

Langmuir, Freundlich Adsorption Isotherms and Kinetics for the Removal of Methylene Blue Dye from Aqueous Solution using Activated Carbon Derived from Pods of *Acacia nilotica* var *astringens* (Sunt tree) by Chemical Activation with $ZnCl_2$

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Abstract

Adsorption of Methylene Blue dye from aqueous solution onto Activated carbon derived from *Acacia nilotica* (Sunt tree) by chemical activation with $ZnCl_2$, (SUNT-C2) has been studied using batch-adsorption techniques. This study was carried out to examine the adsorption capacity of the low-cost adsorbent (SUNT-C2) for the removal of Methylene Blue dye from aqueous solution. The influence of pH, initial dye concentration, adsorbent particle size, adsorbent dose and contact time on the adsorption process were also studied. Results revealed that adsorption rate initially increased rapidly, and the optimal removal efficiency was reached within about 100 mins. Further increase in contact time did not show significant change in equilibrium concentration; that is, the adsorption phase reached equilibrium. The adsorption isotherms could be fitted well by the Langmuir and Freundlich models. Also the adsorption process followed pseudo first order rate kinetics. Results indicate that, a new, environment friendly, freely abundant, locally available, low-cost adsorbent, (SUNT-C2) was an attractive candidate for the removal of cationic dyes from dye wastewater.

Keywords: Adsorption, *Acacia nilotica*, (SUNT-C2) activated carbon, Methylene Blue dye, pseudo first order rate kinetics, FTIR.

1. Introduction:

A large variety of dyestuffs is available under the categories of acid, basic, reactive, direct, disperse, sulphur and metallic dyes [1]. Dyes are synthetic aromatic compounds, which have various functional groups [2]. Some dyes and their degradation products may be carcinogens and toxic, and consequently their treatment cannot depend on biodegradation alone [3,4]. The treatment technologies can be divided into three categories: biological, chemical and physical [5]. Among these methods, adsorption is widely used for its maturity and simplicity. Therefore, extensive research has been conducted to find an effective and efficient alternative for the removal of dyes. The most commonly used adsorbent in the dye adsorption process is activated carbon. Activated carbon has the advantage of exhibiting a high adsorption capacity for colour pollutants due to their high surface area and porous structure [6]. Although activated carbon is an effective and efficient adsorbent, its application is limited due to high cost and minimal decomposition. Therefore, alternative low-cost adsorbents such as chitin [7], coffee [8], tea waste [9], orange peel [10], rice husk [11], bark [12] and coir pith [13] have been studied.

The aim of this research was to produce a novel adsorbent from *Acacia nilotica* var *astringens* (Sunt tree), as such, considering that numerous alternative materials have been investigated to adsorb dyes from aqueous solution, using Methylene Blue as the model basic dye. The equilibrium data were analyzed using Langmuir and Freundlich adsorption isotherm models. Adsorption Kinetics process was also evaluated using pseudo-first-order model.

2. Materials and Methods:

2.1 Materials:

2.1.1 Preparation of the adsorbate solutions:

The dye used in this study, Methylene Blue, has many uses in different fields, such as biology, chemistry, and textile industry [14]. The relative molecular mass of Methylene Blue is 373.9, with three molecules of water. The molecular formula is $C_{16}H_{18}ClN_3S \cdot 3H_2O$. The structure of Methylene Blue is shown in Fig. 1. The basic dye, Methylene Blue, was used without further purification. A stock solution of 1000 mg L^{-1} was prepared by dissolving 1 g of the dye in 1 liter double distilled water. The experimental solutions were

prepared by diluting the dye stock solution in accurate proportions to different initial concentrations from 10-200 mg L⁻¹, and each of them was stored in 500-ml reagent bottles.

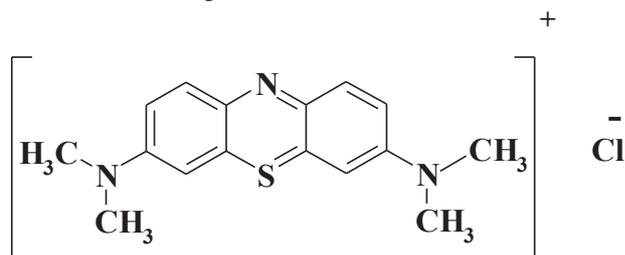


Figure 1. The structure of Methylene Blue Dye

2.1.2 Preparation of the Modified Adsorbent (SUNT-C2):

The adsorbent used in this study was powdered, activated carbon obtained from pods of *Acacia nilotica* var *astrangens* (Sunt tree), collected from El-Obeid (Western Sudan) and authenticated by the department of Botany, University of Khartoum; the carbonization was done at high temperatures (525°C). The activated carbon (hard part), named SUNT-C2, was obtained with 10% ZnCl₂ solution and residence time of 48hrs and was pre-treated according to the method reported in the literature [15-17].

