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Kinetic and Thermodynamic Studies of the Adsorption of Methylene Blue on Processed and Unprocessed Cotton Fibre

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Abstract:
The use of cotton fibre (processed and unprocessed) for the adsorption of methylene blue and indigo solution at different contact time with temperature, pH and temperatures were investigated. The adsorbent showed good potential for adsorption of methylene blue at 298 K and 308 K with maximum uptake of 4.00 mg/g for processed and unprocessed cotton respectively. Experimental data were analyzed by using two adsorption isotherms (Langmuir and Freundlich). Langmuir model shows best fit compared to Freundlich model. Pseudo – second order best describe their adsorption kinetic on the experimental data. Thermodynamic parameters such as $\Delta H°$, $\Delta G°$ and $\Delta S°$ proved that adsorption mechanism of methylene blue is spontaneous and endothermic in the ranges of temperature 288 – 308 K for processed cotton fibre while it was also spontaneous and exothermic in the range of temperature 288 – 308 K for unprocessed cotton fibre. This results of this study showed that cotton fibre (processed and unprocessed) can be used as adsorbent for the adsorption of methylene blue.

Keywords: *Methylene blue, adsorption, cotton kinetics*

1. Introduction

Chemical kinetics is the study of rates of chemical processes, effect of various variables, and rearrangement of atoms formation of intermediates. The factors that affect the speed of reactions and the mechanism by which reactions proceed are; nature of reactants, the concentration of the reactants, the temperature at which the reaction takes place and catalyst or inhibitors that affect the reactions (Zumdahl, 2002). Kinetics is the area of chemistry concerned with reaction rates, from which reaction rate laws and rate constants are derived.

Chemical thermodynamics studies the nature of the role of entropy in the process of chemical reactions and has provided the bulk of expansion and knowledge of the field. (Clark,2004). Chemical thermodynamics is the study of the interrelation of heat and work with chemical reactions or with physical changes of state.it involve the application of mathematical methods to the study of chemical questions and the spontaneity of processes.

Adsorption the word was coined in 1881 by German physicist Heinrich Kayser. It is defined as the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface.it is a surface-based process or phenomenon. Adsorption is present in many natural, physical, biological and chemical systems and is widely used in industrial applications such as heterogeneous catalysts (Czelej *et al*., 2016), activated charcoal. Adsorption is usually described through isotherms, that is, amount of adsorbate on the adsorbent as a function of its concentration (if liquid) or pressure (if gas) at constant temperature.

1.1. Dye

A dye is a coloured substance that has affinity to the substrate to which it is being applied. Dye possess colour because they absorb light in the visible spectrum (400-700nm), they have at least one chromophore (colour bearing group), have a conjugated system that is, a structure with alternating double and single bonds and exhibit resonance of electrons, which is a stabilizing force in organic compounds. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber. Dye may be natural or synthetic. The majority of natural dyes are from plant sources – roots, berries, bark, leaves, and wood, fungi, and lichens. The first human - made (synthetic) organic dye, Mauveine, was discovered serendipitously by William Henry Perkin in 1856. Synthetic dyes cost less, they offered a vast range of new

colors, and they imparted better properties to the dyed materials. Dyes are now classified according to how they are used in the dyeing process. Dyes currently occupy an important place in the industrial sector. They are widely used in paper, cosmetic, food industry, particularly in the textile industry (Garg *et al*.,2005). These releases consisting surfactants, dispersing and wetting, dyes and trace metals are toxic to most living organisms (Richard *et al*., 2015, Ndi *et al*., 2013). Hence, the extensive use of dyes in everyday life has created problems both in food and in the environment (Zhenwang *et al*., 2000). Synthetic dyes are one of the main pollutant groups of water and waste water. Dye concentration in wastewater causes problems in several ways: the presence of dyes in water, even in low quantities, is highly visible and undesirable, inhibit the growth of aquatic biota and interferes with gas solubility in water bodies (Wang *et al*.,2005b, Garg *et al*.,2004 & O-zer & Durson 2007). Direct discharge of dyes containing effluents into the environment may cause the formation of toxic carcinogenic breakdown products. The highest rates of toxicity were found amongst basic and diazo dyes (Lata *et al*., 2007). There are conventional method methods for treating dye containing wastewaters these include: electrochemical treatment, coagulation and flocculation, chemical oxidation, liquid -liquid extraction and adsorption (Fan *et al*., 2008, Tak-Hyun *et al*., 2004, Oguz &Keskinler , 2007 & Wang *et al*., 2005b). Adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substance (Lata et al., 2007).

1.1.1. Methylene Blue

Methylene blue is a cationic dye with a molecular formula $C_{16}H_{18}N_3SCl$ belongs to the family of xanthines. It is also known as methylthioninium chloride, when dissolved in water have a dark blue colour, it has strong affinity for solid surfaces (Leupin & Badruzzaman, 2005) particularly for the surfaces of opposite charge. Methylene blue is widely used as REDOX indicator in analytical chemistry and also used for the determination of the specific surface of clay minerals (Lavine *et al*., 2001). Solutions of methylene blue are blue in an oxidizing environment, but will turn colourless when exposed to a reducing agent. Most industrial effluents contain methylene blue, it is non-biodegredable and highly toxic to humans, plants and aquatic animals.in human beings methylene blue may cause nausea, vomiting, diarrhoea, headache, blindness and dizziness. The structure is as shown below

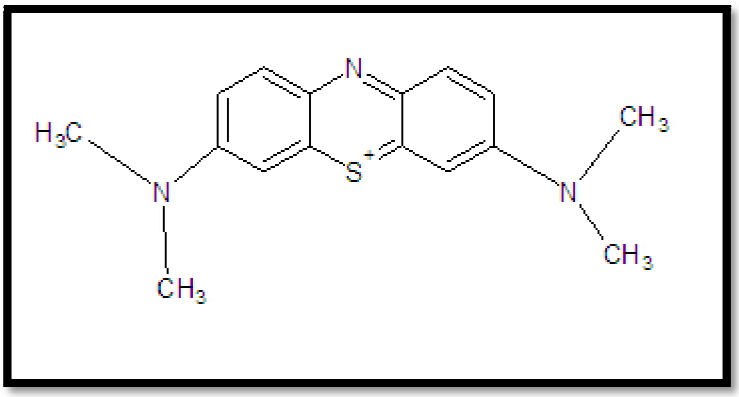

Figure1: Structure of Methylene Blue

1.2. Cotton

Cotton is a soft, fluffy staple fiber that grows in a boll, or protective case around the seed of cotton plant. It belongs to the genus Gossypium in the mallow family of Malvaceae. It is a shrub native to tropical and subtropical region around the world including America, India and Africa. It is currently the leading plant fibre crop and is grown commercially in the temperate and tropical region (Khadi et al., 2010). It is often spun into yarn or thread and used to make soft, textile. Cotton fibre is cellulosic fibre composed of mainly alpha –cellulose (88.0-96.5%) (Hsieh, 2007). The specific chemical compositions of cotton fibres vary by their varieties, growing environment (soil, water and temperature) and maturity, the non–cellulosic include: protein, waxes, pectin, inorganics and other substances. The non –cellulosic component in the cotton fibres, such as the waxes and pectin are most responsible for the hydrophobicity or low water wettability of raw cotton fibres (Hsieh 2007).

1.3. Factors Affecting Adsorption

1.3.1. pH

The pH of dye solution seems to be the most important parameter in the whole adsorption process (Jain & Shrivastava, 2008). It affects both the structure of the adsorbent and the adsorbate and the mechanism of adsorption.

The effect of pH on dye solution has been studied by many researchers and the results indicated that the pH values of solution could significantly influence adsorption. The effect of pH on the adsorption of methylene blue on wheat shells shows that dye uptake increase with increasing pH, and it increased from 5.76 to 9.57 mg/g for an increase in pH from 2 to 9, at higher pH

values (5-9) , the dye adsorption was almost constant (Yasemin & Haluk, 2006). This was explained to be because the surface of wheat shells may contain large number of active sites and the solute uptake can be related to the active sites, at higher pH, the surface of wheat shells may become negatively charged, which enhances the positively charged methylene blue cation through electrostatic forces of attraction. (Yasemin & Haluk, 2006).

Another result from the adsorption of methylene blue onto activated carbon prepared from *Bos indicus* gudali bones shows that the discoloration is not significantly influenced by varying the pH. Thus, there was a light increase in the percentage of adsorption in acidic environment also that the increasing trend of removal of methylene blue with increasing pH is dependent on the nature of the adsorbent (Mohammad *et al*., 2012, Richard *et al*., 2015).

In another report a consistent increase in adsorption capacity of carbon nano tubes with methylene blue was noticed as the pH increased from 2-4, whereas in the range 4-12 the adsorption amount was only slightly affected by the pH (Zohre *et al*., 2010).

Some authors have reported that methylene blue adsorption usually increases as pH increases (Gupta *et al*., 2004, Singh *et al*., 2003).

The effect of pH on the adsorption of methylene blue onto activated carbon fiber and granular activated carbon showed that the amount of methylene blue adsorbed show a slight increase as pH increases also showed the maximum methylene blue adsorption onto both samples are at pH 11 (Hatem *et al*., 2013).

