

Acetic Acid Adsorption onto Activated Carbon Derived from Pods of *Acacia nilotica* var *astringens* (Sunt tree) by Chemical Activation with $ZnCl_2$

Mutasim H. Elhussien^{1*} Yusuf M Isa²

1.Chemistry Department, Faculty of Education, Nile Valley University, Atbara, Sudan

2.Chemical Engineering Department, Durban University of Technology, Durban, South Africa

*E-mail of the corresponding author: mutasim1966@yahoo.com

Abstract

The purpose of this study is to prepare and investigate the adsorption behavior of acetic acid onto two samples of activated carbon prepared from *Acacia nilotica* var *astringens*, Sunt tree, (SUNT-C1 and SUNT-C2). Applicability Langmuir, Freundlich, Temkin and Dubinin-Radushkevitch models of adsorptions isotherm have been tested, while acetic acid initial concentration varied between (0.010 – 0.300) mol/dm³. A comparative study of adsorption capacities of these samples was performed. The obtained data were compared and fitted well with the four models; there exist a correlation between physico- chemical properties of the activated carbons and the sorption processes. The maximum monolayer coverage (Q_m) from Langmuir isotherm model was determined to be 1.016mg/g. Also from Freundlich Isotherm model, the sorption intensity (n) which indicates favourable sorption and the correlation value are 1.11 and 1.09 respectively.

Keywords: Adsorption, *Acacia nilotica* var *astringens*, activated carbon, FTIR

1. Introduction

Activated carbons are carbonaceous materials that can be distinguished from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces [1]. These materials are characterized by their extraordinary large specific surface areas, well-developed porosity and tunable surface-containing functional groups [2]. For these reasons, activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water and wastewater [3].

Due to the growing need for activated carbons in our society and the high cost of raw materials and production, many researchers have attempted using various wastes such as tires, [4] resins, [5] agricultural byproducts [6-8] and dried sewage sludge [9], [10] as raw materials and proposed new production methods [11], [12] for activated carbons with potential applications in pollution control. Furthermore activated carbons are increasingly used as an economic and stable mass separation agent for the removal of surfactants to raise the final product quality in many industrial processes. Activated carbons also play an important role in many areas of modern science and technology such as purification of liquids and gases, separation of mixtures, and catalysis [13]. Adsorption on activated carbon is governed by the chemical nature of the aqueous phase, the solid phase, and the chemical nature of the adsorbing organic species [14]. Analysis of the surface physical properties of the carbon includes determination of the total surface area, extent of micro porosity, and characterization of the pore size distribution.

The main problem in the interpretation of solution-adsorption studies lies in the relative unavailability of comparisons of the data obtained by different research groups and is due to differences in the nature of the carbons, in the conditions of the adsorption processes and in the methodology applied in the analysis [15].

This work is based on the identification and comparison of the adsorption properties of ACs obtained from pods of *Acacia nilotica* var *astringens* (Sunt tree) under different conditions. Acetic acid is an organic pollutant with specific surface area close to that of nitrogen which is not only used in adsorption experiments, but also as a reference substance in aqueous phase satisfying Giles's conditions [2, 15-21]. Hence acetic acid is used in this investigate the performance of the prepared activated carbons.

In this study the adsorption properties of Sunt tree (SUNT-C1 and SUNT-C2), using Langmuir, Freundlich, Temkin and Dubinin-Radushkevitch models of adsorptions isotherm were determined and analyzed. The influence of physico- chemical properties of the activated carbons in the sorption process were also considered.

2. Materials and Method

2.1 Preparations of the Activated Carbon:

The adsorbent used in this study was powdered, activated carbon obtained from pods of *Acacia nilotica* var *astringens* (Sunt tree), collected from El-Obeid (Western Sudan) and authenticated by the department of Botany, University of Khartoum; the carbonisation was done at high temperatures (525°C). SUNT-C1 activated carbon

(light part), was obtained with 10% ZnCl₂ solution and residence time of 3hrs, while SUNT-C2 activated carbon (hard part), was obtained with 10% ZnCl₂ solution and residence time of 48hrs and were pre-treated according to the method reported in the literature [9,11]. These two samples were used in this study.