In a typical activation, the sample was screened and washed with de-ionized water to remove dirt impurities, then dried in the oven at 110°C for 3 hours. The modification was done by chemical treatment of 250 g of the sample with ZnCl₂ as mentioned above. The modified sample was washed again with de-ionized water until the pH being in the range of (6.9 ± 0.2), the pH was determined using a pH meter (model ATPH-6). Afterwards, the sample was dried in the oven at about 95°C to remove moisture. The dried sample was ground and sieved in the mesh to collect the fraction between 550µm and 90µm; this was done to increase the surface area of the adsorbent. The collected fraction was grouped into the following series; series-a: 90-125, series-b: 125-250, and series-c: 250-550, then preserved in a desiccator for later use.

2.2 Methods:

2.2.1 Batch Equilibrium Experiments:

All chemicals used were analytical/laboratory grade. The adsorption experiments were conducted in an experimental apparatus at the desired conditions. A rotary shaker at 150 rpm using 250 ml shaking flasks containing 50 ml of the dye solutions at different concentrations and initial pH values. The corresponding amount of the adsorbent was added to each flask, and then the flasks were sealed to insure no volume change during the experiments. The samples were shaken for predetermined time interval, and then withdrawn, and the dye solutions separated from the adsorbent by centrifugation and filtration respectively. The pH values for the separated dye solutions were again measured. Dye concentrations were estimated by measuring their absorbance at maximum wavelength (λ_{max}= 480 nm) using Spectronic-21D spectrophotometer, Germany.

The amount of dye adsorbed (mg/g) was calculated using the formulae reported by Vanderborght and Van Griekenm [18]:

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

$$\% \text{ removal} = 100 (C_o - C_e) / C_o \dots \dots \dots (2)$$

Where q_e is the amount of the dye adsorbed by the SUNT-C2 sample in (mg/g), C_o and C_e are the initial and equilibrium concentrations of the dye respectively (in mg/L), V is the volume of the dye solution (L) and w is the adsorbent mass of SUNT-C2 (in g). All experiments were duplicated and the mean values are reported. The maximum deviation was observed to be 2%. The effect of each parameter (pH, initial dye concentration, adsorbent particle size, adsorbent mass and contact time) for each of the three series were studied in an experiment by varying the parameter under consideration, while all the other parameters were maintained as constant. The negative control (with no adsorbent) was used to ensure that the adsorption is only due to SUNT-

C2 sample and not to the reaction vessels. The data were fitted into Langmuir and Freundlich isotherms models [19, 20].

FTIR analysis was done using IPRestige-21, FTIR-84005, SHIMADZU Corporation (Kyoto, Japan). 0.1 g sample of SUNT-C2 was mixed with 1 g of KBr, spectroscopy grade (Merck, Darmstadt, Germany), in a mortar. Part of mixture was transferred to the FTIR analyzer and the corresponding spectrogram was obtained showing 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 Sample Characterizations:

The physico-chemical parameters of SUNT-C2 sample, modified with $ZnCl_2$ is shown in Table. 1. The FT-IR spectrum showed the absorption bands at these regions (2880-3490 cm^{-1}), (1315-1760 cm^{-1}), (1000-1260 cm^{-1}), and (475-750 cm^{-1}). The sample showed a broad band with two maxima at 2880 cm^{-1} which is attributed to C-H interaction with the surface of the carbon and at 3445 cm^{-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-C2 sample

Physical Aspect	Crystallinity (XRD)	Energy Dispersive X-ray Analyses	FTIR Results Surface functional groups
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 Effect of initial pH on adsorption capacity:

The effect of pH on the adsorption of dye onto SUNT-C2 samples, series a: (90-125 μm), b:(125-250 μm) and c:(250- 550 μm) were examined at 50 mg/L dye solution and 100 minutes as a contact time with 2.00 g of the adsorbent at room temperature. The initial pH values were adjusted to (3, 4, 5, 6, 7, 8, 9 and 10) with 0.1M HCL or 0.1M NaOH using the pH meter. The results, presented in Fig. 2, showed that, the removal was minimum at the initial pH 3 and the dye adsorption increases with increasing the pH up to 8. The dye removal beyond pH 8 was not significant, that is why pH 8 was selected for further studies.

