

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 with 2:1; 1:1 impregnation ratio at various concentrations of 0.5M; 1M; 1.5M using the batch adsorption mode to 2,4-dinitrophenol. 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 agent in our study and the best ratio will be used for the continuation of our work. The activated carbon will be characterized by Fourier transform-infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and proximate analysis (pH_{ZCN}, pH, Bulk density, moisture content, ash content, volatile matter, fixed carbon content and matter soluble in water). The experimental isotherms were analyzed using two, three and four parameter sorption isotherm models. Three errors 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. According to chi-square test (χ^2), it appears that the Freundlich (two parameters), Hill (three parameters) and Marczewski-Jaroniec (four parameters) models describe better the adsorption data.

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

1. INTRODUCTION

At present, the problems of pollution become alarming and extending more and more following the spectacular increase in industrial activities. Concerns intensify day by day, especially in terms of contamination of drinking water resources. In the two last decades, several research tasks were devoted to the description of the principal pollutants likely to increase the vulnerability of these resources. A report has shown that phenol and its derivatives present the most dangerous pollutants. 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 Sugarcane 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

31 advantage of using agricultural by-products as raw materials for manufacturing activated carbon is
32 that these raw materials are renewable and potentially less expensive to produce.

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

39 In this study, we shall to examine nonlinear isotherms regressions method in more details and use
40 these models to describe the adsorption 2,4-dinitrophenol by activated carbon obtained from cotton
41 cakes.

42 2. Material and methods

43 2.1 Material

44 Processed cotton cake was collected from Zang, Department of Mayo-Tsanaga, far Nord region
45 Cameroon [6]. They were cut into small pieces of about 0.5 to 1 cm in size, dried in sunlight until all
46 the moisture was evaporated.

47 2.1.1 Preparation of Activated Carbon

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

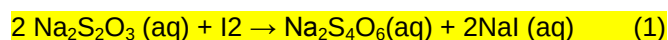
61 2.1.2 Characterization of Activated Carbons

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

65 • Iodine number

66 To gain further knowledge of the porous structure of activated carbon, the adsorption of iodine
67 from liquid phase was adopted by other researchers in the characterization of sludge-based activated
68 carbons [15, 16]. The adsorption of aqueous I_2 is considered a simple and quick test for evaluating
69 the microporosity of activated carbons associated with pore diameter less than 2 nm. The iodine
70 number, defined as the amount of iodine adsorbed per gram of activated carbon at an equilibrium

concentration of 0.02 N, was measured according to the procedure established by the American Society for Testing and Materials [16]. Activated carbon of mass 0.1 g, was mixed with 30mL of 0.02N iodine solutions and stirred for 3 h. After filtration, 10 mL of the filtrate was titrated with 0.005N sodium thiosulphate solution using starch as indicator. The titration equation (1) is giving below



• Water soluble matter

1 g of carbon sample was added to 100 mL of distilled water and stirred for about 30 minutes and then filtered. The residue was dried, cooled and weighed. Mass loss was calculated using Equation 2 [10].

$$\text{Water soluble matter (\%)} = \frac{\text{Mass of crucible with sample (g)} - \text{Mass of crucible after weight loss (g)}}{\text{Mass of crucible with sample (g)} - \text{Mass of crucible (g)}} \times 100 \quad (2)$$

• Moisture content

A previously weighed crucible was weighed with 1g of powder, air dried activated carbon. It was then placed on a hot plate maintained at 110°C it was taken out, cooled in a desiccator before being weighed again. The ratio of the mass lost per the powder to its original mass gave the moisture content of the sample [8,9] .

• Bulk Density

A 25 cm³ specific gravity bottle was weighed empty, and later when carefully filled to the mark with powder activated carbon. The difference in the masses gave the mass of the powder activated carbon [8,9]. The bulk density was calculated from the equation:

$$\text{bulk density} = \frac{\text{weight of powder}}{25} \quad (3)$$

• Ash content/volatile matter [10,16]

The standard test method for ash content-ASTM D2866-94 was used. A crucible was pre-heated in a muffle furnace to about 500°C, cooled in a desiccator and weighed. 1.0g of activated carbon samples were transferred into the crucibles and reweighed. The crucibles containing the samples were then placed in a cold muffle furnace and the temperature was allowed to rise to 500°C. It was removed and allowed to cool in a desiccator to room temperature (25°C) and reweighed again. The ash content was calculated using the equation.

$$\text{Ash (\%)} = \frac{\text{Ash weight (g)}}{\text{Oven dry weight}} \times 100 \quad (4)$$

Volatile matter was calculated using the equation;

$$\text{Volatile matter (\%)} = \frac{\text{weight of volatile component (g)}}{\text{Oven dry weight}} \times 100 \quad (5)$$

• Fix carbon [10]

The fixed carbon content is determined by subtracting the sum of percentage compositions of moisture content, the volatile matter content and the ash content from 100. The value obtained is the amount of fixed carbon present in the sample expressed as a percentage.

• Determination of pH_{zcp}

The pH of zero charge point of the activated carbons were carried out by adding 0.1 g of carbon to 30 mL solution of 0.1 M NaCl whose initial pH had been measured and adjusted with 0.1 M NaOH and 0.1M HCl varying between 2-10. The containers were sealed and placed on an agitator for 48 hours after which the pH was measured. The pH_{pzc} occurs if there is no change in the pH after contact with adsorbent [16].

• pH

The pH of the activated carbons was determined by putting 50 mL of distilled water and 0.5 g of each of the carbons in different washed bottles. The mixtures were agitated for 24 h at room temperature. After which, the mixtures were filtered and the pH of the filtrates was measured [8].

• Boehm titration [12]

The Boehm titration method was used for this analysis. 0.1 g of the activated carbon was added to a separate 50 mL solution of NaHCO₃ (0.1 M), Na₂CO₃ (0.1 M) and NaOH (0.1 M) for acidic groups and 0.1 M HCl for basic groups respectively at room temperature under agitation for 24 h. Subsequently, the aqueous solutions were back-titrated with HCl (0.1 M) and NaOH (0.1 M). The number and type of acidic sites were calculated by considering that NaOH neutralizes carboxylic, lactonic and phenolic groups, Na₂CO₃ neutralizes carboxylic and lactonic groups and that NaHCO₃ neutralizes only carboxylic groups. Carboxylic groups were therefore quantified by direct titration with NaHCO₃. The difference between the groups titrated with Na₂CO₃ and those titrated with NaHCO₃ was assumed to be lactones and the difference between the groups titrated with NaOH and those titrated with Na₂CO₃ was assumed to be phenol. Basic sites were determined by titration with HCl. In order to neutralize basic groups remaining HCl in the solution was back-titrated with 0.1 M NaOH.