The samples were screened and washed with de-ionized water to remove dirt impurities after which were they dried in the oven at 110°C for 3 hours. The dried samples were ground and sieved in the mesh to collect the fraction between 250µm and 150µm; this was done to increase the surface area of the carbons. The modification was done by chemical treatment of 50g of the sieved samples with ZnCl₂ as described above, and then heated on the magnetic stirrer at 100°C until it totally formed a paste. The modified samples were washed with de-ionized water until the pH being in the range of (6.7 - 6.9), the pH was determined using a pH meter (model ATPH-6). Then the two samples were dried in the oven at about 95°C to remove moisture.

2.2 Batch Equilibrium Experiments:

All chemicals used were analytical/laboratory grade. The adsorption experiments were conducted in an experimental apparatus in an appropriate condition. An agitator digital thermostatic water bath (Model HH-S6 / China) was used for shaking the flasks while controlling the temperature (25±0.01°C). Batch equilibrium experiments were designed in six screw cap Erlenmeyer flask 100 cm³ each, 0.1 g of activated carbon was placed and acetic acid concentrations were varied in an order between (0.010-0.300 mol/dm³). The flasks were shaken for four hours (to the optimized value of the shaking time needed to reach equilibrium). After reaching the contact period between the activated carbon and the acetic acid aqueous solution, the content of each flask was filtered using vacuum suction. A sample of each filtrate was removed and titrated with standardized sodium hydroxide solution.

The amount of adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm [16]:

$$q_e = (V/w)(C_o - C_e) \dots \dots \dots 1$$

Where q_e is the concentration of the organic substance adsorbed on the activated carbon in (mg/g), C_o and C_e are the initial and equilibrium concentrations of the solute respectively (in mg/cm³), V is the volume of the solution (cm³) and w is the adsorbent mass (in g). The data were fitted into the following isotherms models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevitch [17].

FTIR analysis was done using IPRestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan). Samples of 0.1 g were mixed with 1 g of KBr, spectroscopy grade (Merk, Darmstadt, Germany), in a mortar. Part of each mixture was transferred to the FTIR analyzer and a corresponding spectrograms were obtained showing the wave lengths of the different functional groups in the sample which were identified by comparing these values with those in the library.

3. Results and discussion

3.1 Samples Characterizations:

The physico-chemical parameters of the SUNT-C1 and SUNT-C2 samples, treated with ZnCl₂ solutions are shown in table -1.

The FT-IR spectrum showed the absorption bands at these regions (2880-3490cm⁻¹), (1315-1760cm⁻¹), (1000-1260cm⁻¹), and (475-750cm⁻¹) for the two samples.

The two samples showed a broad band with two maxima at 2880cm⁻¹ which is attributed to C-H interaction with the surface of the carbon and at 3445cm⁻¹ is due to an O-H stretching mode. Moreover the indicated bands in the range of 3250-3675 cm⁻¹ have also been attributed to the hydrogen-bonded OH group of alcohols and phenols. However, the band at 1490 cm⁻¹ may be attributed to the aromatic carbon-carbon stretching vibration. The two peaks at 1120-1150 cm⁻¹ showed the fingerprint of this carbon. The sharp absorption band at 1125 cm⁻¹ is ascribed to either Si-O [21] or C-O stretching in alcohol, ether or hydroxyl groups. [21], [22] The band at 1150 cm⁻¹ can also be associated with ether C-O symmetric and asymmetric stretching vibration (-C-O-C- ring)[22]. This band could also be attributed to the anti-symmetrical Si-OSi stretching mode as a result of existing silica within the samples [22].