After adsorption experiments, at low pH, the dyes became protonated. The electrostatic repulsion between the protonated dyes and the positively charged adsorbent sites results in decreasing the adsorption. Thus higher adsorption at higher pH may be due to the increased protonation by neutralization of the negative charges at the surface of the adsorbent which facilitates diffusion process and providing much active sites for the adsorbent.

3.3 Effect of initial dye concentration on adsorption capacity:

The effect of initial dye concentration onto the three series samples of SUNT-C2 were carried out at pH 8 solution, with 2.00 g of activated carbon and 100 min. as a contact time. The initial concentrations were prepared by diluting a known volume from stock standard solution to 50 ml volumetric flask with double distilled water to prepare (10, 20, 30, 40, 50, 100, 150 and 200 mg/L). The obtained results are shown in Fig.3. When the dye concentration was increased from 10 to 200mg/L the adsorption increased from 77.1%, 74.4%, and 63.85% to 87.33%, 82.25% and 71.62% for the three series a, b, and c respectively.

3.4 Effect of adsorbent particle size on adsorption capacity:

The effect of the adsorbent particle size of the three series samples (2.00 g SUNT-C2) on the dye adsorption was determined at 50 mg/L initial dye concentration, pH 8 and 100 min. as a contact time. The results are shown in Fig. 4. The dye adsorption increases as the adsorbent particle decrease, this can be explained as smaller particle

have large surface area than those of larger particle, hence adsorbs more dye during the initial stages. Therefore series a: (90-125µm) was been selected for adsorption isotherm experiments.

3.5 Effect of adsorbent mass on adsorption capacity:

The effect of the adsorbent sample of SUNT-C2 was studied by varying its dose (0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 g) with 50 mg/L initial dye concentration, pH 8 and 100 min. as a contact time. The results in Fig. 5 represented that the adsorption percentage increase as the adsorbent mass increase, and this attributed to increased adsorbent surface area and presence of more adsorption sites.

3.6 Effect of contact time on adsorption capacity:

The contact time effect on adsorption capacity of SUNT-C2 was carried out using 50 ml dye solution of 50 mg/L initial concentration at pH 8 with 2.00 g of each of the three activated carbon series at different contact times (15, 30, 45, 60, 75, 80 , 100, and 180 min). Figure 6 represents the relationship between contact time and adsorption. The adsorption capacity increases with increasing contact time and reached to the equilibrium approximately in 100 min.

3.7 Adsorption Isotherms:

The experimental adsorption isotherms were fitted to mathematical Langmuir and Freundlich isotherms models. For the Langmuir model, the following equation was used [8, 16]:

$$1/q_e = \left(1/Q_0 K_L\right) \cdot 1/C_e + 1/Q_0 \dots \dots \dots 3$$

Where q_e and C_e correspond to the milligrams of dye adsorbed per one gram of the activated carbon and the residual dye concentration in the solution when in equilibrium and K_L and q_0 are Langmuir constant and maximum capacity of adsorption for this model.

Freundlich isotherm constants were calculated with the equation:

$$\ln(q_e) = \ln(K_f) + \frac{1}{n} \ln C_e \dots \dots \dots 4$$

Where K_f and n are the Freundlich constants characteristic of the activated carbon system.

The Langmuir model is valid for modeling monolayer adsorption onto a homogenous surface with constant adsorption energy; the Freundlich equation posits a heterogeneous surface and considers that molecules attached to a surface site will have an effect on the neighboring sites. The results of Langmuir and Freundlich isotherm models are shown in Figures 7 and 8 respectively. The adsorption data using series- a: (90-125µm), pH=8, Initial concentration=50 mg/L, Time=100 min., adsorbent dose =2.00 g., were analyzed in terms of both Langmuir and Freundlich equations, and the values obtained for the respective constants are shown in Table 2.

The maximum monolayer coverage capacity (q_0) from Langmuir isotherm model was determined to be - 85.14 mg/g, with K_L (Langmuir isotherm constant) - 0.0567 L/mg respectively, indicating that the equilibrium sorption was much favourable. The linear correlation coefficient R^2 for this model (0.9336) implying that, the Langmuir isotherm model was suitable to explain the adsorption of Methylene Blue onto activated carbons (SUNT-C2) derived from *Acacia nilotica* var *astringens*.