2.1.3 Batch equilibrium experiments and analytical method

Stock solution of 2,4-dinitrophenol at the concentration of 500 mg/L was prepared by dissolving 0.250 g of sodium 2,4-dinitrophenol in 0.5 L of distilled water. Experimental solutions at desired concentrations were obtained by dilution of the stock solution with distilled water pre-adjusted to pH 2. The initial concentrations of the experimental solutions of 2,4-dinitrophenol were determined at 20, 25, 30, 35, 40, 45 and 50 mg/L. 30 mL of the experimental solutions were placed in bottles and then 0.05 g prepared activated carbon was added to each bottle. After agitation for about about 2 hours, the solution was filtered, and the filtrate analyzed to obtain the residual concentration 2,4-dinitrophenol by using the UV/Vis spectrophotometer at λ_{max} value of 320 nm.

2.2 Modelling Theoretical Background

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

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

Parameter	Isotherms	Non-linear forms	Reference
Two	Langmuir	$Q_e = \frac{Q_m K C_e}{1 + K C_e}$	[17]
	Freundlich	$Q_e = K_f C_e^{1/n}$	[17]
	Dubinin-Radushkevich	$Q_e = Q_m \exp(-K \epsilon^2)$; $\epsilon = RT \ln(1 + 1/C_e)$;	[18]
	Temkin	$Q_e = Q_m \frac{RT}{\Delta Q} \ln(A C_e)$	[19]
	Jovanovic	$q_e = q_m (1 - e^{-k_j C_e})$	[20]
Three	Redlich-Peterson	$q_e = \frac{A C_e}{1 + B C_e^\beta}$	[21]
	Sips	$q_e = \frac{K_s C_e^\beta}{1 + a_s C_e^\beta}$	[21]
	Toth	$\frac{q_e}{q_m} = \frac{K_L C_e}{[1 + (K_L C_e)^n]^{1/n}}$	[21]

	Hill	$q_e = \frac{q_{SH} C_e^{nH}}{K_D + C_e^{nH}}$	[21]
	Kahn	$Q_e = \frac{Q_{max} b_k C_e}{(1 + b_k C_e) a_k}$	[21]
	Fritz-Schlunder	$q_e = \frac{q_{mFS} K_{FS} C_e}{1 + q_{mFS} C_e^{MFS}}$	[22]
Four	Baudu	$q_e = \frac{q_m b o C_e^{1+x+y}}{1 + b o C_e^{1+x}}$	[23]
	Marczewski-Jaroniec	$q_e = q_{MMJ} \left(\frac{(K_{MJ} C_e)^{n_{MJ}}}{1 + (K_{MJ} C_e)^{n_{MJ}}} \right)^{M_{MJ}/n_{MJ}}$	[21]

2.3 Error functions analysis

In general, when values of error function are low, it means there is an agreement between the experimental and calculated data and the model converges and becomes favourable. Their error functions are listed in table 2 below.

Table 2: Error functions and their equations

Error function	Abbreviation	formula	Reference
Residual Root Mean Square Error	RMSE	$\sqrt{\left(\frac{1}{n-2} \sum_{i=1}^n (q_{e,exp} - q_{e,calc}) \right)^2}$	[24]
Hybrid fractional error function	HYBRID	$\frac{100}{n-p} \sum_{i=1}^n \frac{(q_{e,i,means} - q_{e,i,calc})^2}{q_{e,i,meas}}$	[23]
Average relative error	ARE	$\frac{100}{n-p} \sum_{i=1}^n \frac{(q_{e,i,calc} - q_{e,i,means})}{q_{e,i,meas}}$	[25]
Nonlinear Chi-Square Test	χ^2	$\sum_{i=1}^n \frac{(q_{ecal} - q_{emeas})^2}{q_{emeas}}$	[26]
Sum of Absolute Errors	EABS	$\sum_{i=1}^p (q_{e,i,means} - q_{e,i,calc})$	[21]
coefficient of determination	R^2	$\frac{\sum_{i=1}^n (q_{ecal} - q_{mexp})^2}{\sum_{i=1}^n (q_{ecal} - q_{mexp})^2 + (q_{ecal} - q_{meas})^2}$	[21]

3 Results and discussion

3.1 Characterization of Activated Carbons

• Burn off and yield

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

Table 3: Burn-off and yield of the chemical activation of the activated carbon using phosphoric acid and potassium hydroxide

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 in the process of activation of carbons obtained from cotton cake varies between 34-45% which indicates that activation resulting from a reaction of KOH and H₃PO₄ with the precursor, limits the burn-off of volatile matter. As such, Table 3 shows that the burn-off increases with decreasing 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 [27].

• 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 [28]. 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 ₃ PO 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 that could be explained by the reactivity of 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 through the separate lamelle of crystallite. The removal of potassium salts from the internal volume of carbon by washing creates microporosity in the activated carbon [29].

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 activating agent in our study and the best will be used for the continuation of our work. CCK1, CCK2 and CCK3 are obtained as follows:

- ✓ 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 mater, ash content, moisture content and fixed carbon content was examined and show in table 5 below.

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

Properties	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 mater (%)	24.40	29.80	28.40
fixe 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} of all the seven adsorbents are less than 7 and this shows that these absorbents have more acid groups on their surfaces. This results is according to Ahmedna *et al.*, (2000) [30] and Okieimen *et al.*, (2007) [31]. 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 of 250 kg/m^3 for activated carbons to be of practical use [32]. 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 the carbons studied are 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 decrease while the volatile matter rates increase for these carbons. These results show that this material can be used as a good precursor to produce activated carbon [33]. From the data it was clear that all the carbons have a good percentage of fixed carbon.