Table 1: Physico-chemical parameters of SUNT-C1 and SUNT-C2 samples

sample	Physical Aspect	Crystallinity (XRD)	Energy Dispersive X-ray Analyses	FTIR Results Surface functional groups
SUNT-C1	Granular activated carbon	Amorphous	C (77%); O (10%); Si (3%); Cl (7%); Zn (2%); K (1%)	-C ₆ H ₅ -, -CH ₂ -, -CH ₃ -, -CO-, -CH-, -OH
SUNT-C2	Powder activated carbon	Amorphous	C (81%); O (12%); Si (2%); Cl (3%); Zn (2%)	-C ₆ H ₅ -, -CH ₂ -, -CH ₃ -, -CO-, -CH-, -OH

3.2. Adsorption properties:

The various constants characteristics of adsorption for each model and each sample were obtained by using MS Excel of Windows. All the constants deduced from the linear transforms of different isotherms (figures: 1-5) are shown in table-2.

3.2.1. Langmuir Adsorption Isotherm:

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of acetic acid between the solid and liquid phases [8]. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \dots \dots \dots 2$$

Langmuir adsorption parameters were determined by transforming the Langmuir equation (2) into linear form.

$$\frac{1}{q_e} = \left(\frac{1}{Q_o K_L}\right) \cdot \frac{1}{C_e} + \frac{1}{Q_o} \dots \dots \dots 3$$

Where: C_e = the equilibrium concentration of adsorbate (mg/dm^3) q_e = the amount of acetic acid per gram of the adsorbent at equilibrium (mg/g). Q_o = maximum monolayer coverage capacity (mg/g) K_L = Langmuir isotherm constant (dm^3/mg). The values of Q_o and K_L were computed from the slope and intercept of the Langmuir plot of $1/q_e$ versus $1/C_e$ [8, 9-12].

For SUNT-C1 and SUNT-C2 samples, the maximum monolayer coverage capacity (Q_o) from Langmuir isotherm model were determined to be 1.016 and 0.853 mg/g , with K_L (Langmuir isotherm constant) 36.863 and 71.889 dm^3/mg respectively, indicating that the equilibrium sorption was much favourable in SUNT-C2 sample. In fact, the higher the K_L value, the stronger the affinity between acetic acid and the activated carbon (SUNT-C2 was twice stronger than SUNT-C1). In addition, the linear correlation coefficient R^2 for this model are higher (0.997) implying that the Langmuir Isotherm model was suitable to explain the adsorption of acetic acid onto activated carbons derived from *Acacia nilotica* var *astringens* (Sunt tree).

3.2.2. Freundlich Adsorption Isotherm:

This is commonly used to describe the adsorption characteristics for the heterogeneous surface [27]. These data often fit the empirical equation proposed by Freundlich:

$$q_e = K_f C_e^{\frac{1}{n}} \dots \dots \dots 4$$

Where K_f = Freundlich isotherm constant (mg/g); n = adsorption intensity; C_e = the equilibrium concentration of adsorbate (mg/dm^3) q_e = the amount of the acetic acid adsorbed per gram of the adsorbent at equilibrium (mg/g). Linearizing equation 4, we have:

$$\ln(q_e) = \ln(K_f) + \frac{1}{n} \ln C_e \dots \dots \dots 5$$

The constant K_f is an approximate indicator of adsorption capacity, while $1/n$ is a function of the strength of adsorption in the adsorption process [6,10]. However, K_f and n are parameters characteristic of the sorbent-sorbate system. The value of Freundlich constant, n , determines if the adsorption of the acetic acid on studied activated carbon is favorable or not. If the exponent n , lies between 1 and 10, the adsorption is favorable. The two values are 1.09 and 1.11 (approximately identical) on the bases of which it appears that the adsorption of acetic acid on SUNT-C1 and SUNT-C2 was favorable. The functional groups (showed by FTIR

results in table-1) present at the surface of the two materials particularly the carbonyl (CO) and the hydroxyl (OH) explains why the sorption is favorable on the two samples. On the other hand Freundlich model has values of correlation coefficient of 0.993 and 0.997 for SUNT-C1 and SUNT-C2 respectively which restricts the utility of the model to describe acetic acid adsorption onto these two samples.