1.3.2. Adsorbent Dosage

Adsorbent dosage is an important parameter because this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage was studied on methylene blue adsorption on wheat shells by Yasemin & Haluk (2006) by keeping all other experimental conditions constant, the result showed that as the adsorbent concentration increased, the percentage of adsorption also increases, but the amount adsorbed per unit mass of the adsorbent decreased considerably it was reported that it was due to the adsorption sites remaining unsaturated during adsorption (Yasemin & Haluk 2006).

Richard et al., (2015) reported the amount of methylene blue adsorbed decreases as the mass of activated carbon increases, it may be as a result of aggregation of the adsorbent particles on the surface of activated carbon animal which causes a decrease in the surface area available for adsorption, thus the larger the surface area, the larger the amount adsorbed.

1.3.3. Effect of Temperature

A study of the temperature dependence of adsorption reaction gives a valuable knowledge about enthalpy, entropy changes during adsorption and temperature affects the solubility of the adsorbate and the equilibrium constant for adsorption. Zohre *et al*., (2010) studied the effect of temperature on the adsorption of methylene blue on carbon nano tubes, the experiment was performed at temperature of 290, 300 & 310K and it showed that the influence of temperature on the adsorption of dye (methylene blue) onto carbon nano tubes increase with increasing temperature the adsorbent shows the endothermic nature of adsorption.

The adsorption ability of wheat shells for methylene blue increased with increase in temperature that is, from 16.56 to 21.50 mg/g by increasing the temperature of the solution from 303 to 323K which indicates the process is endothermic.

The adsorption capacity of activated carbon prepared from Bos indicus gudali bones with methylene blue increases with temperature, it may be as a result in the mobility of dye ion with temperature.

1.3.4. Thermodynamics Parameter of Adsorption

The thermodynamic parameters namely free energy ($\Delta G°$), Enthalpy ($\Delta H°$) and entropy ($\Delta S°$) have an important role to determine spontaneity and heat change for the adsorption process. Thermodynamic parameters were calculated using the following relations (Karago *et al*., 2008, Pehlivan & Arslan 2007 and Richard et al., 2015).

$\Delta G° = -RT \ln K_c$

The equilibrium constant qe and ce are amount adsorbed (mg/g) and concentration of solution (mg/L) respectively.

R = universal gas constant (8.314 J/mol/K)

T = is temperature in K. ($\Delta H°$) and ($\Delta S°$) parameters can be calculated from the slope and intercept respectively from a graph of $\ln K_c$ vs. $1/T$. $\Delta G°$ can be determined using ln Kc values for different temperatures.

Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes showed that ΔG° is negative which means the process is spontaneous and ΔH° is positive which indicates that the adsorption process is endothermic for methylene blue (Zohre *et al*., 2010).

A kinetics and thermodynamics study of methylene blue adsorption on wheat shells showed that ΔG° is negative which means the process is spontaneous and ΔH° is positive which indicates that the adsorption of methylene blue onto wheat shells is an endothermic process. ΔS° was observed to be positive which indicate the affinity of the adsorption for methylene blue (Yasemin & Haluk, 2006)

A study on batch equilibrium, kinetic and thermodynamic studies on adsorption of methylene blue in aqueous solution onto activated carbon prepared from *bos indicus gudali* bones, thermodynamic parameters such as $\Delta H°$, $\Delta G°$ and $\Delta S°$ proved that adsorption mechanism of Methylene blue onto activated carbon prepared from *Gudali* bones is possible, and thermodynamically spontaneous and exothermic (Richard *et al*.,2015).

In another study, kinetic and thermodynamic studies of indigo adsorption on some activated bio-solids showed that the thermodynamic parameter of the adsorption process fitted very well with the experimental data, the Gibb's free energy ($\Delta G°$) for all adsorption reaction were negative which indicate that the process is spontaneous (Abayomi & Jamiu, 2011).

1.3.5. Equilibrium Parameters of Adsorption

Equilibrium data commonly known as adsorption isotherms are basic requirements for the design of adsorption systems. Classical adsorption models (Langmuir, Freudlich, Redlich –Perterson, Tempkin and Sips) are used to describe how adsorbates interact with adsorbent thus, the correlation of equilibrium data using either a theoretical or empirical equation for interpretation and prediction of adsorption data is essential.

1.3.6. Adsorption Kinetics Studies

The adsorption kinetics shows the evolution of the adsorption capacity through time and it is necessary to identify the types of adsorption mechanism in a given system. The following models are used to describe the adsorption kinetics behaviour pseudo-first order and pseudo-second order.

2. Materials and Method

2.1. Sample Collection

2.1.1. Collection of Adsorbent (Cotton)

In this study, *Gossypium L.* cotton fibre (processed and unprocessed) a low cost and abundant adsorbent were used for the adsorption studies. The cotton fibre (processed) used in this research work were purchased in July / August , 2017 from Angwan lambu Keffi, Nasarawa State, Nigeria, and the unprocessed cotton was purchased from Keffi market, Nasarawa State, Nigeria.

2.1.2. Collection of Adsorbate (Dye)

The adsorbate used in this study is methylene blue dye; it was purchased from BDH chemical product.

2.2. Sample Preparation

2.2.1. Preparation of Adsorbent

The adsorbents (processed and unprocessed) were air-dried at room temperature for 24 hours before use.

2.2.2. Preparation of Adsorbate

The adsorbate (methylene blue) was oven – dried for 2 hours at 110^{o}C before use. It was prepared with deionized water. Stock solutions (100 mgL^{-1}) of the dye was prepared, which was diluted to the required initial concentration

2.2.3. Preparation of Buffer

Phosphate buffer (standard) was prepared at pH 7.0 using 29.1 mL of 0.1M NaOH and 50 mL of 0.1M KH_2PO_4 and it was made to 1000 mL with deionized water in a 1000 mL volumetric flask, it was thoroughly stirred using magnetic stirrer ,then a pH – meter was used to confirm the pH of the buffer. Other buffers at different pH were made from the standard pH by adjusting the buffer with 0.1M HCl and 0.1M NaOH.

2.2.4. Preparation of 0.1M HCl

The percentage purity and specific gravity of the acid were gotten from its bottle to determine the molarity of the acid. Thus, 4.42 mL of concentrated HCl was measured and made up to 500 mL in a standard flask with deionized water.

2.2.5 Preparation of 0.1 M NaOH

2.0 g of NaOH was weighed using analytical weighing balance and dissolved in 100mL of deionized water and made to mark in a 500mL volumetric flask.

2.3. Experimental Procedure

2.3.1 Influence of Contact Time on Adsorption

The effect of contact time of adsorbents with dye was investigated using 10 mgL^{-1} initial concentration of dye at different temperatures (288, 298 and 308K). 1.0 g of adsorbent (cotton fibre) were weighed and mixed with 100 mL of dye solution. The mixtures were stirred at time intervals of 5, 10, 15, 20, 40 and 60 minutes using magnetic stirrer. After adsorption the filtrates in both cases were analyzed using visible spectrophotometer by monitoring the absorbance changes in methylene blue at wavelength of 660 nm, the experiment was carried out in triplicate.

2.3.2. Influene of pH on Adsorption

5.0 mL of the dye solution was mixed with 45 mL of buffer solutions at different pH (5.6, 6.6, 7.0, 7.6, 8.6 and 9.0). The pH of the solutions were adjusted with 0.1 M HCl and 0.1 M NaOH where necessary using pH meter. 0.5 g of the adsorbents (cotton fibre) was weighed and added to the mixture at the prepared pH at constant temperature and time 298 K. After adsorption, the mixtures were analyzed using a visible spectrophotometer by monitoring the absorbance changes at 660nm for the adsorbate.

2.3.3. Influence of Temperature on Adsorption

To study the effect of temperature on methylene blue, 10 mL of the dye solutions were mixed with 50 mL of deionized water. 0.25 g of each of the adsorbents (cotton fibre) were added to the dye solutions at different temperature (288, 298, 308 K) at given time (75 mins), after adsorption the mixtures were analyzed using spectrophotometer by monitoring the absorbance changes at 660 nm for the methylene blue

2.3.4. Calculation of Dye Uptake

Dye uptake by the adsorbents was calculated using the following mass balance equation for the adsorbent (Zohre *et al*., 2010; Yasemin & Haluk 2006).

$$q = (C_0 - C_e)\frac{V}{M} \quad (2.1)$$

Where; q is the amount of dye adsorbed by the cotton fibre (mg/g)
C_o is the initial dye concentration in mg L^{-1}
C_e is the final dye concentration in mg L^{-1}
V is the volume of solution in L
M is the adsorbent weight in g

2.3.4.1. Kinetic Study

The adsorption kinetic shows the evolution of the adsorption capacity through time and it would be necessary to identify the types of adsorption mechanism in a given system. The following models are used to describe the adsorption kinetics behavior: Pseudo-first order model and Pseudo-second order model.

2.3.4.2. Pseudo- First Order: Lagergren Model

The adsorption kinetics can be described by a pseudo-first order equation as suggested by Lagergren.

$$\frac{dqt}{dt} = k_1(q_e - q_t) \quad (2.1)$$

Where q_e is the amount of dye adsorbed at equilibrium per unit weight of the adsorbent (mg/g),
q_t is the amount of as adsorbed at any time (mg/g) and
k_1 is the pseudo first-order rate (constant/min).
The values of log (q_e–q_t) were correlated with t. From the plot of log (q_e–q_t) versus t, k_1 and q_e can be determined from the slope and intercept respectively.