Figure 1 below show the curve that determines the pH of the zero point charge

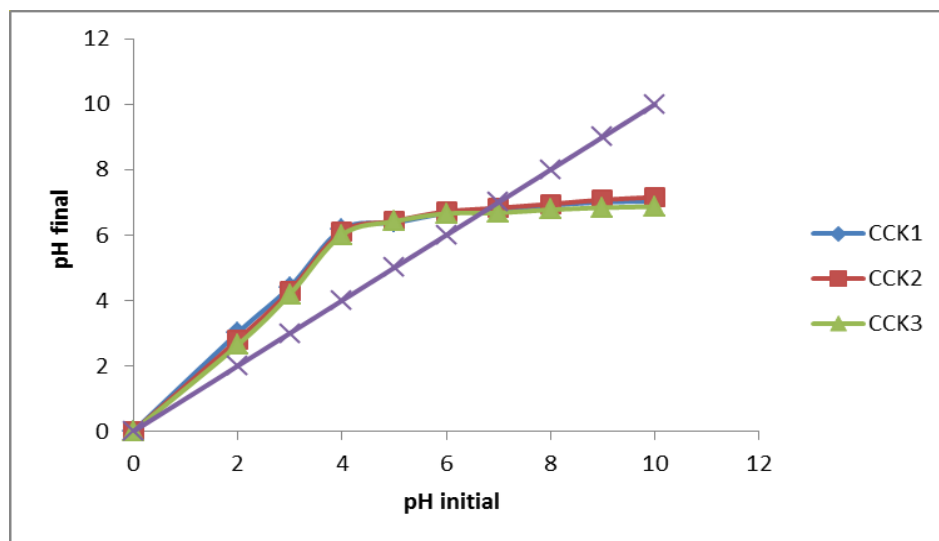


Figure 1: curve that determines the pH of the zero point charge

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

The FTIR Analysis result showing the absorbance spectra of the cotton cake and activated carbons powder is shown in figures 2 below.

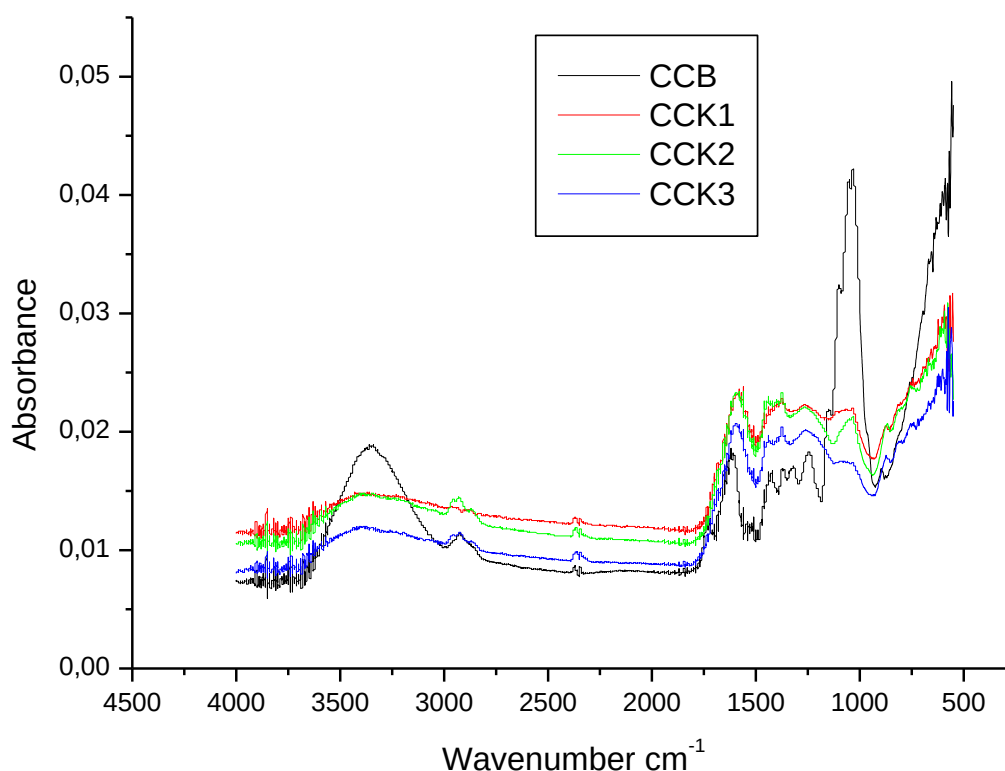


Figure 2: Fourier transform infrared spectra of cotton cake and cotton cake based activated carbon

The FTIR Analysis result depicts the absorbance spectra of the cotton cakes powder. From figure 1, CCB spectra's vibrations implies the presence of either a free O-H or alcohol at the broad band with wave numbers between 3200 cm^{-1} to 3400 cm^{-1} . A vibration band at 3317 cm^{-1} was attributed to the presence of acetylenic stretching. The region between 2920 and 2550 cm^{-1} is assigned to C-H stretching vibrations. Also, 1605 cm^{-1} adsorption bands were attributed to quinonic, a monosubstituted alkene and carboxylate structures mean while the adsorption band of 1728 cm^{-1} was attributed to a carboxylic tautomeric structure (C=O). The bands located at 1100 and 1120 cm^{-1} are related to C-O stretching vibrations in alcohols and phenols [34]. Halogeno-alkanes could also be allocated at vibrations between 500 cm^{-1} and 800 cm^{-1} .

This behavior suggests that the activated carbon is mainly an aromatic polymer of activated carbon. The most important bands and peaks appearing on the spectrum of CCK1 are the same presented on CCK2 and CCK3 but with low intensities of peaks O-H and C-H and that can be explained by the carbonization which is at the origin of the atoms of C, O, H, in the form of CO_2 , H_2O , aldehyde [35]. This comparison shows us an increase in the intensity of the peaks C-H and C=C of spectrum CCK1, 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:

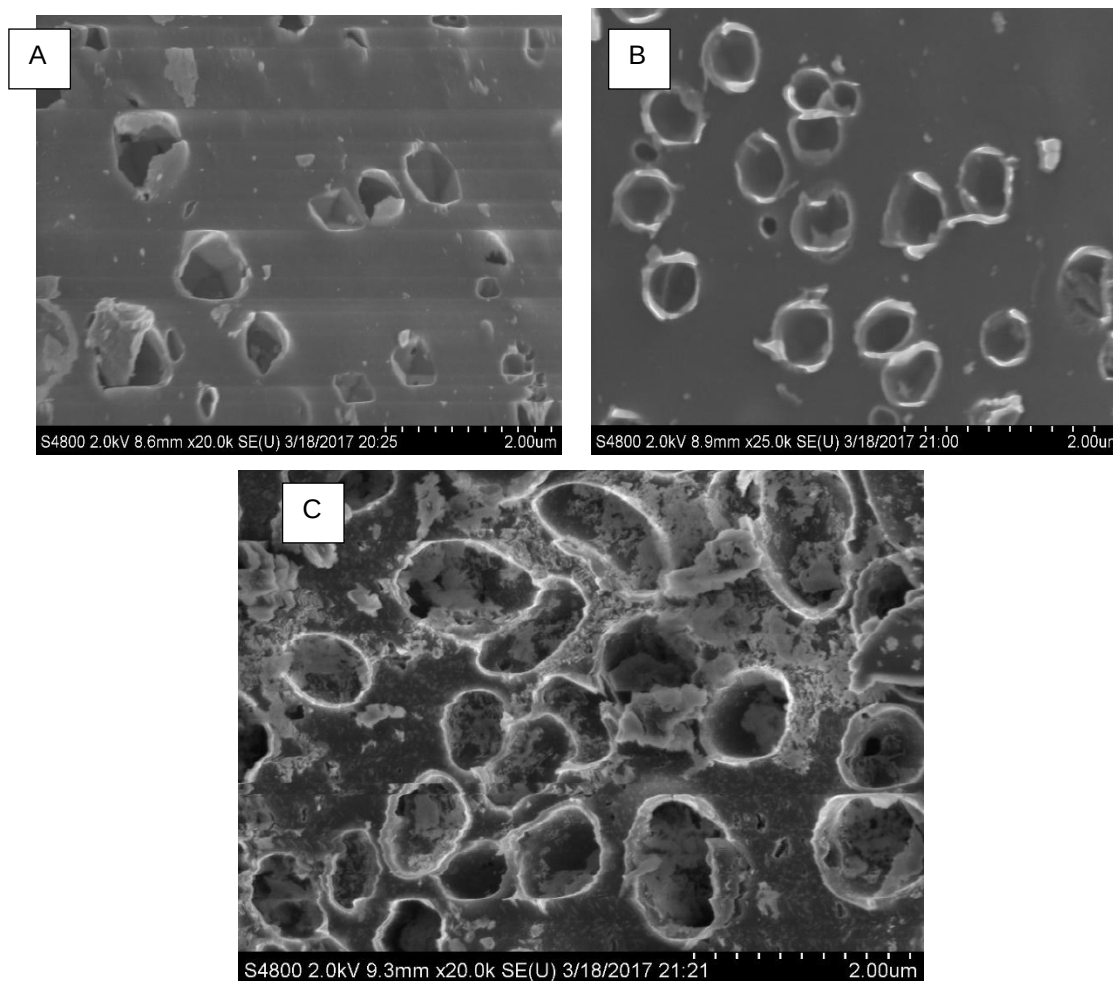


Figure 3: SEM micrographs of activated carbon of samples: A) CCK1; B) CCK2 and C) CCK3

Figure 3 show that the adsorbent have rough texture with homogeneous 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 [36]. 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 [29]. 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 absorbents 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

Functional groups	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.

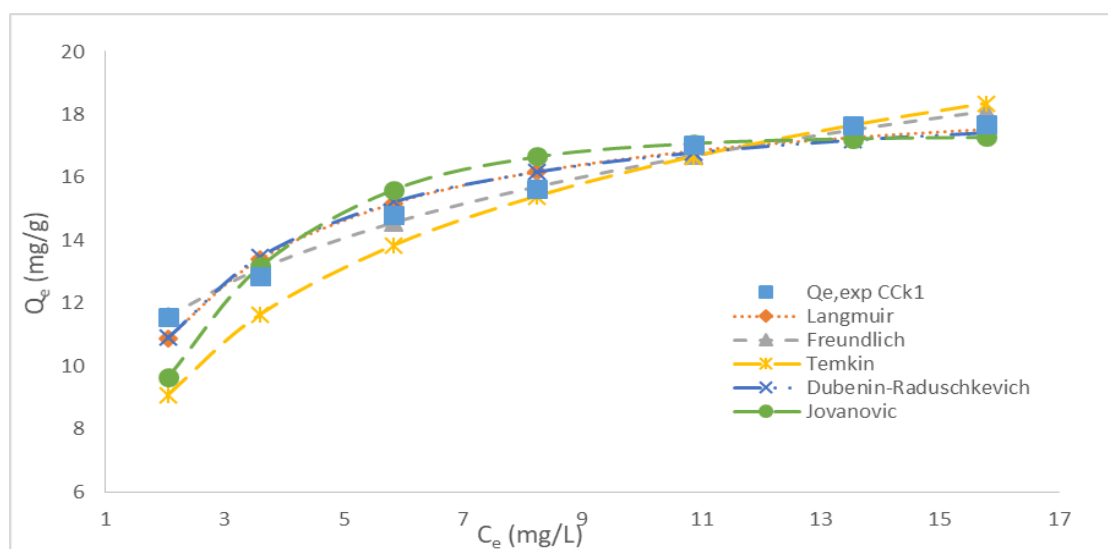


Figure 4: Comparison of measured and calculated q_e values for two-parameter isotherms onto activated carbon CCK1

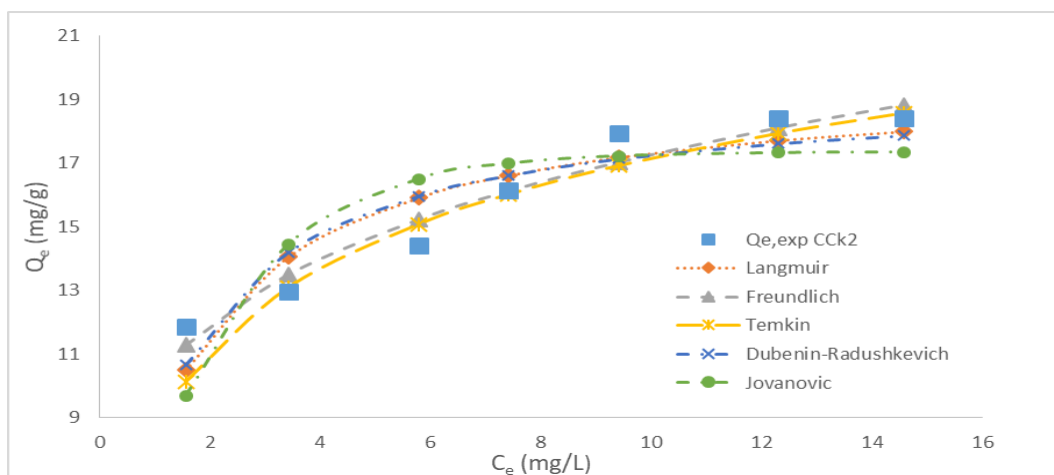


Figure 5: Comparison of measured and calculated q_e values for two-parameter isotherms onto activated carbon CCK2

