitting values of non-linear regression analysis, in addition to the error calculations, are mentioned in Table 7 to 9 below.

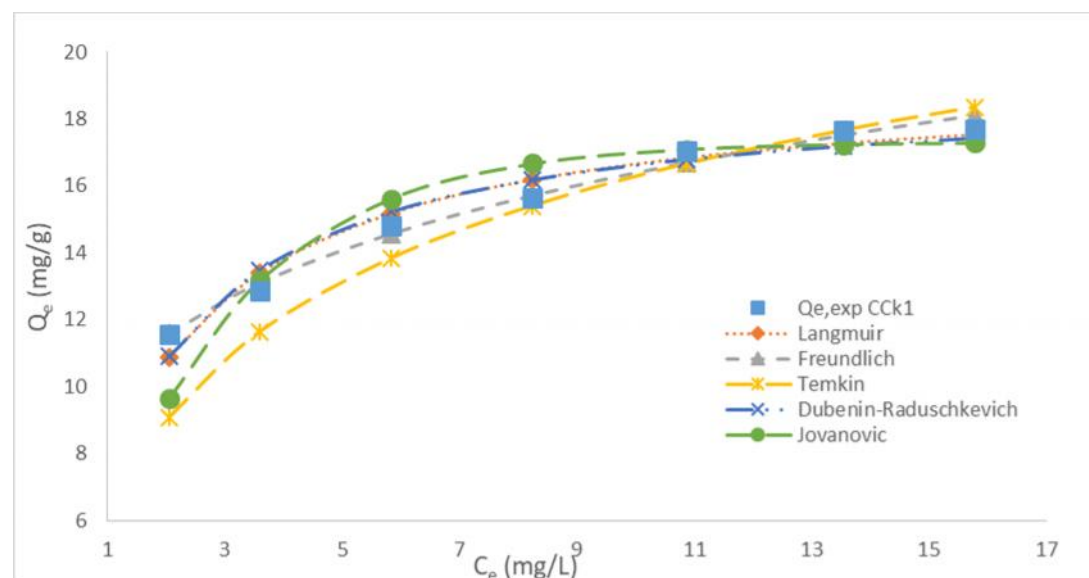


Figure 4: Comparaison of measured and calculated q_e values for two-parameter isotherms onto activated carbon CCK1