The value of Freundlich parameters K_f and n were determined to be 3.558[(mg/g) (L/mg)^{1/n}] and 0.7948 respectively indicating that, adsorption of Methylene Blue onto activated carbons (SUNT-C2) is favorable. The linear correlation coefficient R^2 (0.9670) explain that, this isotherm model was suitable to the dye type adsorption.

3.8 Adsorption Kinetics:

The adsorption kinetics of Methylene Blue dye by SUNT-C2 series- a: (90-125µm), pH=8, Initial concentration=50 mg/L, Time=100 min., adsorbent dose =2.00 g., illustrated in Fig.6 shows that, the removal rates of dyes from solutions were very rapid during the initial stages of the adsorption process. A very rapid adsorption of dye uptake capacities increased with time and reached equilibrium values in approximately 100 min. The amount of the dye adsorbed at time (t) is shown in Fig. 9.

The kinetic data were treated with the following Lagergren's pseudo – first order rate equation [8], [10]:

$$\ln(q_e - q_t) = \ln q_e - k_{ad} t \dots \dots \dots (5)$$

Where q_e and q_t refer to the amount of the dye adsorbed at equilibrium and time (t), respectively, and k_{ad} is the rate constant which could be calculated from the linear plot of $\ln(q_e - q_t)$ versus t , The plot is shown in

Fig.10 . The higher value of the correlation coefficient showed that, the data conformed well to the pseudo – first order rate kinetic model, Table (2).

Table (2): Langmuir, Freundlich Isotherm constants and Pseudo - first order kinetic parameters for the adsorption of Methylene Blue onto SUNT-C2 sample.

Langmuir			Frenudlich			Pseudo - first order kinetic parameters		
q_0 (mg/g)	K_L (L/mg)	R^2	n	$K_f[(\text{mg/g})(\text{L/mg})^{1/n}]$	R^2	q_e , (mg/g)	K_{ad} , min^{-1}	R^2
- 0.0567	- 58.14	0.9336	0.7948	3.558	0.9670	26.133	0.0346	0.9772

Conclusion:

This study confirmed that, activated carbon prepared from SUNT tree pods could effectively remove Methylene Blue from aqueous solutions. The optimal pH for favorable adsorption of dye was 8. The change of particle size had an effect on dye removal. The study also showed that the adsorption equilibrium was reached approximately in 100 min. The effect of dye concentration, dose of adsorbent should also be taken into account. Adsorption isotherm data fitted Langmuir and Freundlich models, so the adsorption was physisorbtion. Also the adsorption process followed pseudo first order rate kinetics.

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Figure 2.Effect of pH on % of dye removal by SUNT –C2: initial concentration=50 mg/L, time=100 min., adsorbent dose =2.00 g., particle sizes; a: (90-125 μm), b:(125-250 μm) and c:(250- 550 μm).

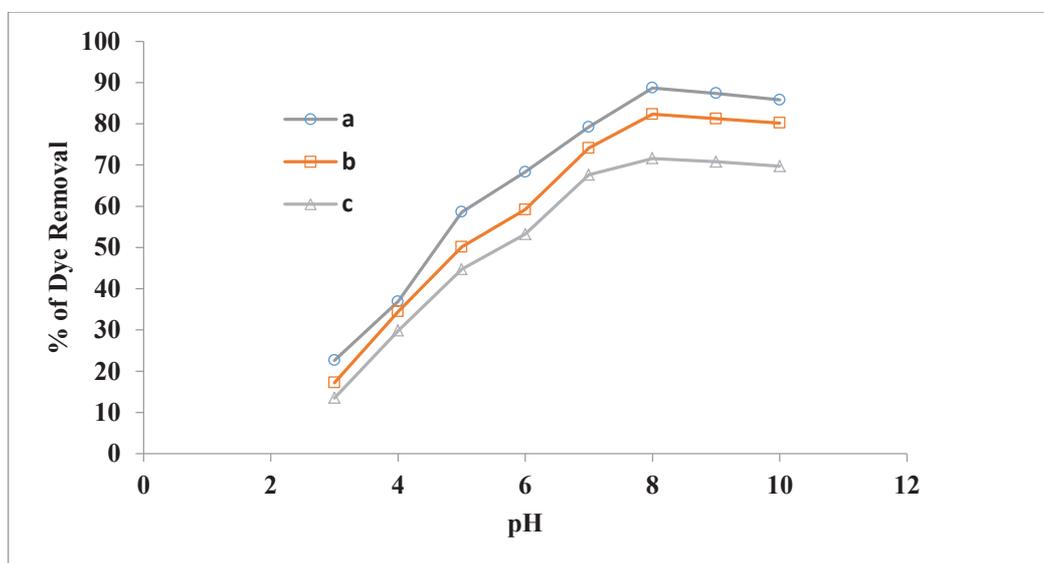


Figure 3. Effect of initial dye concentration on % of dye removal by SUNT –C2: pH=8, time=100 min., adsorbent dose =2.00 g., particle size ;a: (90-125 μ m), b:(125-250 μ m) and c:(250- 550 μ m).