2.3.4.3. Pseudo-Second Order Model

The pseudo second-order kinetic rate equation is expressed as

$$\frac{dqt}{dt} = k_2(q_e - q_t)^2 \quad (2.3)$$

Where k_2 is the rate constant of the pseudo second-order adsorption equation (g / mg. min). The constants q_e and K_2 were obtained by plotting t/q versus t in equation.

2.4. Adsorption Equilibrium Models

Freundlich and Langmuir isotherm models were used for interpreting the dye adsorption equilibrium, they are the most common and simplest known relationships used in describing adsorption phenomenon (Jalali et al., 2002).

2.4.1. Langmuir Isotherm

The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogenous sites within the adsorbent and has found successful application to many sorption processes of monolayer adsorption. It can be written as

$$q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \quad (2.3)$$

q_m and k_L are Langmuir constants related to the adsorption capacity and energy of adsorption respectively. For the Langmuir equation the favorable nature of adsorption can be expressed in terms of dimensionless separation factor of equilibrium parameter, which is defined by:

$$R_L = \frac{1}{1 + k_L C_o} \quad (2.4)$$

Where; k_L is the Langmuir constant
C_o is the initial concentration of the adsorbate in solution.

The values of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$) or expressed by plotting C_e / q_e against C_e a straight line with Q_m and b as slope and intercept respectively.

2.4.2. Freundlich Isotherms

The Freundlich isotherm is an empirical equation employed to describe heterogeneous system. The Freundlich equation is

$$q_e = k_F C_e^{1/n} \quad (2.5)$$

Where k_F is a constant indicative of the adsorption capacity of the adsorbent (mg1- (1/n) L 1/n g−1) and n is an empirical constant related to the magnitude of the adsorption driving force. The magnitude of 1/n quantifies the favourability of adsorption and the degree of heterogenicity of the adsorbent surface. The plot of log q_e versus log C_e gives straight lines with slope of 1/n which shows that the adsorption of the dye follows Freundlich isotherm.

3. Result and Discussion

Table 1Shows the mean concentration of the stock solution of methylene blue at 660 nm wavelength

Mean Absorbance	Mean Concentration(mg/L) × 10^{-5}	S.D	S.E	%C.V
1.000	13.000	0.001	0.0002	0.047

Table 1: Initial Concentration of Stock Solution of Methylene Blue at Wavelength 660 Nm
S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage

Time	Mean	S.D Concentration(Mg/ L) × 10^{-5}	S.E	% C.V
5	3.990	0.014	0.008	4.394
10	3.980	0.005	0.003	1.466
15	3.870	0.009	0.005	2.933
20	2.500	0.011	0.007	5.948
40	3.500	0.012	0.007	4.560
60	3.700	0.004	0.003	1.516

Table 2: Effect of Contact Time of Adsorbent with Methylene Blue on Unprocessed Cotton at 15°C (288 K)
S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 1.0 G, Volume of Adsorbent = 100 Ml, Concentration of Adsorbate = 10 Mg/L, Wavelength = 660 Nm

Table 2 shows the mean concentration of the effect of contact time on adsorption with methylene blue on unprocessed cotton (natural cotton) at 288K (15°C) there is a decrease from 5 – 10 mins and a slight increase from 20 – 60 mins. The highest mean concentration was recorded at 5 mins ($3.99 \times 10^{-5} \pm 0.01$ mg/L) and the mean concentration was recorded at 20 mins ($2.50 \times 10^{-5} \pm 0.01$ mg/L).

Time	Mean Concentration(Mg/ L) × 10^{-5}	S.D	S.E	% C.V
5	3.60	0.009	0.005	3.282
10	3.83	0.018	0.010	6.022
15	3.40	0.012	0.007	4.515
20	3.84	0.014	0.008	4.786
40	3.73	0.003	0.001	0.868
60	3.99	0.009	0.006	3.192

Table 3: Effect of Contact Time of Adsorbent with Methylene Blue on Unprocessed Cotton at 25°C (298 K)
S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 1.0 G, Volume of Adsorbent = 100 Ml, Concentration of Adsorbate = 10 Mg/L Wavelength = 660 Nm

Table3. Shows the mean concentration of the effect of contact time on adsorption with methylene blue on unprocessed cotton (natural cotton) at 298K (25°C), it was observed that there was no definite pattern for the increase or decrease of the

mean concentration, but the highest mean concentration was seen at 60 mins ((3.99 x 10^{-5} ± 0.01 mg/L) and the lowest mean concentration was seen at 15 mins (3.40 × 10^{-5} ± 0.01 mg/L).

Time	Mean Concentration(Mg/ L) × 10^{-5}	S.D	S.E	% Cv
5	3.31	0.048	0.003	1.879
10	2.84	0.002	0.001	1.079
15	3.41	0.006	0.003	2.252
20	3.23	0.003	0.001	1.003
40	2.86	0.009	0.005	3.857
60	3.75	0.036	0.021	12.286

Table 4: Effect of Contact Time of Adsorbent with Methylene Blue on Unprocessed Cotton at 35°C (308K) S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 1.0 G, Volume of Adsorbent = 100 Ml, Concentration of Adsorbate = 10 Mg/L and Wavelength = 660 Nm

Table4. Shows the mean concentration of the effect of contact time on adsorption with methylene blue on unprocessed cotton (natural) at 308 K, the highest mean concentration was seen at 60 mins (3.75 × 10^{-5} ± 0.04 mg/L) and the lowest mean concentration was at 10 mins (2.84 × 10^{-5} ± 0.002 mg/L)

pH	Mean Concentration(mg/ L) × 10^{-5}	S.D	S.E	% C.V
5.6	4.17	0.01	0.0027	1.4449
6.6	6.24	0.01	0.0043	1.5319
7.0	6.23	0.01	0.0028	1.0206
7.6	6.32	0.01	0.0025	0.8872
8.6	6.84	0.01	0.0033	1.0889
9.0	4.22	0.01	0.0038	2.0327

Table 5: Effect of Ph on Adsorption of Methylene Blue on Unprocessed Cotton S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 0.5 G, Volume of Adsorbent = 50 Ml, Concentration of Adsorbate = 10 Mg/L, Wavelength = 660 Nm, Time = 20 Mins and Temperature = 298 K

Table .5 Shows the mean concentration on adsorption of methylene blue on unprocessed cotton (natural cotton) at pH (5.6 – 9.0), it was observed that there was a sharp increase from pH 5.6 (4.17 × 10^{-5} ± 0.01 mg/L) to pH 6.6 (6.24× 10^{-5} ± 0.01) and a gradual increase from pH 6.6 (6.24 × 10^{-5} ± 0.01) to pH 8.6 (6.84 × 10^{-5} ± 0.01 mg/L) at which the highest mean concentration was recorded , the lowest mean concentration was recorded at pH 5.6 (4.17 × 10^{-5} ± 0.01 mg/L).

Temp.(K)	Mean Concentration(Mg/ L) × 10^{-5}	S.D	S.E	% C.V
288	6.58	0.01	0.0031	1.0485
298	5.90	0.01	0.0049	1.8877
308	8.56	0.01	0.0056	1.4608

Table 6: Effect of Temperature on Adsorption of Methylene Blue on Unprocessed Cotton S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 0.25 G, Volume of Adsorbent = 60 Ml, Wavelength = 660 Nm, Time = 75 Mins

Table 6 Shows the effect of temperature on adsorption of methylene blue on unprocessed cotton (natural) 288 – 308K , the highest concentration was recorded at 308 K (8.56 × 10^{-5} ± 0.01 mg/L) and the lowest was recorded at 298K (5.90 × 10^{-5} ± 0.01 mg/L).

Time (Min.)	Mean Concentration(Mg/ L) × 10^{-5}	S.D	S.E	% C.V
5	3.26	0.02	0.012	8.087
10	2.88	0.01	0.007	5.418
15	2.76	0.03	0.018	14.543
20	1.74	0.01	0.006	7.551
40	2.03	0.00	0.001	1.085
60	2.26	0.01	0.004	4.240

Table 7: Effect of Contact Time of Adsorbent with Methylene Blue on Processed Cotton at 15°C (288 K) S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 1.0 G, Volume of Adsorbent = 100 Ml, Concentration of Adsorbate = 10 Mg/L, Wavelength = 660 Nm

Table 7 Shows the mean concentration of the effect of contact time on adsorption with methylene blue on processed cotton (synthetic) at 288 K, there was a regular trend of change in the mean concentration with increase in time, but a sudden decrease was seen at time 20 mins ($1.74 \times 10^{-5} \pm 0.01$ mg/L) at which the lowest mean concentration was recorded and the highest mean concentration was recorded at time 5 min ($3.26 \times 10^{-5} \pm 0.02$ mg/L)

Time (Min)	Mean Concentration(Mg/ L) × 10^{-5}	S.D	S.E	% C.V
5	1.94	0.01	0.0035	4.0302
10	1.89	0.00	0.0005	0.6487
15	2.43	0.00	0.0014	1.3316
20	2.36	0.01	0.0039	3.7693
40	2.29	0.01	0.0045	4.3682
60	2.46	0.02	0.0098	8.9303

Table 8: Effect of Contact Time of Adsorbent with Methylene Blue on Processed Cotton at 25°C (298 K) S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 1.0 G, Volume of Adsorbent = 100 Ml, Concentration of Adsorbate = 10 Mg/L, Wavelength = 660 Nm

Table 8: Shows the mean concentration of the effect of contact time on adsorption with methylene blue on processed cotton (synthetic) at 298 K , the highest concentration was seen at 60 mins ($2.46 \times 10^{-5} \pm 0.02$ mg/L) and the lowest mean concentration was seen at 10 mins ($1.89 \times 10^{-5} \pm 0.00$ mg/L).