3.2.3 The Temkin adsorption Isotherm:

This isotherm contains a factor that explicitly takes into the account of adsorbent–adsorbate interaction. The model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [7, 10, 14]. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy) was carried out by plotting the quantity sorbed q_e against $\ln C_e$ and the constants were determined from the slope and intercept. The model is given by the following equations [10]:

$$q_e = \left(\frac{RT}{b}\right)\ln(A_T C_e) \dots \dots \dots 6$$

$$q_e = \left(\frac{RT}{b}\right)\ln(A_T) + \left(\frac{RT}{b}\right)\ln(C_e) \dots \dots \dots 7$$

$$q_e = B \ln(A_T) + B \ln(C_e) \dots \dots \dots 8$$

where: $B = RT/b$

Where: A_T = Temkin isotherm equilibrium binding constant (dm^3/g), b = Temkin isotherm constant, R = universal gas constant ($8.314\text{J}/\text{mol}\cdot\text{K}$), T = Temperature at 298K . and B = Constant related to heat of sorption (J/mol).

From the plot shown in fig 2 Temkin constant, b , is positive, then the adsorbent–adsorbate interactions are gravitational and in the contrary case, they are repulsive [7]. For the two studied samples SUNT-C1 and SUNT-C2, these constants are positive; $3.4 \times 10^5 \text{J}\cdot\text{g}/\text{mol}^2$ and $3.1 \times 10^5 \text{J}\cdot\text{g}/\text{mol}^2$ respectively, thus the acetic acid – carbon interaction are gravitational confirming the result obtained by the Langmuir model. Also, the following values, A_T , Temkin isotherm equilibrium binding constant were estimated to be 1.73×10^3 and $2.48 \times 10^3 \text{dm}^3/\text{mg}$ for the two samples respectively, the model has values of correlation coefficient of 0.955 and 0.970 respectively.

3.2.4 Dubinin–Radushkevich isotherm model (DRK model):

This isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [14, 15]. The model has been often successfully fitted high solute activities and the intermediate range of concentrations data.

$$q_e = Q_{DR} \cdot \exp \left[-B_{DR} \left(RT \ln \left(1 + 1/C_e \right) \right)^2 \right] \dots \dots \dots 9$$

$$\ln q_e = -B_{DR} \cdot R^2 \cdot T^2 \left[\ln \left(1 + 1/C_e \right) \right]^2 + \ln Q_{DR} \dots \dots \dots 10$$

Where q_e = amount of adsorbate in the adsorbent at equilibrium (mg/g); Q_{DR} = theoretical isotherm saturation capacity (mmol/dm^3); B_{DR} = Dubinin–Radushkevich isotherm constant (mol^2/J^2). The model gives information on the binding energies. The calculations of the average energy, E , of a molecule adsorbed, expresses the energy released when a molecule of adsorbate passes from the solution into the adsorbent [15.]The energy was calculated from equation (11) :

$$E = \left(1/2 B_{DR} \right)^{1/2} \dots \dots \dots 11$$

where R , T and C_e represent the gas constant ($8.314 \text{J}/\text{mol K}$), absolute temperature (K) and adsorbate equilibrium concentration (mg/dm^3), respectively. The equation 9 is linearized to equation 10 which is used in the plot of DRK graph in figure (3). The constant such as Q_{DR} , and B_{DR} were determined from the appropriate plot. From the linear plot of DRK model, Q_{DR} were determined to be 1.24 and $1.67 \text{mmole}/\text{dm}^3$, while the mean free energy, $E = 6.45$ and $6.00 \text{kJ}/\text{mol}$, where B_{DR} values were found to be 1.2×10^{-8} and $1.4 \times 10^{-8} \text{mol}^2/\text{J}^2$ with correlation coefficients 0.9976 and 0.9958 for SUNT-C1 and SUNT-C2 respectively. The mean free energy, E , for the two samples indicating a physisorption process. It appears just like in case of Temkin adsorption

isotherm, the two samples are strongly attached to acetic acid, however it is important to notice that this model seems to be very suitable to explain the acetic acid adsorption more than Temkin model where R^2 are greater than 0.97.