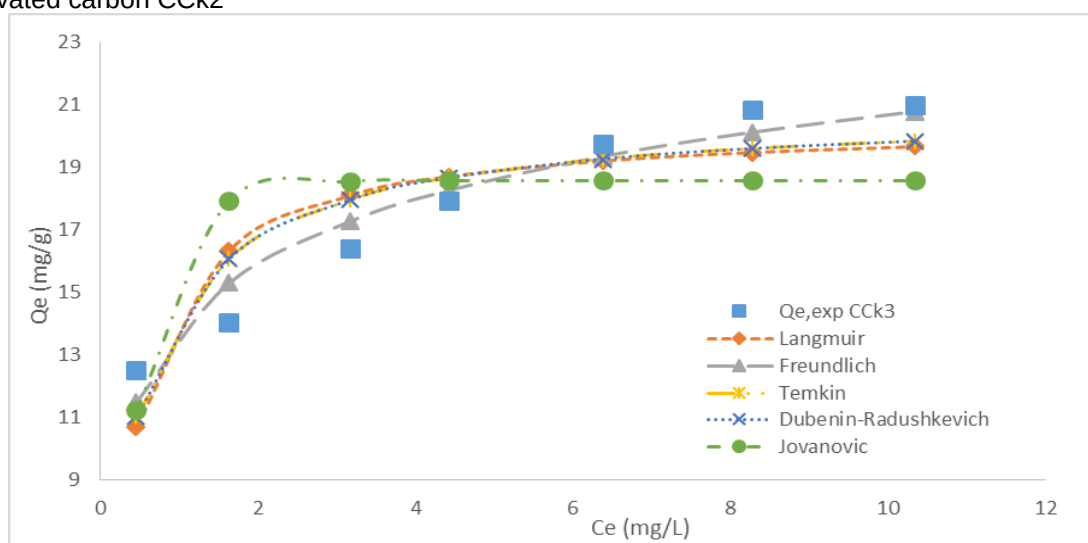


Figure 6: Comparison of measured and calculated q_e values for two-parameter isotherms onto activated carbon CCK3

289 **Table 7:** optimum isotherm parameters and their statistical comparison values for two-parameter
290 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.	Dubinin-Radushkevich	$Q_{\max}(\text{mg.g}^{-1})$	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						

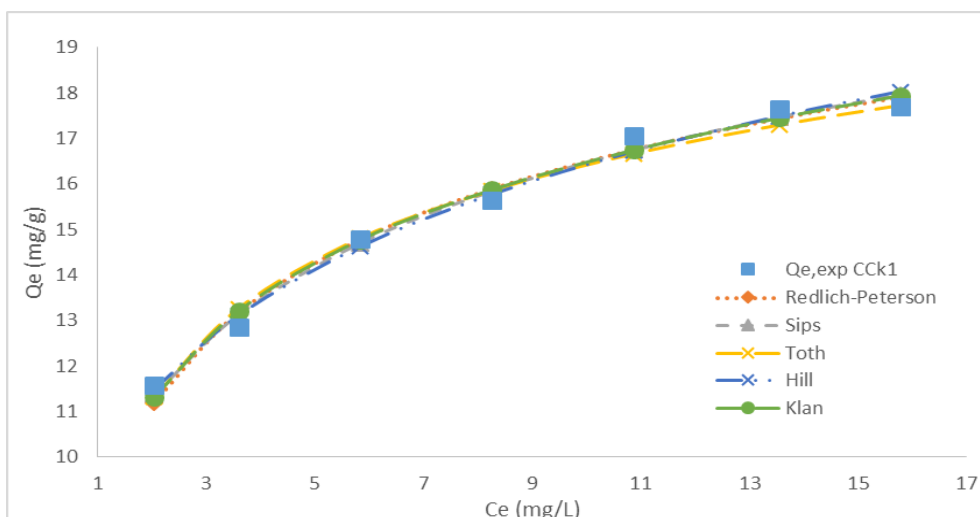


Figure 7: Comparison of measured and calculated q_e values for three-parameter isotherms onto activated carbon CCK1

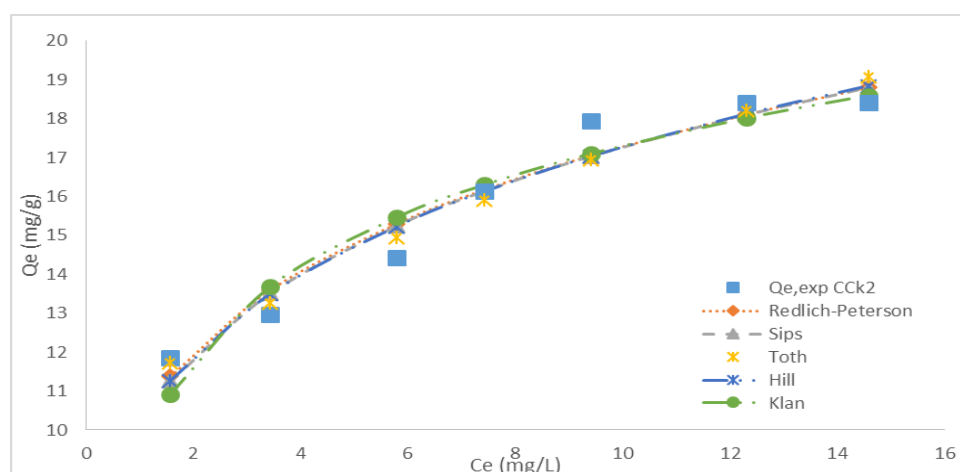


Figure 8: Comparison of measured and calculated q_e values for three-parameter isotherms onto activated carbon CCK2

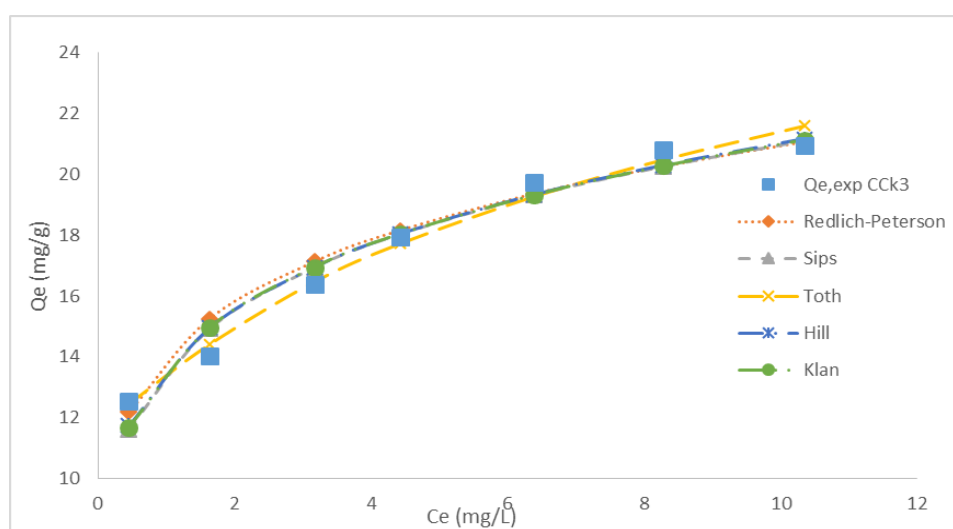


Figure 9: Comparison of measured and calculated q_e values for three-parameter isotherms onto activated carbon CCK3