Time (Min)	Mean Concentration(Mg/ L) × 10^{-5}	S.D	S.E	% C.V
5	2.81	0.001	0.0005	0.3780
10	2.63	0.003	0.0014	1.2328
15	2.53	0.024	0.0143	12.7072
20	3.36	0.001	0.0007	0.4822
40	3.14	0.007	0.0043	3.0469
60	2.93	0.002	0.0009	0.7543

Table 9: Effect of Contact Time of Adsorbent with Methylene Blue on Processed Cotton at 35°C (308 K) S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 1.0 G, Volume of Adsorbent = 100 Ml, Concentration of Adsorbate = 10 Mg/L, Wavelength = 660 Nm

Table 9: Shows the mean concentration of the effect of contact on adsorption with methylene blue on processed cotton (synthetic) at 308 K, the highest mean concentration was seen at 20 min ($3.36 \times 10^{-5} \pm 0.001$ mg/L) and the lowest mean concentration was seen at 15 mins ($2.53 \times 10^{-5} \pm 0.02$ mg/L).

pH	Mean Concentration (mg/ L) × 10^{-5}	S.D	S.E	% C.V
5.6	3.51	0.004	0.0021	1.3182
6.6	4.41	0.004	0.0022	1.1371
7.0	4.78	0.003	0.0018	0.8392
7.6	5.24	0.001	0.0005	0.2338
8.6	3.93	0.004	0.0021	1.2474
9.0	5.25	0.002	0.0009	0.4204

Table 10: Effect of Ph on Adsorption of Methylene Blue on Processed Cotton
S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage
Weight of Adsorbent = 0.5 G, Volume of Adsorbent = 50 Ml, Concentration of Adsorbate = 10 Mg/L,
Wavelength = 660 Nm, Time = 120 Mins and Temperature = 298 K

Table 10: Shows the mean concentration on adsorption methylene blue with processed cotton (synthetic) at pH 5.6 – 9.0 , it was observed that , there was a gradual increase from pH 5.6 (3.51 × 10^{-5} ± 0.004 mg/L) to pH 7.6 (5.24 × 10^{-5} ± 0.001 mg/L) and a sharp decrease in pH 8.6 and a sharp increase in pH 9.0 (5.25 × 10^{-5} ± 0.002 mg/L) which the highest mean concentration was recorded and the lowest mean concentration was recorded at pH 5.6

Temp.(K)	Mean Concentration(Mg/ L) × 10^{-5}	S.D	S.E	% C.V
288	8.93	0.02	0.0099	2.4984
298	9.26	0.01	0.0054	1.3217
308	7.63	0.04	0.0248	7.3091

Table 11: Effect of Temperature on Adsorption of Methylene Blue on Processed Cotton
S.D = Standard Deviation, S.E = Standard Error of Mean, C.V = Coefficient of Variation in Percentage Weight of Adsorbent = 0.25 G, Volume of Adsorbent = 60 Ml, Wavelength = 660 Nm And Time = 75 Mins

Table 11: Shows the mean concentration of the effect of temperature on adsorption of methylene blue on processed cotton (synthetic) from 288 – 308K , the highest mean concentration was recorded at 298 K (9.26 × 10^{-5} ± 0.01 mg/L) and the lowest mean concentration was recorded at 308 K (7.63 × 10^{-5} ± 0.04 mg/L)

3.1. Effect of Temperature

A study of the temperature dependence of adsorption reactions gives valuable knowledge about the enthalpy and entropy changes during adsorption. The adsorption of methylene blue onto cotton fibre (processed and unprocessed) were studied at 288, 298 and 308K. For unprocessed cotton in Fig. 8 it was seen that the amount of methylene blue adsorbed increases as temperature increases from 288 - 298 K but reduces from 298 K to 308 K. From Fig.9 (processed) it was seen that the amount of methylene blue adsorbed from 288 K decreases to 298 K and increases from 298K to 308K, although there was no trend or pattern of increment of amount of methylene blue adsorbed. Report from some studies showed that amount of dye increases as temperature increases because the mobility of dye molecules increases with temperature.

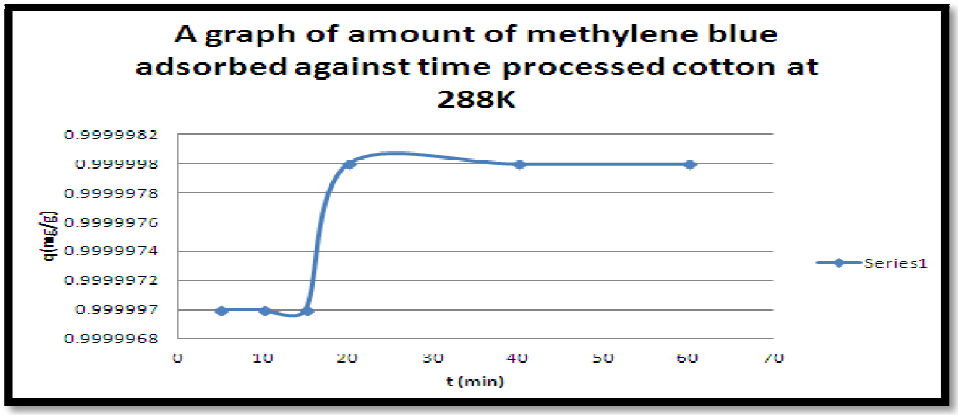

Figure1: Effect of Contact Time on the Adsorption of Methylene Blue on Processed Cotton (T = 288 K, W = 1.00 G, And V= 0.1 L)

It was observed that there was an increase in the amount of methylene adsorbed, it was almost equal from 5 – 15 mins. and 20 – 60 mins., this could be as a result of increase in time tend to increase to amount of methylene blue adsorbed (Fig.3.1)

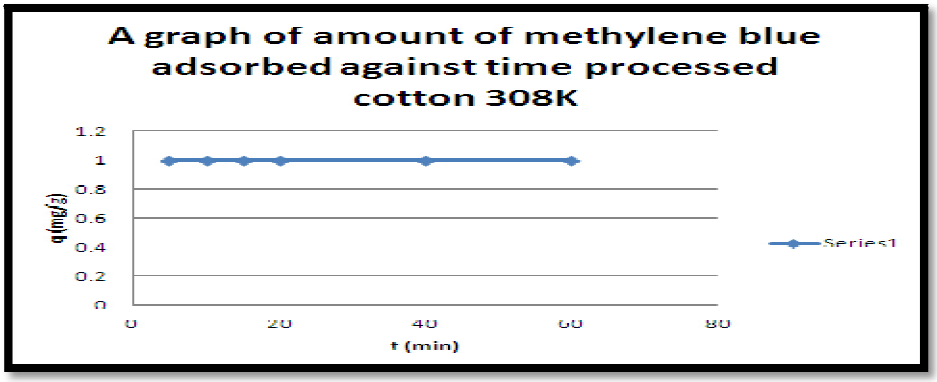

Figure 2: Effect of Contact Time on the Adsorption of Methylene Blue on Processed Cotton (T = 308 K, W = 1.00 G, and V= 0.1 L)

It is observed that at this temperature, time does not affect the amount of methylene adsorbed it may be because it is at room temperature thus, the reaction could be said not to be time dependent at this temperature Fig.2.

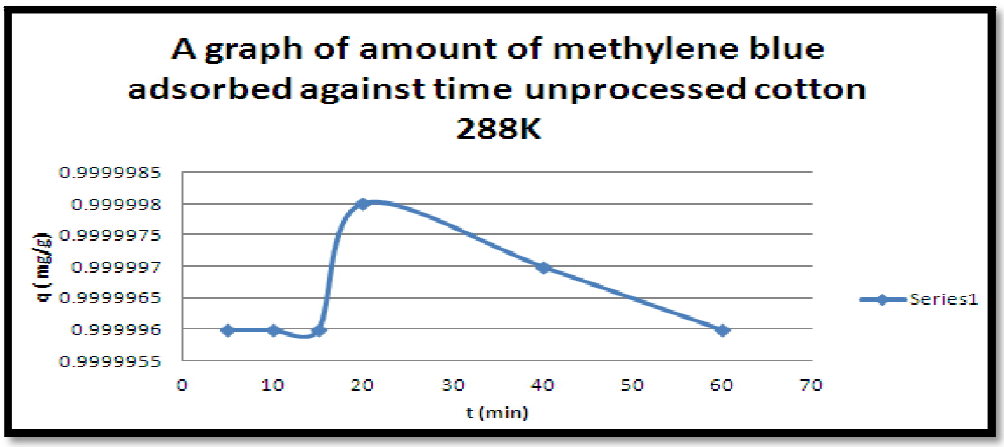

Figure 3: Effect of Contact Time on the Adsorption of Methylene Blue on Unprocessed Cotton (T = 288 K, W = 1.00 G, and V= 0.1 L)

Here, the amounts of methylene blue adsorbed were almost uniform but there was an increase from 15 min to 20 min Fig.3.5.