Table 2. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Acetic Acid onto SUNT-C1 and SUNT-C1 Activated with $ZnCl_2$

Adsorbent	Langmuir			Freundlich			
	Q_0 (mg/g)	K_L (mg/g)	R^2	$1/n$	n	K_f (mg/g)	R^2
SUNT-C1	1.016	36.863	0.9965	0.9029	1.11	18.58	0.9931
SUNT-C2	0.8534	71.889	0.9968	0.9192	1.09	32.21	0.9971
Adsorbent	Temkin			Dubinin-Radushkevitch			
	A_T (dm ³ /mg)	B (J/mol)	R^2	Q_D (mmol/dm ³)	B_D (mol ² /J ²).10 ⁸	E (KJ/mol)	R^2
SUNT-C1	1725.14	0.0735	0.9546	1.24	1.20	6.45	0.9975
SUNT-C2	2475.89	0.0808	0.9699	1.67	1.39	6.00	0.9958

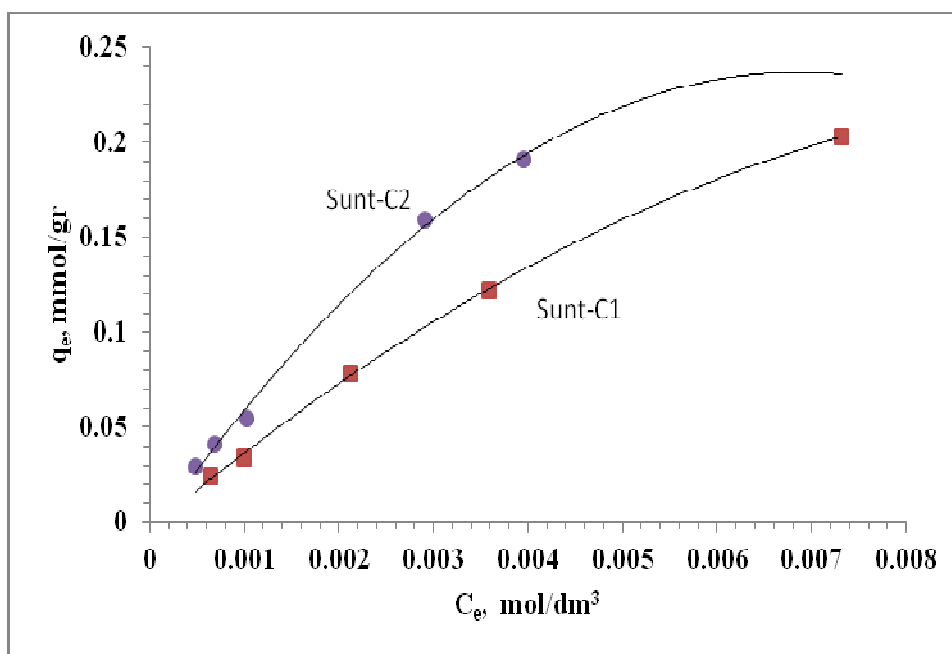


Figure1. Isotherm of adsorption of acetic acid on the activated carbon of Sunt sample