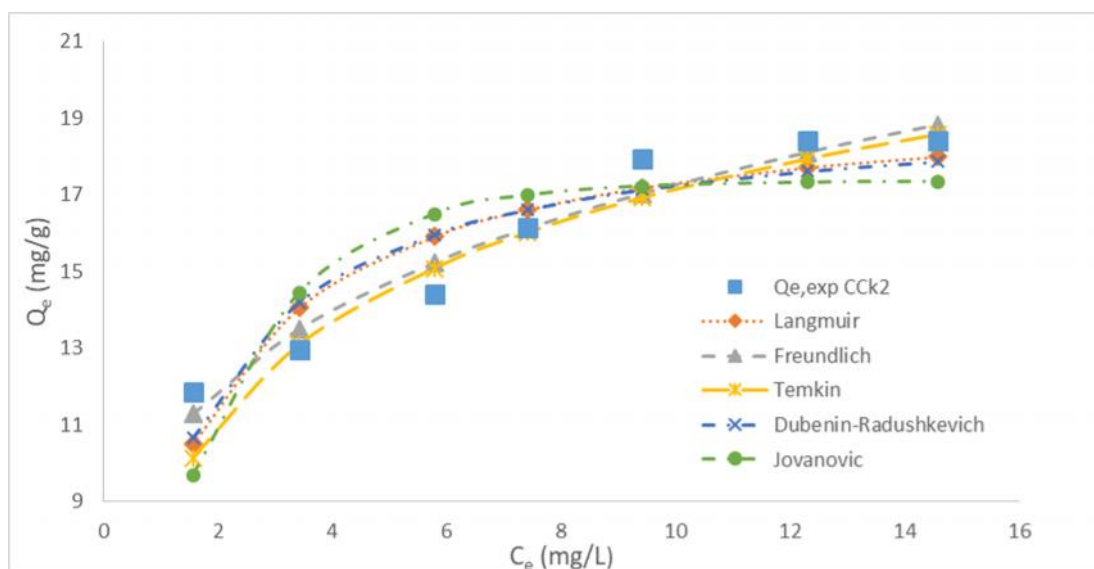


Figure 5: Comparison of measured and calculated q_e values for two-parameter isotherms onto activated carbon CCK2

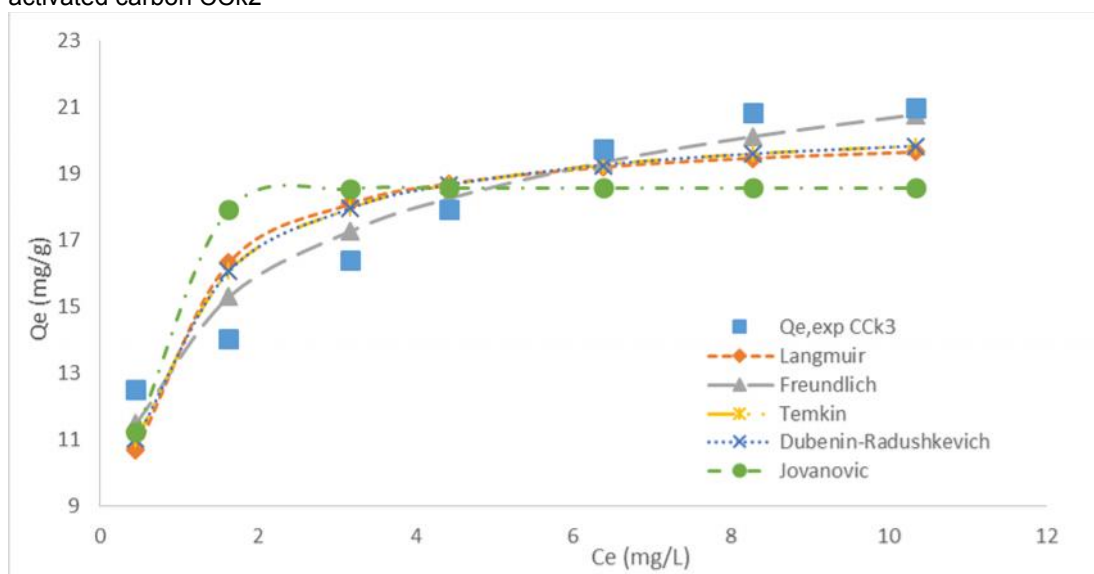


Figure 6: Comparison of measured and calculated q_e values for two-parameter isotherms onto activated carbon CCK3

228 **Table 7:** optimum isotherm parameters and their statistical comparison values for two-parameter
229 models