304 **Table 8:** optimum isotherm parameters and their statistical comparison values for three-parameter
305 models

Models									
N°	Models	constants	values	R ²	RMSE	χ ²	HYBRID	ARE	EABS
CCK1									
	Redlich-Peterson	A (L.g ⁻¹)	25.456	0.987	0.691	0.034	0.843	1.643	1.675
		B (L.mg ⁻¹)	1.966						
		β	0.866						
	Sips	K _s (L.g ⁻¹)	31.800	0.990	0.600	0.024	0.591	1.428	1.511
		a _s ((L.g ⁻¹)	0.414						
		β _s	2.416						
	Toth	Q (mg/g)	13.051	0.983	0.746	0.038	0.937	1.611	1.664
		K _e	0551						
		n (mg/g)	0.935						
	Hill	Q _m (mg/g)	51.078	0.989	0.612	0.023	0.587	1.348	1.470
		K _H (L.g ⁻¹)	4.298						
		n _H	0.309						
	Khan	Q _m (mg/g)	10.352	0.987	0.659	0.030	0.739	1.552	1.612
		b _k (L.g ⁻¹)	2.340						
		a _k	0.841						
CCK2									
	Redlich-Peterson	A (L.g ⁻¹)	511.645	0.941	1.549	0.158	3.983	3.404	3.580
		B (L.mg ⁻¹)	48.986						
		β	0.780						
	Sips	K _s (L.g ⁻¹)	152.034	0.943	1.544	0.159	3.968	3.401	3.564
		a _s ((L.g ⁻¹)	0.071						
		β _s	3.927						
	Toth	Q (mg/g)	8.166	0.954	1.378	0.113	2.796	2.665	3.030
		K _e	-0.345						
		n (mg/g)	0.834						
	Hill	Q _m (mg/g)	2563.36	0.945	1.529	0.155	3.869	3.375	3.549
		K _H (L.g ⁻¹)	251.617						
		n _H	0.232						
	Khan	Q _m (mg/g)	10.545	0.922	1.836	0.240	5.971	4.192	4.249
		b _k (L.g ⁻¹)	2.504						
		a _k	0.836						
CCK3									
	Redlich-Peterson	A (L.g ⁻¹)	110355	0.954	1.632	0.165	4.344	3.193	3.580
		B (L.mg ⁻¹)	7879.0						
		β	0.825						
	Sips	K _s (L.g ⁻¹)	144.61	0.963	1.562	0.168	4.156	3.309	3.600
		a _s ((L.g ⁻¹)	0.104						
		β _s	4.672						
	Toth	Q (mg/g)	11.826	0.986	0.966	0.049	1.229	1.697	2.171
		K _e	-0.127						
		n (mg/g)	0.865						
	Hill	Q _m (mg/g)	2264.1	0.965	1.508	0.153	3.835	3.215	3.525
		K _H (L.g ⁻¹)	165.01						
		n _H	0.190						
	Khan	Q _m (mg/g)	5.371	0.963	1.547	0.162	4.047	3.281	3.586

$b_k(\text{L.g}^{-1})$	156.65
a_k	0.815

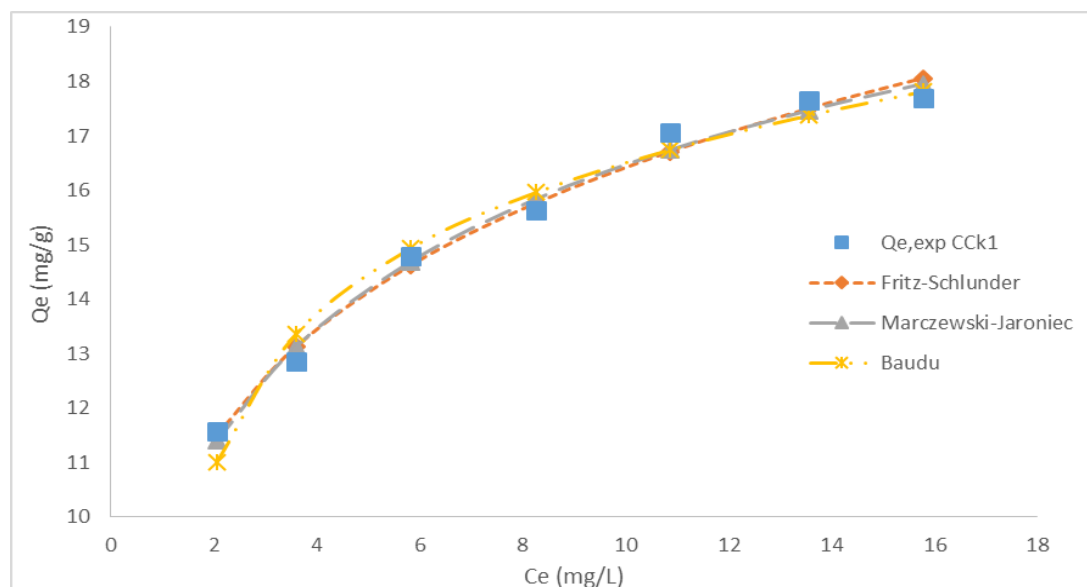


Figure 10: Comparison of measured and calculated q_e values for four-parameter isotherms onto activated carbon CCK1