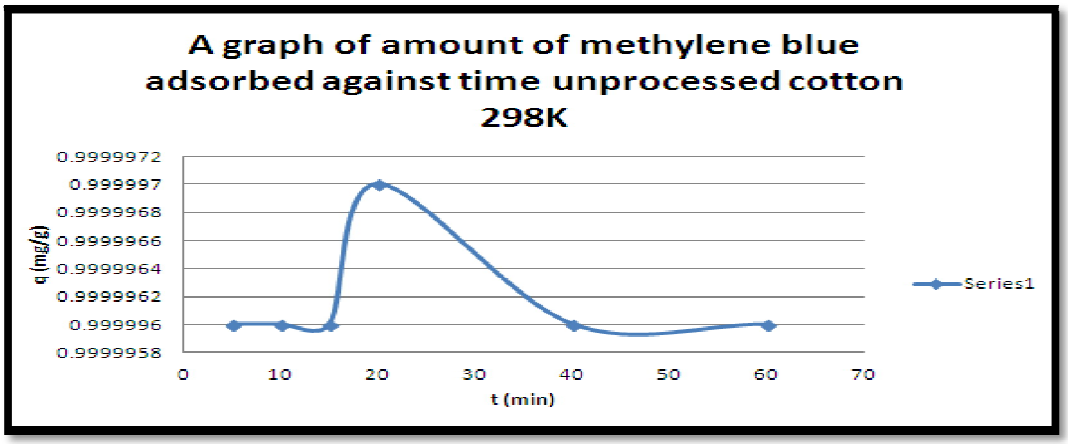

Figure 4: Effect of Contact Time on the Adsorption of Methylene Blue on Unprocessed Cotton (T = 298 K, W = 1.00 G, And V= 0.1 L)

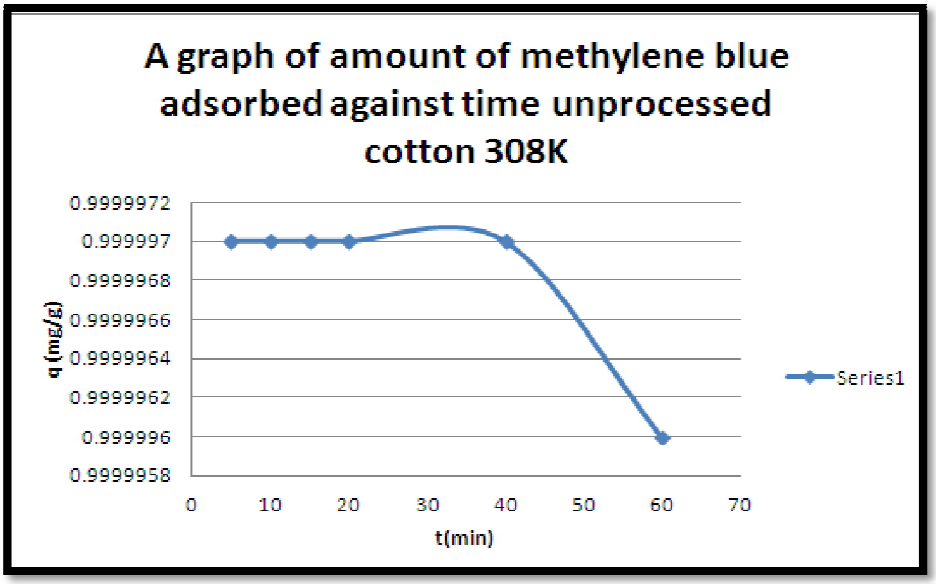

Figure 5: Effect of Contact Time on the Adsorption of Methylene Blue on Unprocessed Cotton (T = 308 K, W = 1.00 G, and V= 0.1 L)

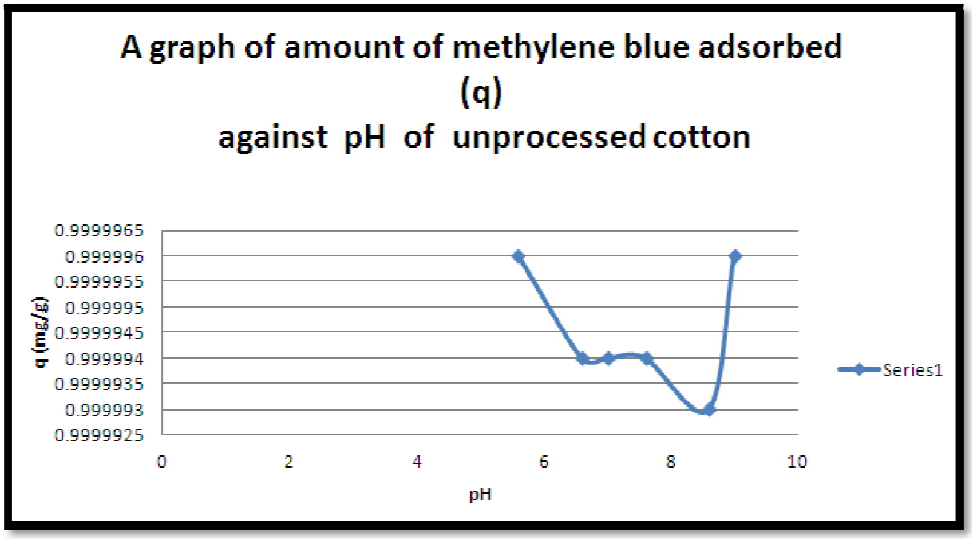

Figure 6: Effect of Ph on the Adsorption of Methylene Blue on Unprocessed Cotton Fibre (T = 288K, C_o = 10 Mg/L, Adsorbent = 0.5g, V = 0.05 L Contact Time = 120 Min)

3.2. Effect of pH

pH is an important factor in any adsorption study, because it influences both the structure of the adsorbent, the adsorbate and the mechanism of adsorption. the efficiency of adsorption at different pH were taken, from Fig. 6 the amount of methylene blue adsorbed were the same at pH 5.6 and 9.0, but the amount adsorbed at pH 6.6 – 8.6 were almost constant. Although it has been reported that methylene blue adsorption usually increases as the pH is increased (Zohre et al., 2010, Guptal et al.,2004). However, it does not explain the constant adsorption by unprocessed cotton fibre. From Fig.7 the amount of methylene blue adsorbed decreases from acidic medium to neutrality, this was entirely different from Fig. 6 above (unprocessed cotton) in other words, it is said that adsorption decreases with pH.

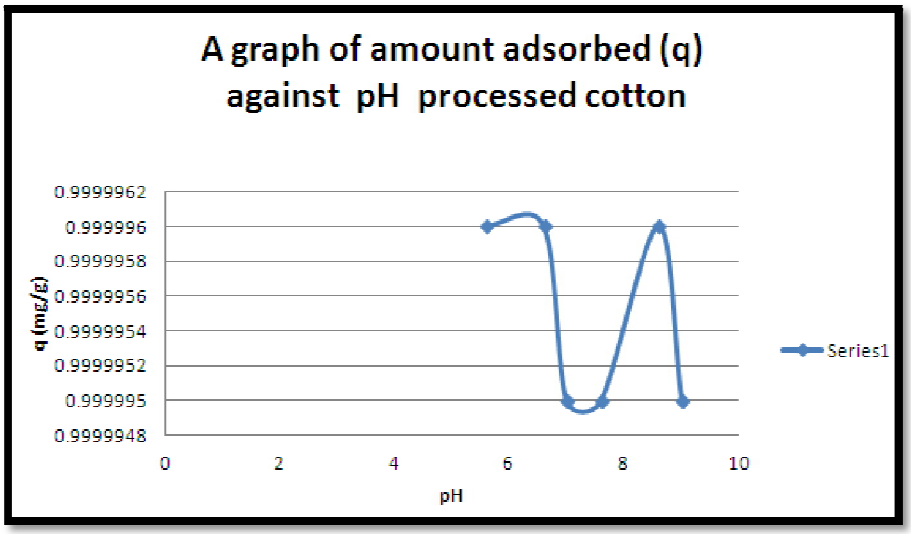

Figure 7: Effect of Ph on the Adsorption of Methylene Blue on Processed Cotton Fibre (T = 288K, C_o = 10 Mg/L, Adsorbent = 0.5g, V = 0.05 L Contact Time = 120 Min)