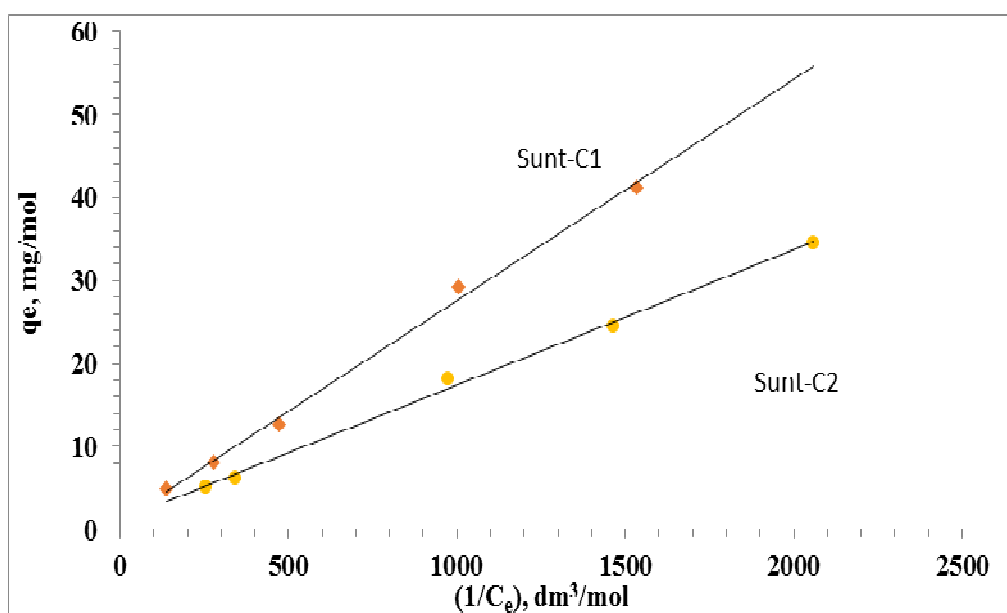


Figure 2. Langmuir Adsorption Isotherm: for Acetic Acid adsorption onto Sunt samples activated with $ZnCl_2$

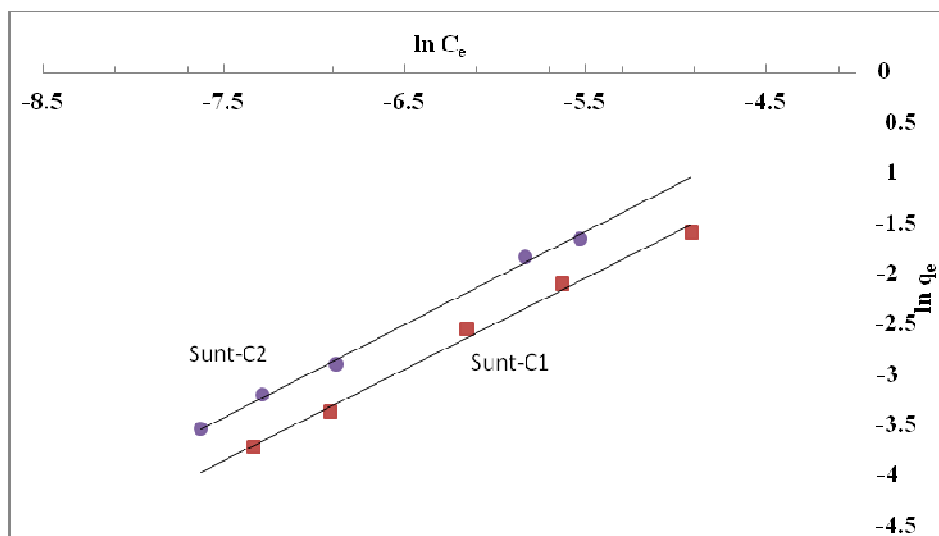


Figure 3. Freundlich Adsorption Isotherm for Acetic Acid adsorption onto Sunt samples activated with $ZnCl_2$