N°	Models	constants	values	R ²	RMSE	χ ²	HYBRID	ARE	EABS
CCK1									
1.	Langmuir	$Q_{\max}(\text{mg.g}^{-1})$	19.273	0.959	1.192	0.105	2.086	2.947	2.933
		$K_L(\text{L.mg}^{-1})$	0.633						
2.	Freundlich	$K_F(\text{L.mg}^{-1})$	9.906	0.987	0.663	0.027	0.540	1.332	1.479
		N	4.575						
3.	Temkin	$a(\text{L.mg}^{-1})$	3.609	0.994	3.044	0.915	15.036	5.015	5.972
		$b(\text{J.mol}^{-1})$	546.02						
4.	Dubinin-Radushkevich	$Q_{\max}(\text{mg.g}^{-1})$	19.005	0.951	1.294	0.121	2.421	3.241	3.254
		$K(\text{L.mg}^{-1})$	0.0002						
5.	Jovanovic	$Q_{\max}(\text{mg.g}^{-1})$	17.318	0.881	2.420	0.516	9.180	5.140	4.934
		$K_J(\text{L.mg}^{-1})$	-0.397						
CCK2									
1.	Langmuir	$Q_{\max}(\text{mg.g}^{-1})$	19.691	0.841	2.590	0.484	9.664	6.201	6.280
		$K_L(\text{L.mg}^{-1})$	0.727						
2.	Freundlich	$K_F(\text{L.mg}^{-1})$	10.182	0.944	1.527	0.155	3.085	3.362	3.538
		N	4.360						
3.	Temkin	$a(\text{L.mg}^{-1})$	9.281	0.912	2.163	0.396	7.026	4.266	4.264
		$b(\text{J.mol}^{-1})$	654.58						
4.	Dubinin-Radushkevich	$Q_{\max}(\text{mg.g}^{-1})$	19.366	0.817	2.672	0.495	10.094	6.433	6.589
		$K(\text{L.mg}^{-1})$	0.0002						
5.	Jovanovic	$Q_{\max}(\text{mg.g}^{-1})$	17.356	0.691	3.841	1.104	21.282	9.289	9.434
		$K_J(\text{L.mg}^{-1})$	-0.521						
CCK3									
6.	Langmuir	$Q_{\max}(\text{mg.g}^{-1})$	20.424	0.738	3.989	1.023	20.690	8.731	9.802
		$K_L(\text{L.mg}^{-1})$	2.443						
7.	Freundlich	$K_F(\text{L.mg}^{-1})$	13.610	0.965	1.504	0.153	3.058	3.200	3.506
		N	5.291						
8.	Temkin	$a(\text{L.mg}^{-1})$	108.57	0.932	2.059	0.283	5.709	4.409	4.824
		$b(\text{J.mol}^{-1})$	838.56						
9.	DR	$Q_{\max}(\text{mg.g}^{-1})$	20.829	0.780	3.517	0.780	15.925	7.695	8.686
		$K(\text{L.mg}^{-1})$	0.0001						
10.	Jovanovic	$Q_{\max}(\text{mg.g}^{-1})$	18.579	0.248	5.827	1.916	42.040	11.841	13.782
		$K_J(\text{L.mg}^{-1})$	-2.063						

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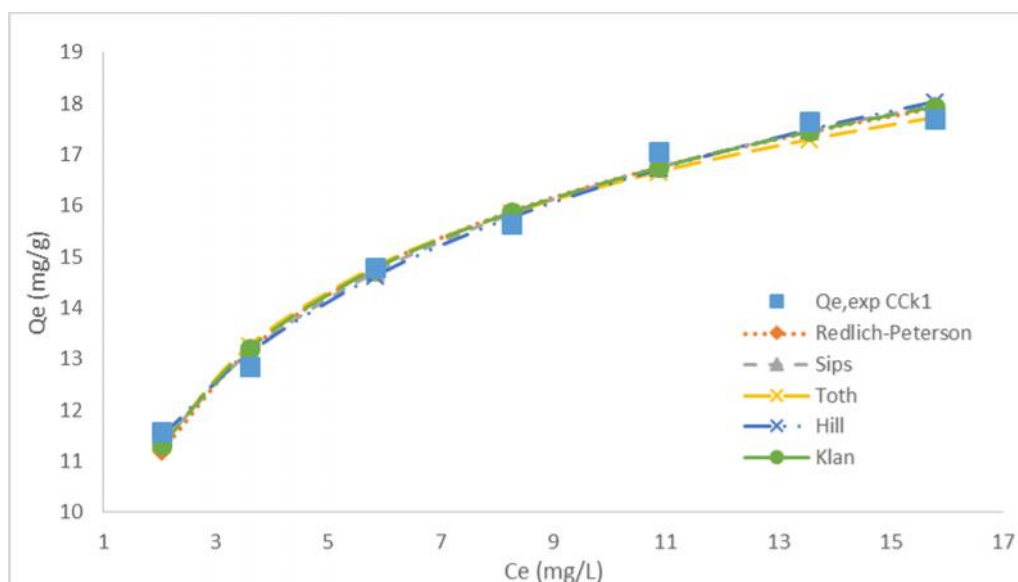