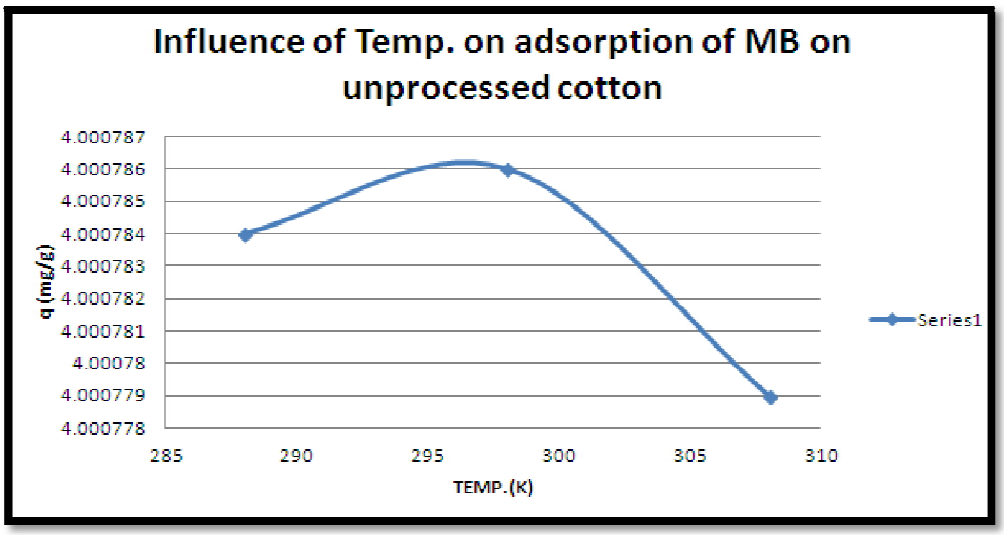

Figure 8: Effect of Temperature on the Adsorption of Methylene Blue on Unprocessed Cotton Fibre

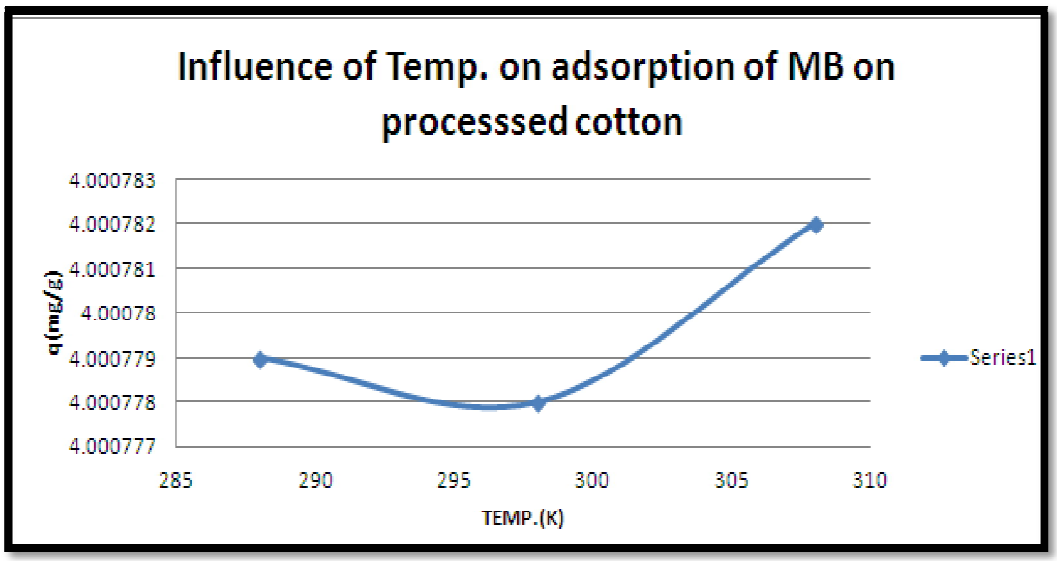

Figure 9: Effect of Temperature on the Adsorption of Methylene Blue on Processed Cotton Fibre

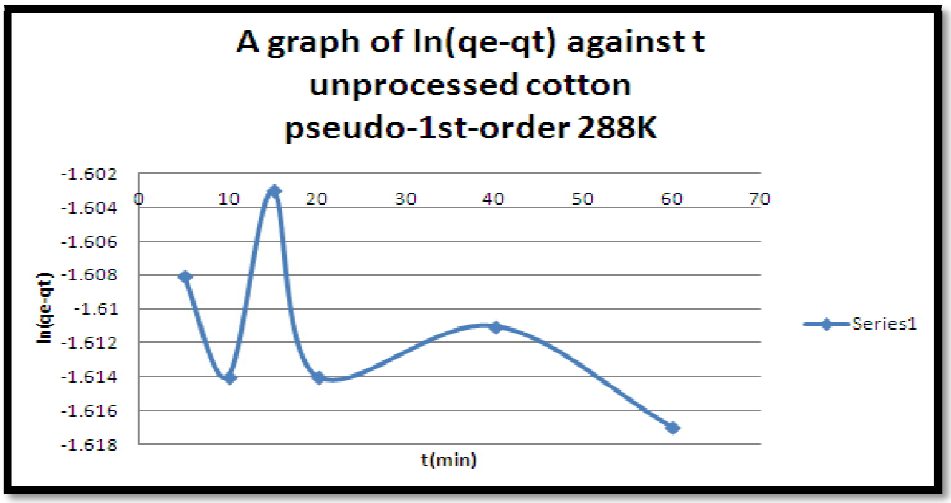

Figure 10: Modeling Methylene Blue Adsorption Kinetics by Unprocessed Cotton Fibre (Pseudo-First Order Model)

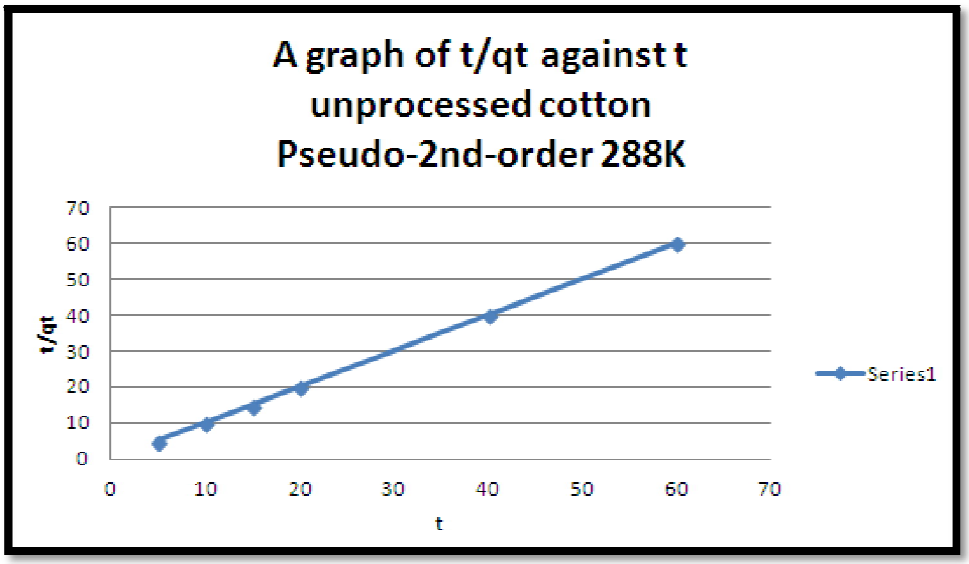

Figure 11: Modeling Methylene Blue Adsorption Kinetics by Unprocessed Cotton Fibre (Pseudo-Second Order Model)

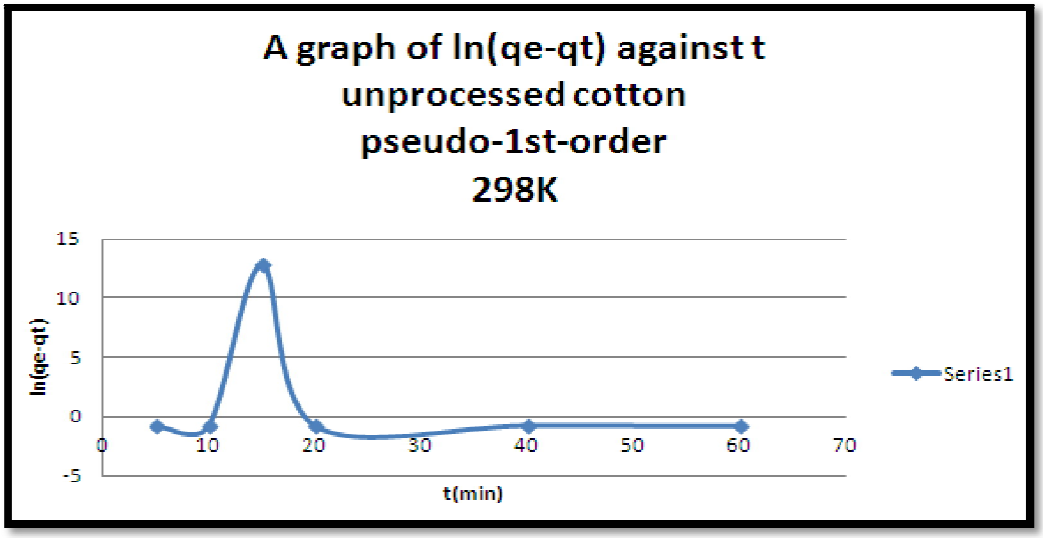

Figure12: Modeling Methylene Blue Adsorption Kinetics by Unprocessed Cotton Fibre (Pseudo-First Order Model)