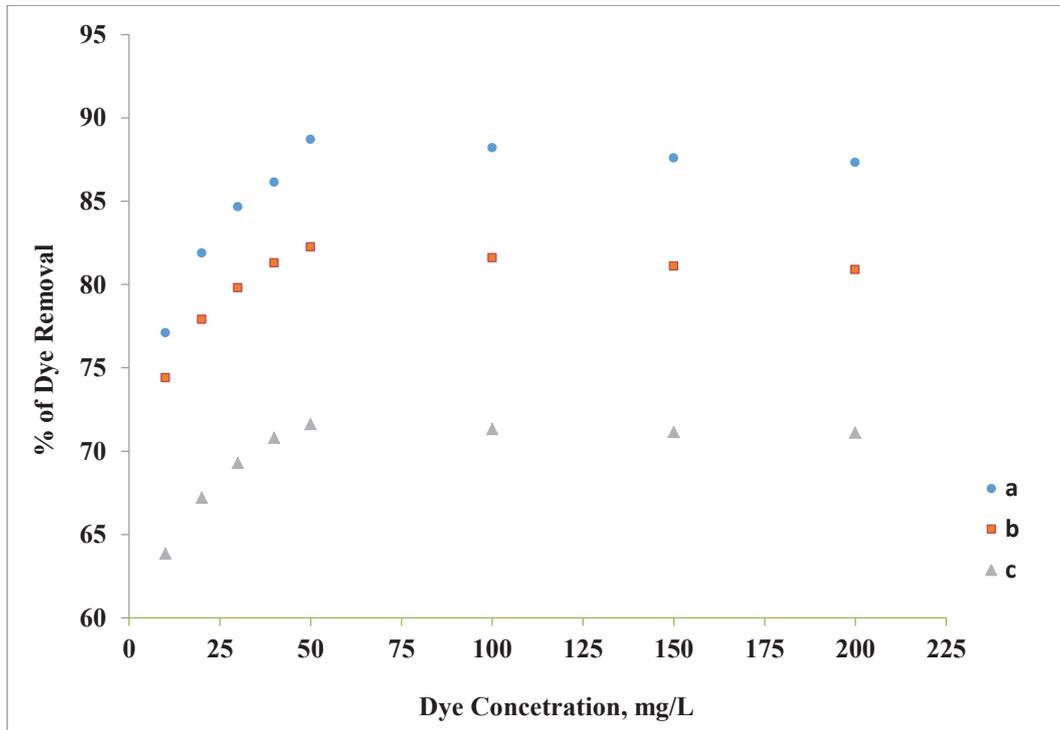


Figure.4 Effect of adsorbent particle size on % of dye removal by SUNT –C2: pH=8, initial concentration=50 mg/L, time=100 min., a: (90-125 μ m), b:(125-250 μ m) and c:(250- 550 μ m).