Figure 7: Comparison of measured and calculated q_e values for three-parameter isotherms onto activated carbon CCK1

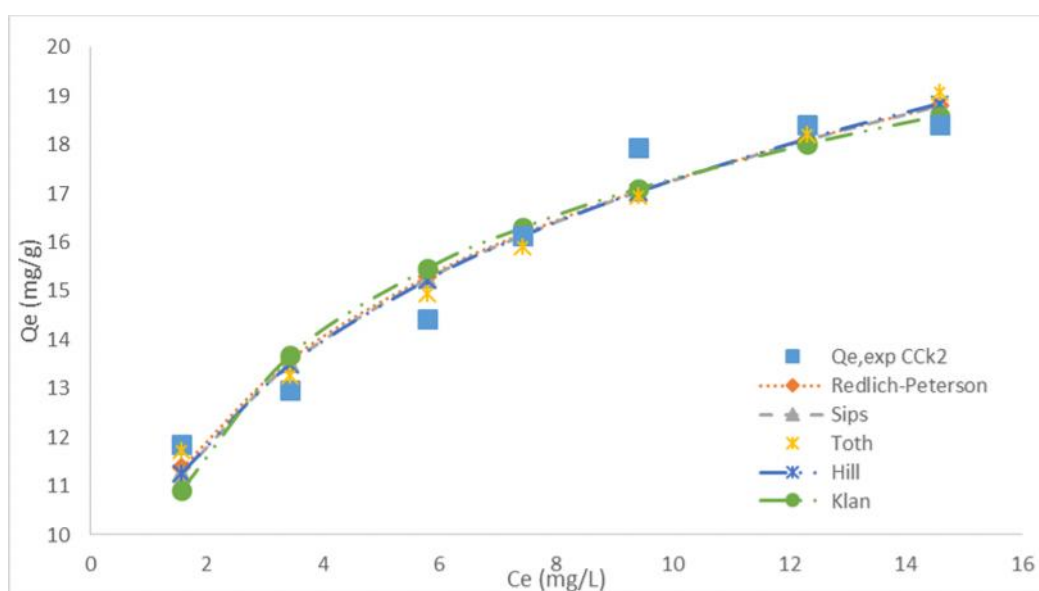


Figure 8: Comparison of measured and calculated q_e values for three-parameter isotherms onto activated carbon CCK2