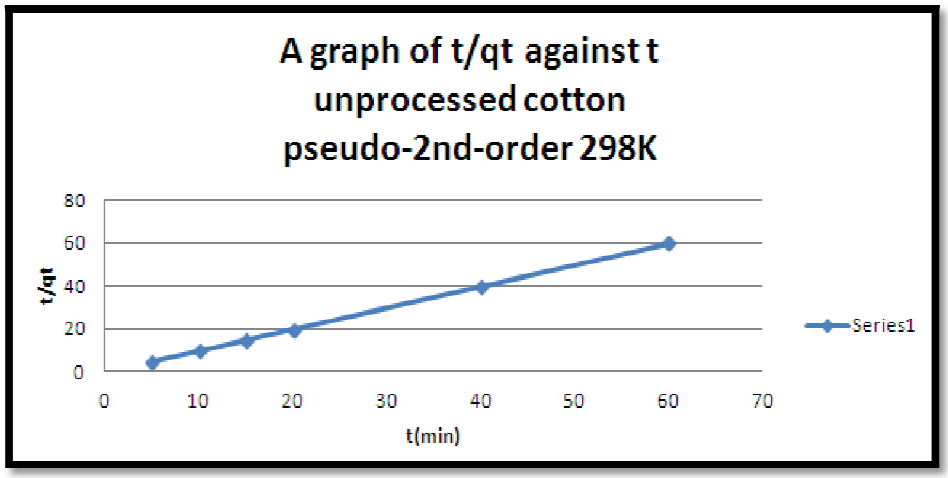

Figure13: Modeling Methylene Blue Adsorption Kinetics by Unprocessed Cotton Fibre (Pseudo-Second Order Model)

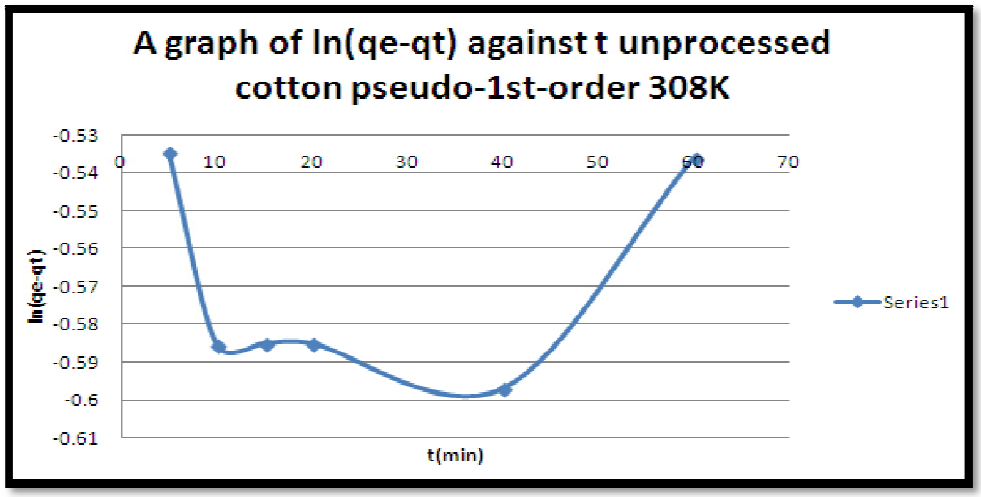

Figure 14: Modeling Methylene Blue Adsorption Kinetics by Unprocessed Cotton Fibre (Pseudo-First Order Model)

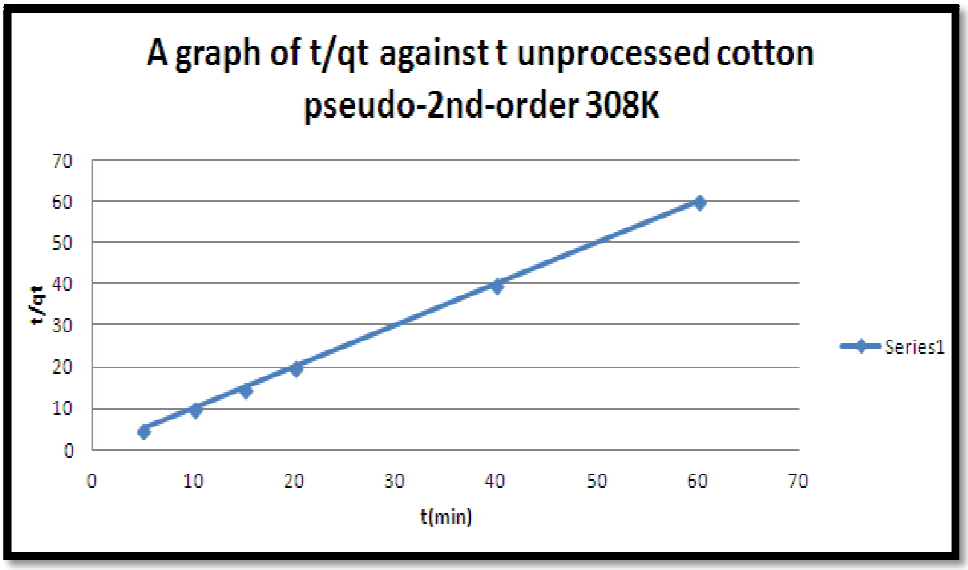

Figure 15: Modeling Methylene Blue Adsorption Kinetics by Unprocessed Cotton Fibre (Pseudo-Second Order Model)

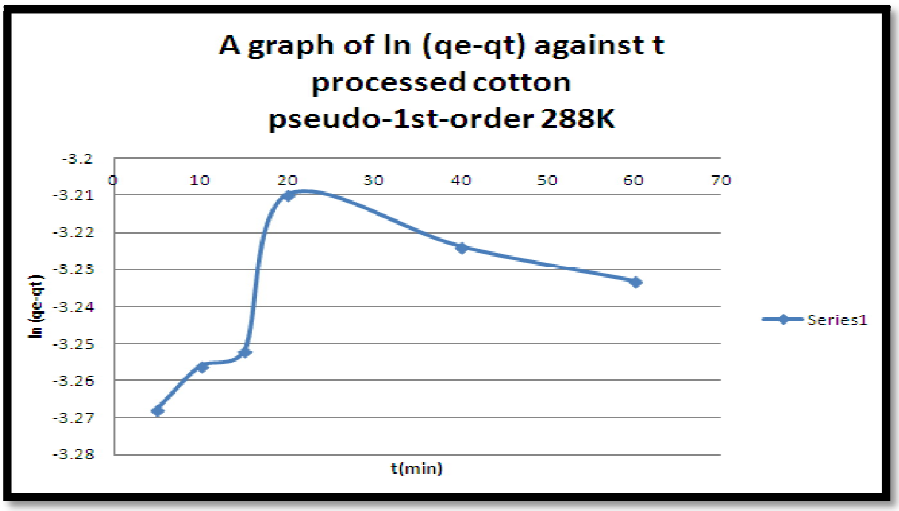

Figure16: Modeling Methylene Blue Adsorption Kinetics by Processed Cotton Fibre (Pseudo-First Order Model)

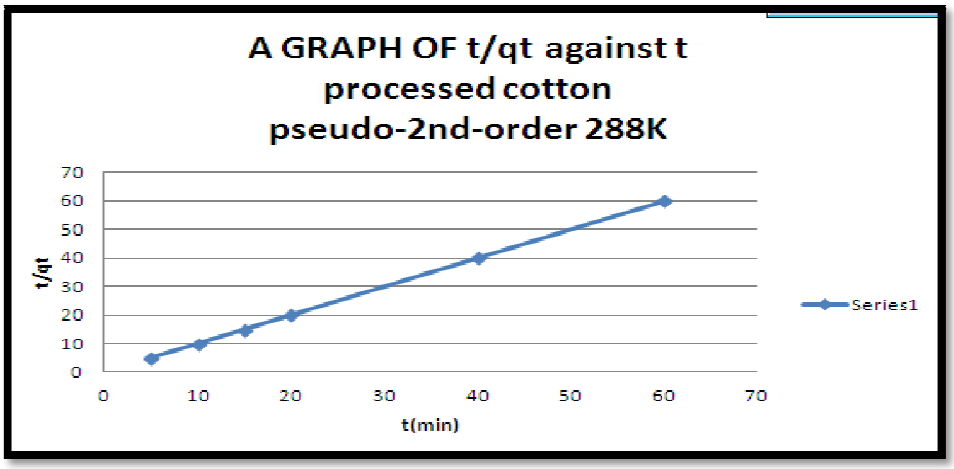

Figure 17: Modeling Methylene Blue Adsorption Kinetics by Processed Cotton Fibre (Pseudo-Second Order Model)