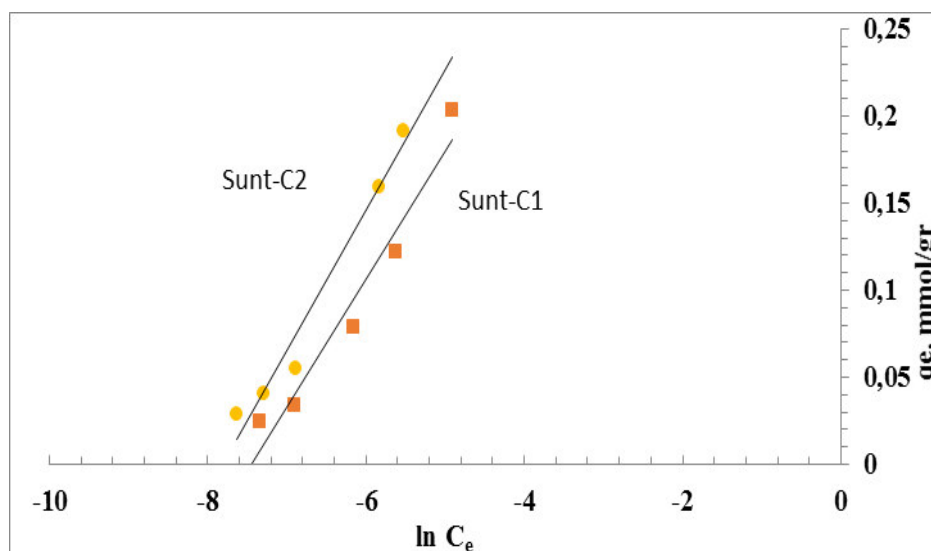


Figure 4. The Temkin adsorption Isotherm for Acetic Acid adsorption onto Sunt samples activated with $ZnCl_2$

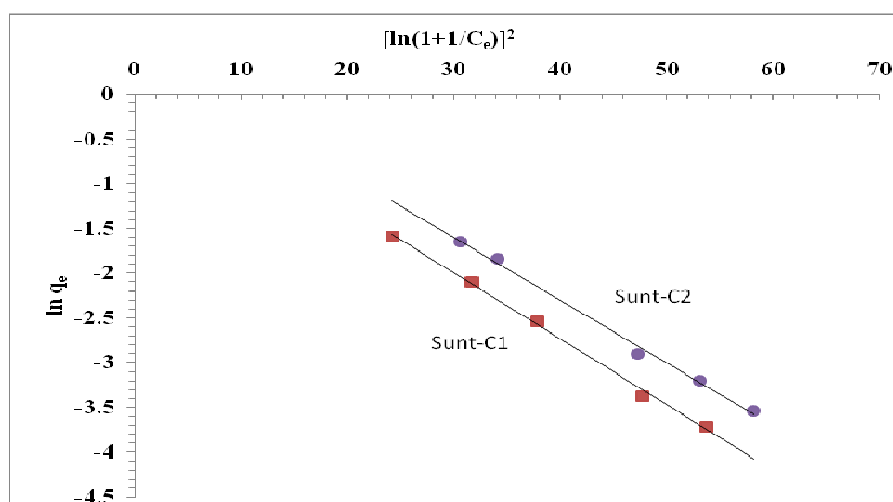


Figure 5. Dubinin-Radushkevich isotherm model for Acetic Acid adsorption onto Sunt samples activated with $ZnCl_2$

4. Conclusion

Activated carbon has been successfully synthesized from pods of *Acacia nilotica var astringens* (Sunt tree) and their performance in the adsorption of acetic acid was evaluated. XRD analyses showed that the samples were amorphous. FTIR analyses confirmed the presence of similar functional groups on both samples. The adsorption characteristics fitted well with the investigated adsorption isotherms. The maximum monolayer coverage (Q_0) from Langmuir isotherm model was determined to be 1.016 mg/g while Freundlich Isotherm model showed a sorption intensity (n) which indicates favourable sorption and the correlation value are 1.11 and 1.09 respectively. Finally, the prepared samples have potentials as adsorbents and can find application in separation and purification technologies.

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