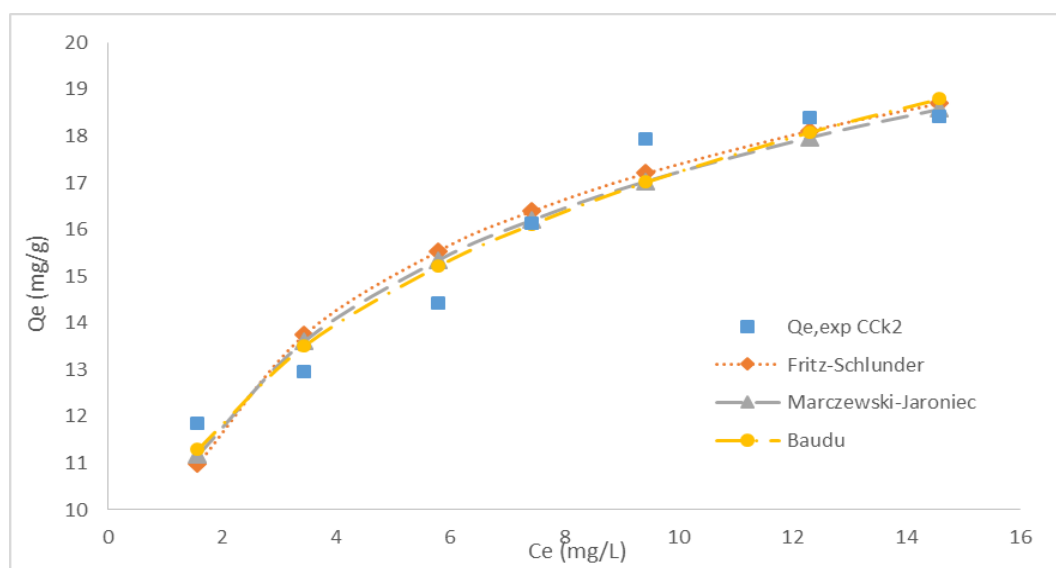


Figure 11: Comparison of measured and calculated q_e values for four-parameter isotherms onto activated carbon CCK2

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						

323

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

328 Two-parameter models

329 Table 7 shows the two isotherm parameters obtained using the Non-linear method. Higher values of
330 R^2 obtained in this study are derived by fitting experimental data into the Temkin isotherm model for
331 both CCK1 sample and Freundlich for both CCK2 and CCK3 samples. In addition, lower values of
332 Chi-square (χ^2), ARE, EABS and Root mean square error (RMSE) for each parameter obtained in
333 both isotherm models with higher R^2 can generate a satisfactory fit to the experimental data. As
334 shown in Table 7, maximum adsorption capacity values obtained using non-linear Langmuir model,
335 were 19.273, 19.691 and 20.424 mg/g for CCK1, CCK2, and CCK3 respectively. The values of n of
336 the model of Freundlich are higher than 1 suggesting that the process occurs on heterogonous
337 surfaces [17]. Based on the energies, the variation of energy of adsorption b (kJ/mol) resulting from
338 the non-linearization of the Temkin model is positive. A positive value of b means that the process of
339 adsorption is exothermic. From the Dubinin-Radushkevich model the adsorption energies are 42.25,
340 45.64 and 67.42kJ/mol onto CCK1, CCK2 and CCK3 respectively, also high than 16 kJ/mol. These
341 observations (values of energies) suggest that intra particular diffusion dominates the adsorption
342 process. Jovanovic cannot describe the experimental equilibrium data, because it is as a lower value
343 of R^2 obtained in this study. In this study, all the values of error function are very small, indicating a
344 favorable adsorption of 2,4-dinitrophenol on these differents adsorbents

345 Three-parameter models

346 Table 8 shows the three isotherm parameters obtained using the non-linear method. It was observed
347 that the correlation coefficient value for all models isotherms study are very good (>0.94) and the low
348 Chi-square (χ^2), ARE, EABS and Root mean square error (RMSE) values, thus it indicates that the
349 models are able to describe equilibrium data perfectly. In the case of Slips model shows high
350 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 [21]. 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 of 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-Schlunder (0.965) isotherms model respectively for both CCK1 CCK2 and CCK3 samples. Finally, they were chosen as the best fitted nonlinear model for the 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 to 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 they having a high R^2 , 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 (according to chi-square test (χ^2)). This results explain the favorable adsorption of 2,4-dinitrophenol in these different adsorbents.

REFERENCES

1-Murillo-Acevedo, Y.S.; Giraldo, L. & Moreno-Piraján, J.C. (2010). Characterization of the Adsorption of 2,4-dinitrophenol from Aqueous Solution onto Bovine Bone Char by Immersion Calorimetry. *Adsorption Science & Technology*, **28**, 8-9.