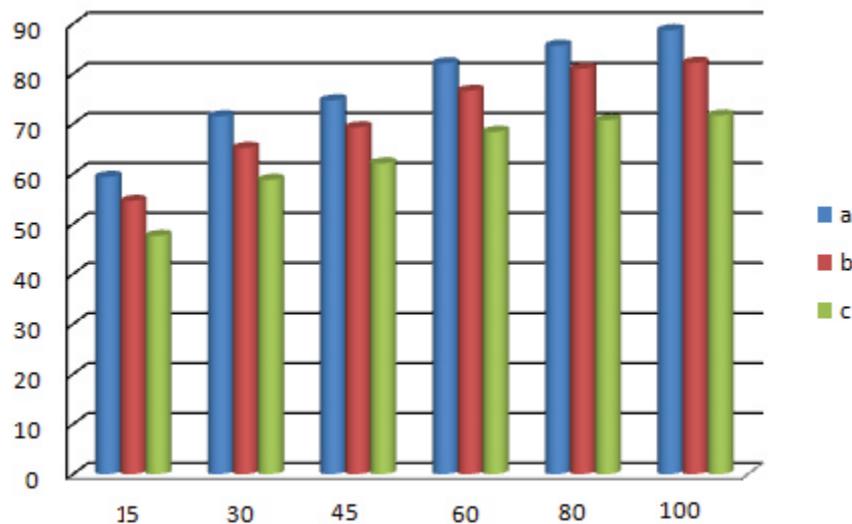


Figure.5 Effect of adsorbent doses on % of dye removal by SUNT –C2: pH=8, initial concentration=50 mg/L, time=100 min., particle size; a: (90-125 μ m), b:(125-250 μ m) and c:(250- 550 μ m).

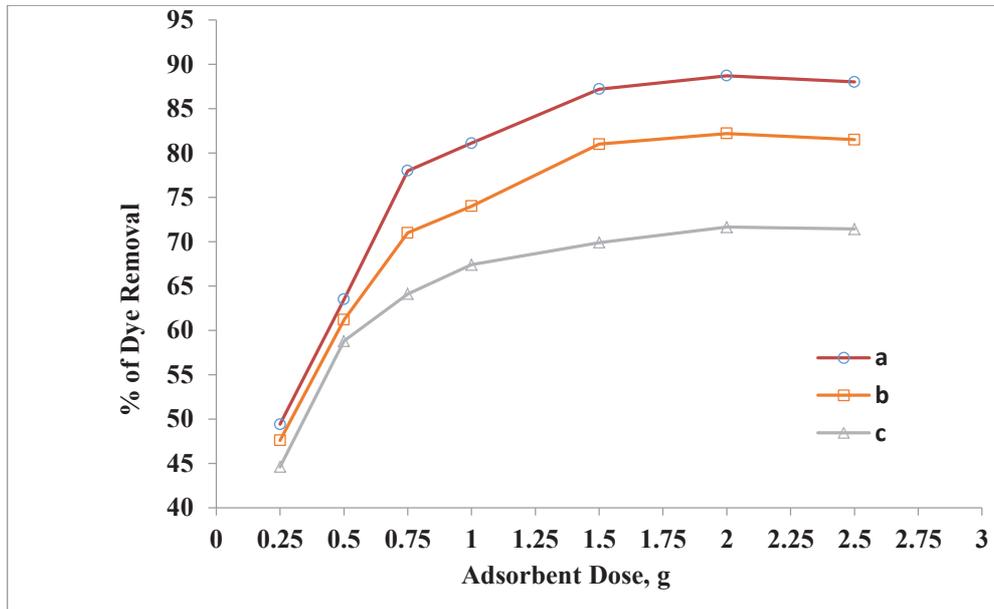


Figure 6. Effect of contact time on % of dye removal by SUNT –C2: pH=8, initial concentration=50 mg/L, adsorbent dose =2.00 g., particle size a: (90-125 μ m), b :(125-250 μ m) and c :(250- 550 μ m).