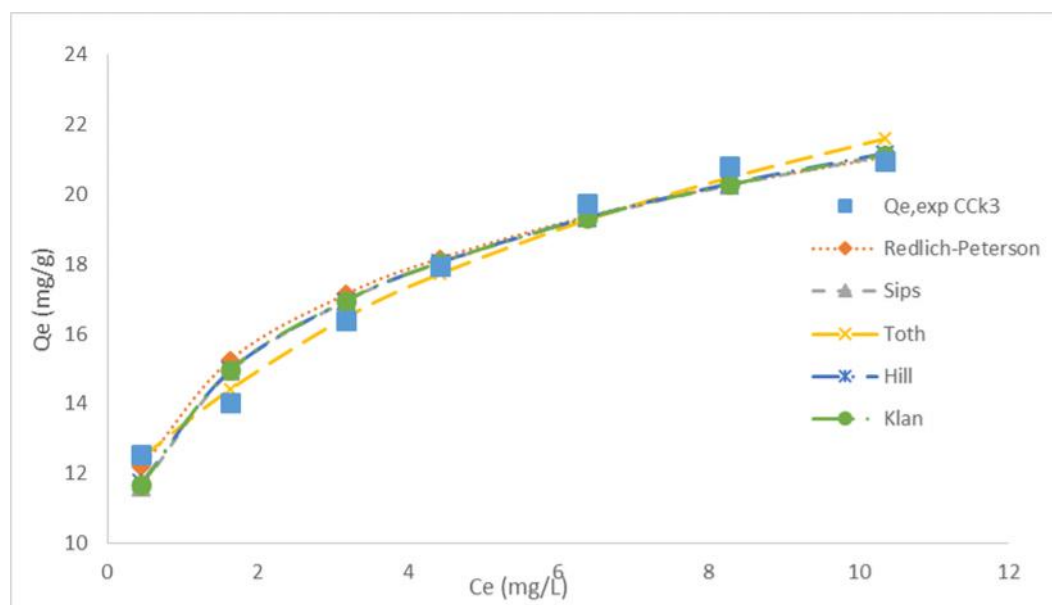


Figure 9: Comparaison of measured and calculated q_e values for three-parameter isotherms onto activated carbon CCK3

Khan	Q_m (mg/g)	5.371						
	b_k (L.g ⁻¹)	156.65	0.963	1.547	0.162	4.047	3.281	3.586
	a_k	0.815						

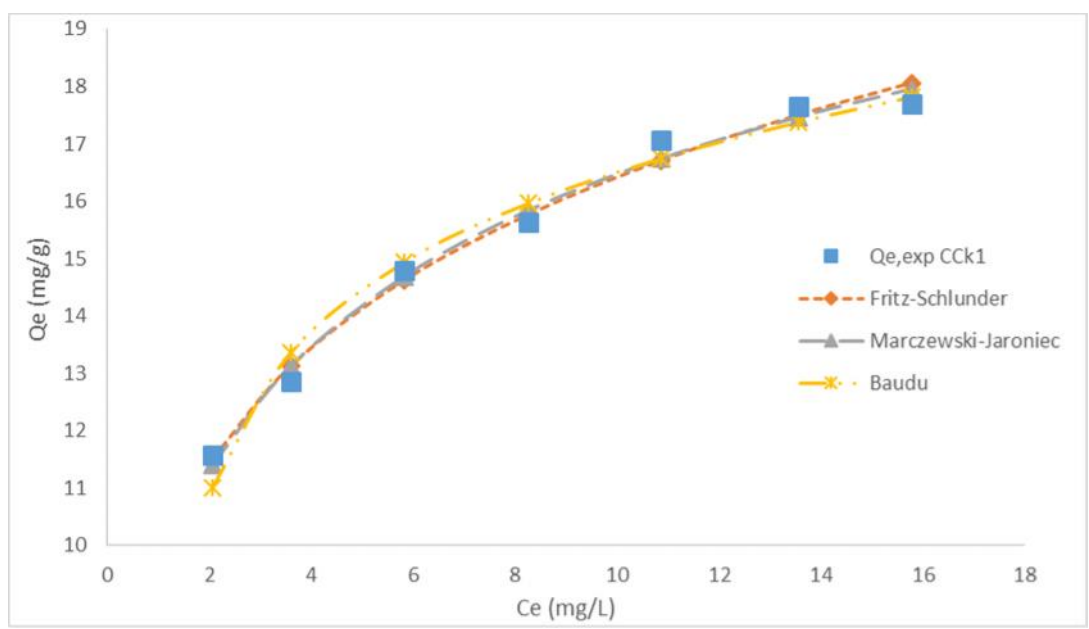


Figure 10: Comparaison of measured and calculated q_e values for four-parameter isotherms onto activated carbon CCK1