- 2- Hutton, E.A.; Ogorevc, B.; Hočevár, S.B.; Weldon, F.; Smyth, M.R. & Wang, J. (2001). An introduction to bismuth film electrode for use in cathodic electrochemical detection, *Electrochemistry Communication*, **3**, 707-711.
- 3-Nadavala, S.K.; Swayampakula, K.; Boddu, V.M. & Abburi, K. (2009). Biosorption of phenol and o-chlorophenol from aqueous solutions on to chitosan-calcium alginate blended beads. *Journal of Hazardous Material*, **162**, 482-489.
- 4-Rubin, E.; Rodriguez, P.; Herrero, R. & Sastre, V.M.E: (2006). Biosorption of phenolic compounds by the brown alga *Sargassum muticum*. *Journal of Chemical Technology and Biotechnology*, **81**, 1093-1099
- 5- Quershi, K.; Bhatti, I.; Kazi, R. & Ansari, A.K. (2007). Physical and Chemical Analysis of activated carbon from Sugarcane Bagasse and use for Sugar Decolorization, *World Academy of Science, Engineering and Technology*, **34**
- 6- Sugumarn, P.; Priya, V.; Susan, P. Ravichandran & Seshadri, S. (2012). Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and Delonix regia Fruit Pod. *Journal of Sustainable Energy and Environ.* **3**, 125-132.
- 7- Kibami, D.; Chubaakum, P.; Rao, K. S. & Sinha, D. (2014). Preparation and characterization of activated carbon from *Fagopyrum esculentum* Moench by HNO₃ and H₃PO₄ chemical activation. *Der Chemica Sinica*, **5**(4), 46-55.
- 8- Tchuifon, T.D.R.; Anagho, S G.; Ketcha, J.M.; Ndifor-Angwafor, G.N. & Ndi, J.N. (2014). Kinetics and equilibrium studies of adsorption of phenol in aqueous solution onto activated carbon prepared from rice and coffee husks. *International Journal of Engineering and Technical Research*, **2**, 166-173.
- 9- Ndifor-Angwafor, G.N.; Bopda, A.; Tchuifon, T.D.R.; Ngakou, S.C.; Kuete, T.I.H. & Anagho, S.G. (2017). Removal of Paracetamol from Aqueous Solution by Adsorption onto Activated Carbon Prepared from Rice Husk. *Journal of Chemical and Pharmaceutical Research*, **9**(3):56-68.
- 10- Pongener, C.; Kibami, D.; Rao, K.; Goswamee, R.L. & Sinha, D. (2015). synthesis and characterization of activated carbon from the biowaste of the plant *manihot esculenta*. *Chemical Science Transactions*, **4**(1), 59-68
- 11- Yang T. & Chong Lua A. (2006). Textural and chemical properties of zinc chloride activated carbons prepared from pistachio-nut shell. *Materials in chemistry and Physics*, **100**, 438-444
- 12- Ndi J.S.; Ketcha J.M.; Anagho S.G.; Ghogomu J.N. and Bilibi E.P.D., (2014). Physical and chemical characteristics of activated carbon prepared by pyrolysis of chemically treated cola nut (*cola acuminata*) shells wastes and its ability to adsorb organics. *International Journal of Advanced Chemical Technology*, **3**, 1-13.
- 13- Khan, A.R.; Ataulloh, R. & Al-Haddad A. (1997). Equilibrium adsorption studies of some aromatic pollutants from dilute aqueous solutions on activated carbon at different temperatures. *Journal of Colloid and Interface Science*, **194**, 154-165.
- 14-Kumar,V.K. (2007). Optimum sorption isotherm by linear and non-linear methods for malachite green onto lemon peel. *Dyes and Pigments*, **74**, 595-597.
- 15-Martin M.J.; Artola A.; Balaguer M.D. & Rigola M. (2003). Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions. *Chemical Engineering Journal*, **94**(3), 231 -239
- 16-ASTM International. (2006). Standard Test Method for Determination of Iodine Number of Activated Carbon: PA 19428-2959, United States, 1 -5
- 17-Al-Duri, B.; McKay, G., (1988). Basic dye adsorption on carbon using a solid phase diffusion model. *Chemical Engineering Journal*, **38** (1), 23-31
- 18- Gunay, A.; Arslankaya, E. & Tosun, I. (2007). Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, *Journal of Hazardous Material*. **146** 362-371.
- 19-Ringot, D.; Lerzy, B.; Chaplain, K.; Bonhoure, J.P.; Auclair E. & Larondelle, Y.(2007). In vitro biosorption of ochratoxin A on the yeast industry by-products: comparison of isotherm models. *Bioresource Technology*, **98**(9), 1812-1821.
- 20- Rania, F. & Yousef, N.S. (2015). Equilibrium and Kinetics studies of adsorption of copper (II) on natural Biosorbent. *International Journal of Chemical/Engineering and Applications*, **6**(5), 319-324.
- 21- Ayawei, N.; Ebelegi, A.N. and Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry*, ID 3039817
- 22- Yaneva, Z.L.; Koumanova, B.K. & Georgieva, N.V. (2013) Linear regression and nonlinear regression methods for equilibrium modelling of p-nitrophenol biosorption by *Rhizopus oryzen*: comparison of error analysis criteria. *Journal of Chemistry*, **2013**, 1-10.

449 23-McKay, G.; Mesdaghinia, A.; Nasser, S.; Hadi, M. & Aminabad, M.S. (2014). Optimum isotherms of
 450 dyes sorption by activated carbon: fractional theoretical capacity and error analysis. *Chemical*
 451 *Engineering Journal*, 251, 236–247.
 452 24-Subramanyam, B. & Das, A. (2009). Linearized and non-linearized isotherm models comparative
 453 study on adsorption of aqueous phenol solution in soil. *International Journal of Environmental Science*
 454 *& Technology*. 6(4):633-40.
 455 25- Foo, K. & Hameed, B. (2010). Insights into the modeling of adsorption isotherm systems.
 456 *Chemical Engineering Journal*, 156(1), 2-10.
 457 26- Chan, L.; Cheung, W.; Allen, S. & McKay, G. (2012). Error analysis of adsorption isotherm models
 458 for acid dyes onto bamboo derived activated carbon. *Chinese Journal of Chemical Engineering*, 20(3),
 459 535-42.
 460 27-Bansal, R.C.; Donnet, J.B. & Stoeckli, F. (1988). "Active Carbon", Marcel Dekker, Inc, New York
 461 28-Benadjemia, M.; Milliere, R.L.; Benderdouche, N. & Duclaux, L. (2011). Preparation,
 462 Characterization and Methylene blue adsorption of phosphoric acid activated carbons from globe
 463 artichoke leaves. *Fuel Processing Technology*, 92, 1203- 1212
 464 29-Sahira, J. & Bhadra, P.P. (2013). Preparation and Characterization of Activated Carbon from lapsi
 465 (*Choerospondias axillaris*) Seed Stone by Chemical Activation with Potassium Hydroxide, *Journal of*
 466 *the Institute of Engineering*, 9(1), 79–88
 467 30- Ahmedna, M.; Marshall, W.E & Rao, R.M. (2000). Granular activated carbons from agricultural by-
 468 products: preparation properties and application in cane sugar refining.
 469 *Bulletin of Louisiana state University Agricultural centre*, 54P.
 470 31- Okieimen, F.E.; Okieimen, C.O. & Wuana, R.A. (2007). Preparation and characterization of
 471 activated carbon from rice husks, *Journal of Chemical Society*, 32, 126-136.
 472 32- Omlin, J. & Cheseaux, L. (2010). Evaluation des charbons actifs en poudre (CAP) pour
 473 l'élimination des micropolluants dans les eaux urbaines. *Rapport d'étude*, Ecole Polytechnique
 474 Fédérale de Lausanne, Lausanne, France, 62 p.
 475 33- Prahas, D.; Kartika, Y.; Indraswati, N. & Ismadji S. (2008). Activated carbon from jackfruit peel
 476 waste by H₃PO₄ chemical activation: pore structure and surface chemistry characterization. *Chemical*
 477 *Engineering Journal*, 140, 32–42.
 478 34- Virote, B.; Srisuda, S & Wiwut, T. (2005). Preparation of activated carbons from coffee residue for
 479 the adsorption of formaldehyde. *Separation and Purification Technology*, 42, 159–168
 480 35- Ndi, J.N. & Ketcha, M. J (2013). The adsorption efficiency of chemically prepared activated carbon
 481 from Cola Nut Shells by ZnCl₂ on methylene Blue. *Journal of Chemistry*. ID 469170, 1-7.
 482 36-Abechi, S.E.; Gimba, C.E; Uzairu, A & Dallatu, Y.A. (2013). Preparation and Characterization of
 483 Activated Carbon from Palm Kernel Shell by Chemical Activation, *Research Journal of Chemical*
 484 *Sciences*, 3(7), 54-61.