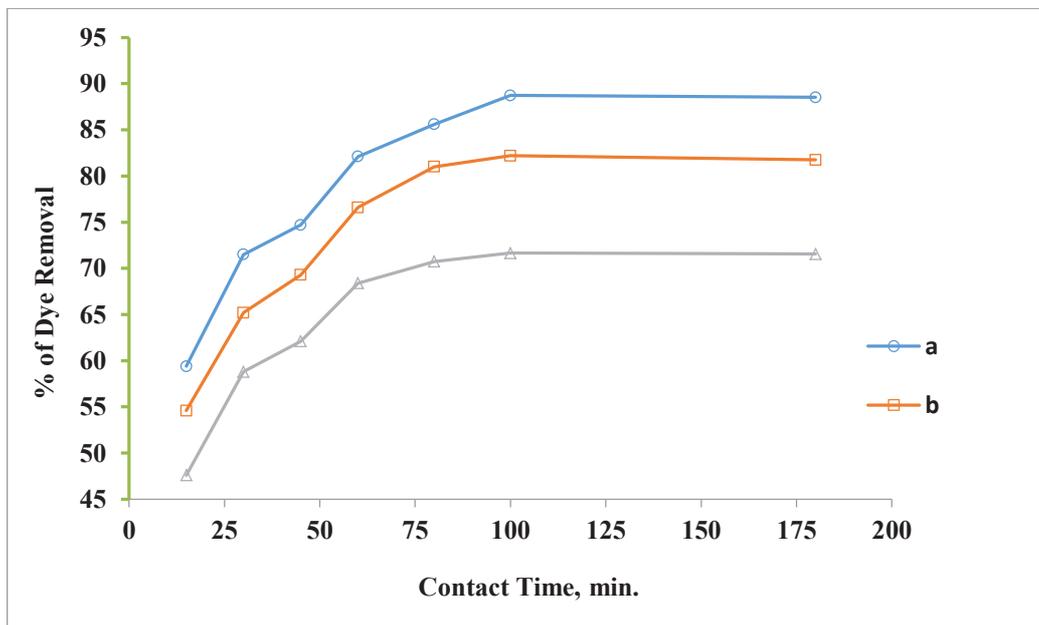


Figure 7. Langmuir adsorption isotherm for dye adsorption by SUNT -C2: pH = 8, initial concentration=50 mg/L, time=100 min., adsorbent dose =2.00 g., particle size; a: (90-125 μ m).

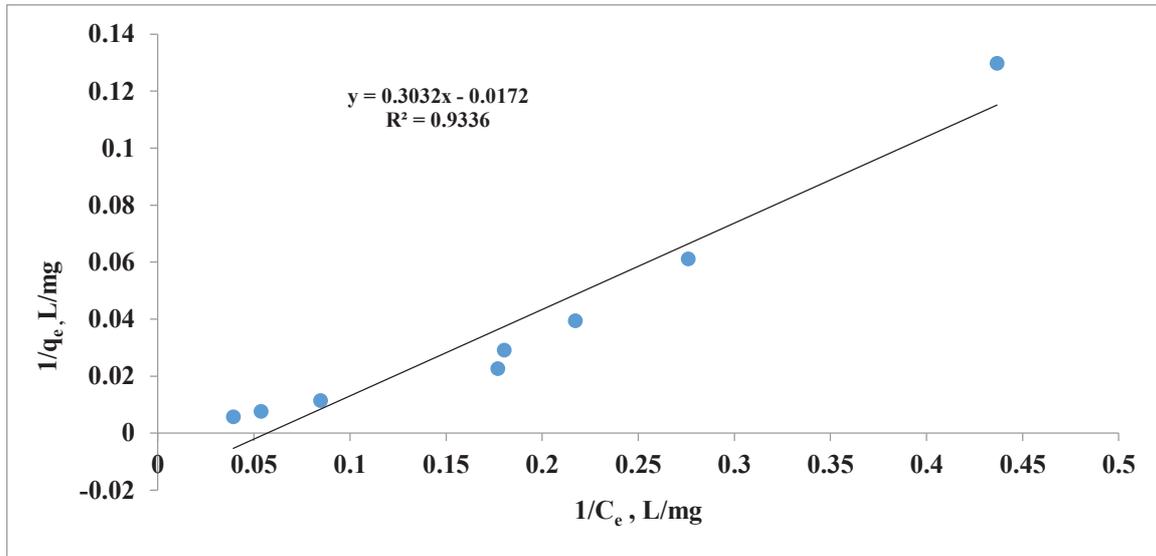


Figure 8. Freundlich adsorption isotherm for dye adsorption by SUNT -C2: pH = 8, initial concentration=50 mg/L, time=100 min., adsorbent dose =2.00 g., particle size; a: (90-125 μ m).