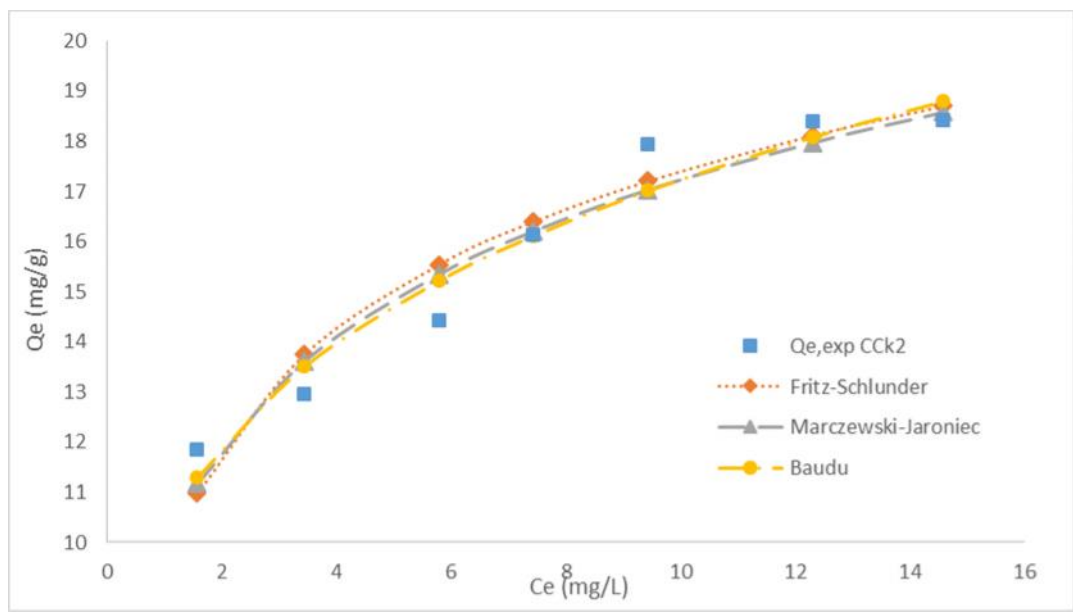


Figure 11: Comparaison of measured and calculated q_e values for four-parameter isotherms onto activated carbon CCK2

	y	0.228						
			CCK3					
Fritz-Schlunder	$q_{mFS} (mg.g^{-1})$	115.82	0.962	1.566	0.167	5.542	3.321	3.624
	$K_{FS} (mg.g^{-1})$	11.096						
	$q_m (mg.g^{-1})$	93.188						
	M_{FS}	0.817						
Marczewski-Jaroniec	$q_{MMJ} (mg.g^{-1})$	138.91	0.958	1.654	0.186	6.200	3.487	3.781
	K_{MJ}	0.130						
	n_{MJ}	0.125						
	M_{MJ}	0.351						
Baudu	$q_m (mg.g^{-1})$	16.413	0.965	1.504	0.153	5.097	3.200	3.506
	b_0	4.854						
	x	-1.000						
	y	0.189						

262

263 In this study, equilibrium data were fitted by five "two-parameter isotherms" (Langmuir, Freundlich,
 264 Temkin, Dubinin-Radushkevich, and Jovanovic) models, five "three-parameter isotherms"(Redlich-
 265 Peterson, Sips, Khan, Hill and Toth) and three four-parameter isotherms"(Fritz-Schlunder, Baudu and
 266 Marczewski-Jaroniec).

267 Two-parameter models

268 Table 7 shows the low isotherm parameters obtained using the Non-linear method. Higher values of
 269 R^2 obtained in this study are derived by fitting experimental data into the Temkin isotherm model for
 270 both CCK1 sample and Freundlich for both CCK2 and CCK3 samples. In addition, lower values of
 271 Chi-square (χ^2), ARE, EABS and Root mean square error (RMSE) for each parameter obtained in
 272 both isotherm models with higher R^2 can generate a satisfactory fit to the experimental data. As
 273 shown in Table 7, maximum adsorption capacity values obtained using non-linear Langmuir model,
 274 were 19.273, 19.691 and 20.424 mg/g for CCK1, CCK2, and CCK3 respectively. The values of n of
 275 the model of Freundlich are high than 1 suggesting that the process that occur on heterogonous
 276 surfaces [15]. Based on the energies, the variation of energy of adsorption b (kJ/mol) resulting from
 277 the non-linearization of the Temkin model is positive. A positive value of b means that the process of
 278 adsorption is exothermic. From the Dubinin-Radushkevich model the adsorption energies are 42.25,
 279 45.64 and 67.42kJ/mol onto CCK1, CCK2 and CCK3 respectively, also high than 16 kJ/mol. These
 280 observations (values of energies) suggest that intra particular diffusion dominates the adsorption
 281 process. Jovanovic cannot describe the experimental equilibrium data, because it as a lower value of
 282 R^2 obtained in this study In this study, all the values of error function are very small, indicate the
 283 favorable adsorption of 2,4-Dinitrophenol on these differents adsorbents

284 Three-parameter models

285 Table 8 shows the three isotherm parameters obtained using the non-linear method. It was observed
 286 that the correlation coefficient value for all models isotherms study are very good (>0.94) and the low
 287 Chi-square (χ^2), ARE, EABS and Root mean square error (RMSE) values, thus it indicates that the

models are able to describe equilibrium data perfectly. In the case of Slips model shows high correlation coefficients value (0.99) for sample CCK1 and Toth model shows high correlation coefficients value (0.954, 0.986) respectively for CCK2 and CCK3 samples. Finally, they were chosen as the best fitted nonlinear model for data. These models are suitable for predicting adsorption on heterogeneous surfaces [19]. The adsorption maximum capacities determined for all samples using the Slips model are higher than those of Toth.

Four-parameter models

Table 9 shows the four isotherm parameters obtained using the Non-linear method. It was observed that the correlation coefficient value is to all models isotherms study are very good (>0.93) and the low Chi-square (χ^2), ARE, EABS and Root mean square error (RMSE) values, thus it indicates that the models are able describe equilibrium data perfectly.

Higher values of R^2 obtained in this study are derived by fitting experimental data into the Marcewski-Jaroniec (0.99), Baudu (0.944) and Fritz-Schunder (0.965) isotherms model respectively for both CCK1 CCK2 and CCK3 samples. Finally, they were chosen as the best fitted nonlinear model for data. These models are able to describe experimental data perfectly. Consequently, they were the most suitable models for this sorption system. The values of the maximum adsorption capacity obtained using all the three four parameters isotherm are not according than those theoretical values calculated by the Langmuir.

Conclusion

A detailed analysis of the fits of several isotherm models to experimental adsorption equilibrium of 2,4-Diniphenol onto activated carbons prepared from cotton cakes was carried out. The activated carbons have burn-off higher to 55% showing a structure of micro and mesopores. The higher Iodine number of the activated carbon has been attributed to the presence of large micropore structure which might have resulted due to the reactivity of the activating agent KOH. The functional groups of the three carbons were determined using FTIR spectroscopy which was confirmed by using Boehm's titration. The best textural characteristics were obtained for the activation of carbonized cotton cakes a KOH/carbon weight ratio of 2/1 and with activating agent 1 .5M. Five two-parameter sorption isotherm models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, and Jovanovic), five three-parameter models (Redlich-Peterson, Sips, Khan, Hill and Toth) and three four-parameter models (Fritz-Schlunder, Baudu and Marczewski-Jaroniec) were investigated from this analysis. The following conclusions are made based on the results obtained. Among CCK1, the Freundlich model (two parameter) better described the experimental data. The Toth model (three-parameter) was found to provide the best fit to the equilibrium experimental data for CCK2 and CCK3. Because there having a high R^2 and the low Chi-square (χ^2), ARE, EABS and Root mean square error (RMSE) values. It was clear that both two-parameter Freundlich and three-parameter Toth isotherms were the best-fitting models for the experiment results. This results explain the favorable adsorption of 2,4-dinitrophenol in these different adsorbents

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