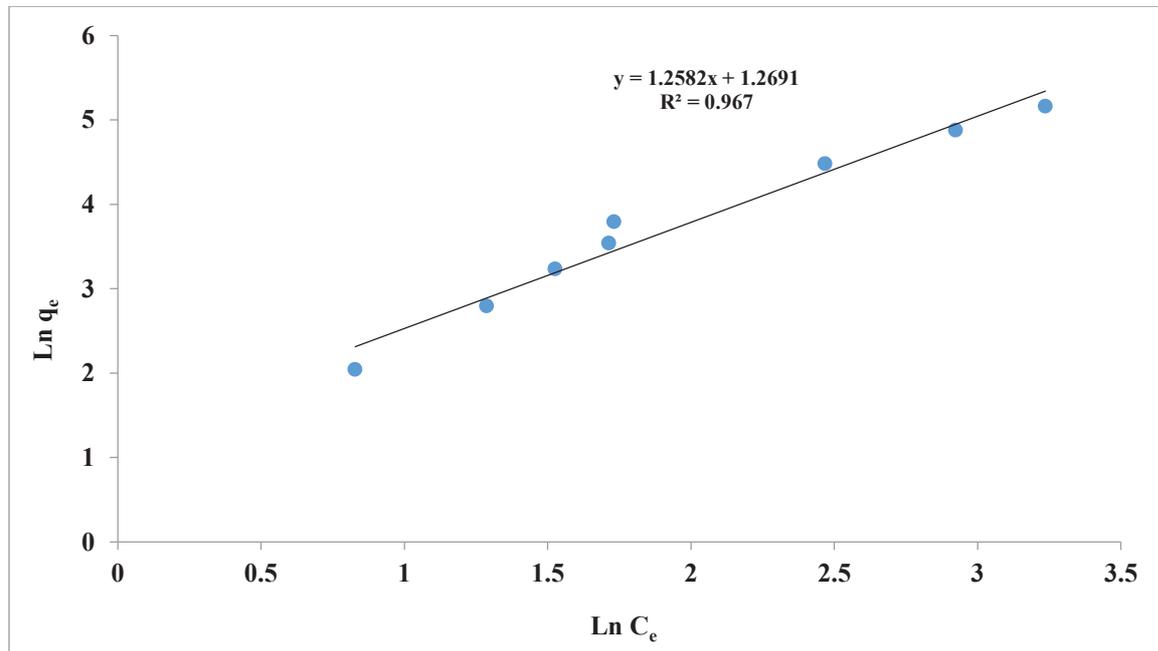


Figure 9. Adsorption kinetics of dye by SUNT -C2: pH = 8, initial concentration=50 mg/L, time=100 min., adsorbent dose =2.00 g., particle size; a: (90-125 μ m).

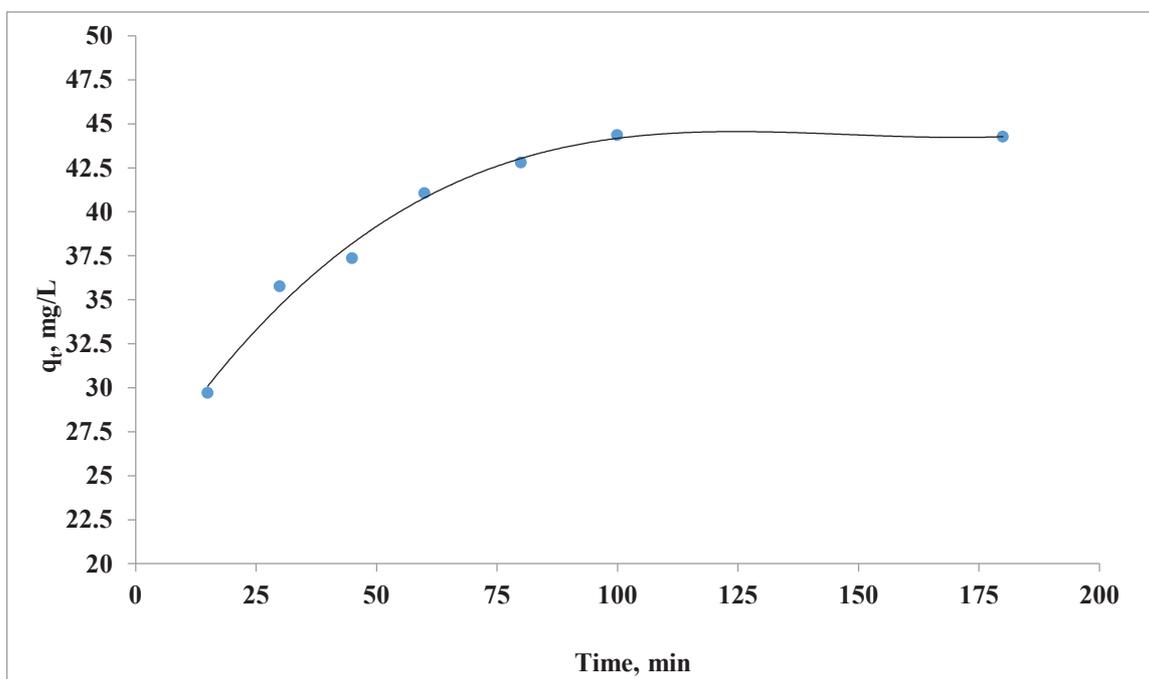


Figure 10. Lagergren pseudo-first order plot for the adsorption of dye by SUNT -C2: pH = 8, initial concentration=50 mg/L, adsorbent dose =2.00 g., particle size; a: (90-125 μ m).