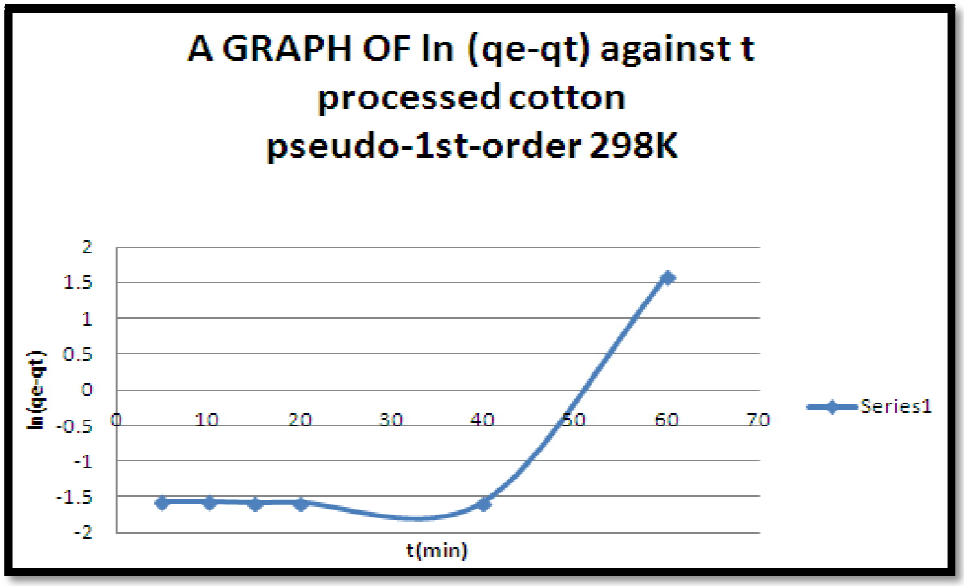

Figure18: Modeling Methylene Blue Adsorption Kinetics By Processed Cotton Fibre (Pseudo-First Order Model)

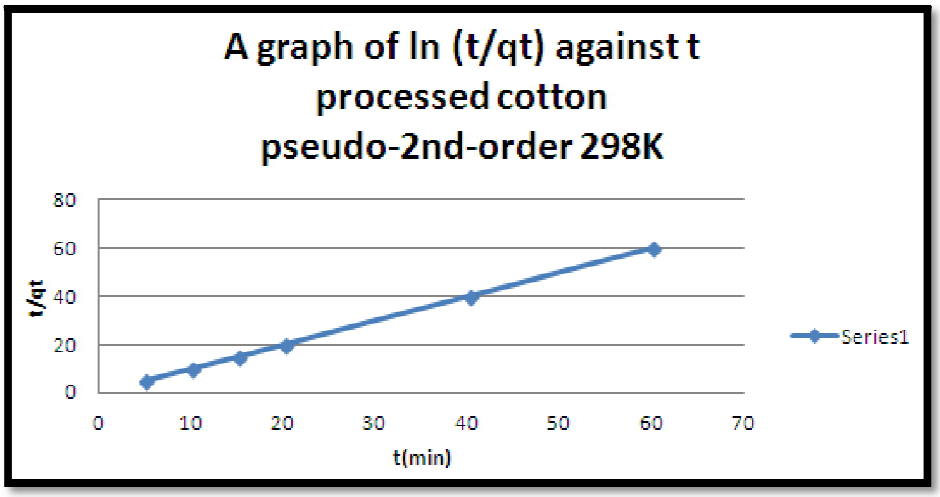

Figure 19: Modeling Methylene Blue Adsorption Kinetics by Processed Cotton Fibre (Pseudo-Second Order Model)

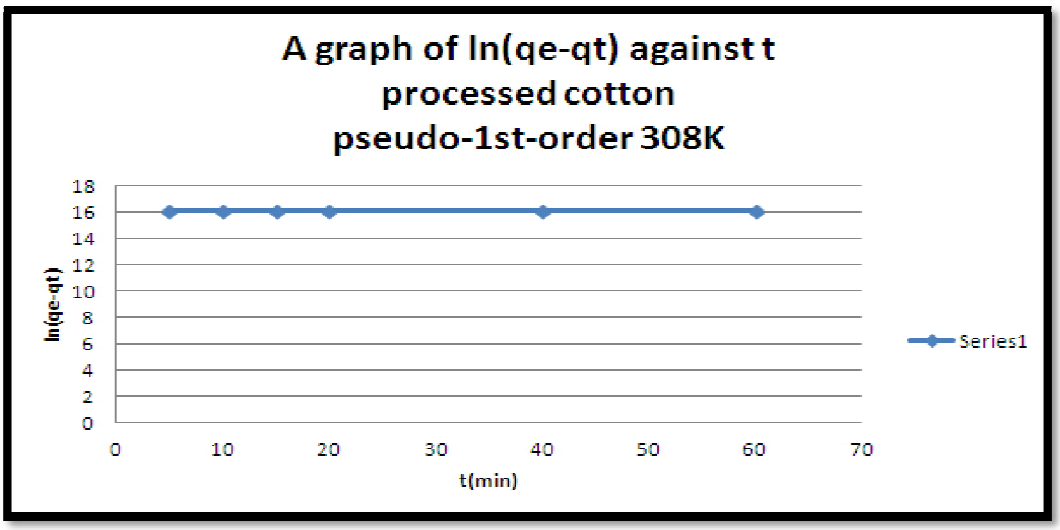

Figure 20: Modeling Methylene Blue Adsorption Kinetics by Processed Cotton Fibre (Pseudo-First Order Model)

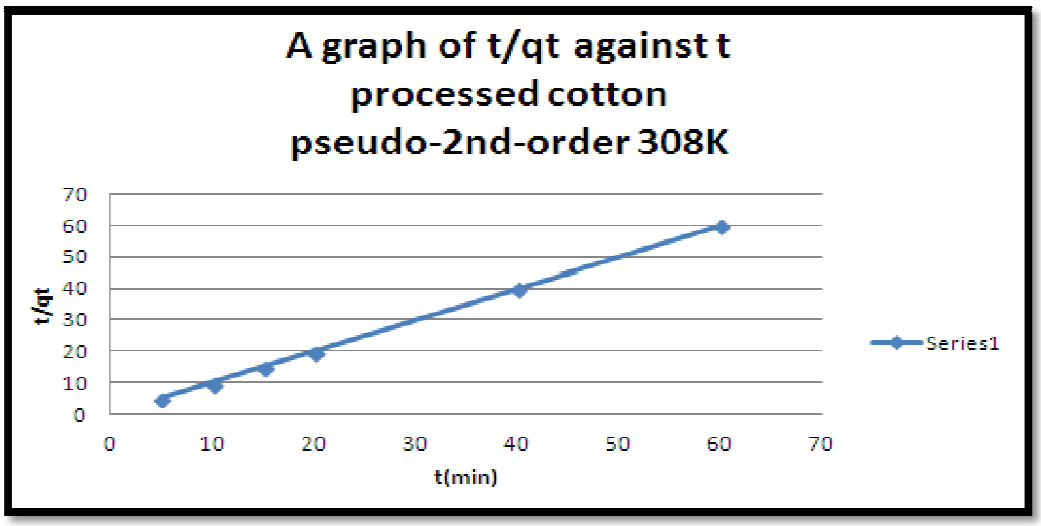

Figure 21: Modeling Methylene Blue Adsorption Kinetics by Processed Cotton Fibre (Pseudo-Second Order Model)

T (K)	ΔG° (Kj.mol^{-1})	ΔH°(Kj.mol^{-1})	ΔS°(Kj.mol^{-1}.k^{-1})	R^2
288	- 27.03			
298	- 28.24	1.17	0.0073	0.454
308	- 28.21			

Table 12: Thermodynamic Parameters of Adsorption of Methylene Blue on Unprocessed Cotton at Different Temperatures

T (K)	ΔG° (Kj.mol^{-1})	ΔH°(Kj.mol^{-1})	ΔS°(Kj.mol^{-1}.k^{-1})	R^2
288	- 26.23			
298	- 27.07	- 0.73	0.014	0.014
308	- 28.46			

Table 13: Thermodynamic Parameters of Adsorption of Methylene Blue on Processed Cotton at Different Temperatures

Cotton type	Model	parameters		T (K)		
			288	298		308
		K_1(min^{-1})	-0.0001	-0.0619	0.0002	
Unprocessed	pseudo-first order	q_e (mg/g)	1.6079	3.0634	0.5766	
		R_1^2	0.3014	0.055		0.0337
		K_2 (g.mg^{-1} .min^{-1})	0.0000	0.0000	0.0000	
	Pseudo-second order	q_e (mg/g)	1.0000	1.0000		1.0000
		R_2^2	1.0000	1.0000		1.0000
		K_1(min^{-1})	0.0006	0.0499		0.000
Processed	pseudo-first order	q_e (mg/g)	3.2545	2.2900	16.118	
		R_1^2	0.2948	0.6646		0.0000
	Pseudo-second order	K_2 (g.mg^{-1} .min^{-1})	0.0000	0.0000	0.0000	
		q_e (mg/g)	1.0000	1.0000		1.0000
		R_2^2	1.0000	1.0000		1.0000

Table 3.14: Adsorption Kinetic Parameters of Methylene Blue on Cotton (Processed & Unprocessed)

		Langmuir isotherm			Freundlich isotherm		
Cotton type	**T(K)**	**Q_m(mg/g)**	**b (l/mg)**	**R^2**	**K_f**	$\frac{1}{n}$	**R^2**
	288	0.8763	0.0000	0.3258	-0.4055	-0.1577	0.0782
Unprocessed	298	1.0000	0.0000	1.0000	0.0218		0.0000
1.0000							
	308	1.0000	0.0000	1.0000	-0.4292	-1.7876	0.0836
	288	1.0193	0.07E-05	0.9908	0.0191		0.0666
0.0351							
Processed	298	1.2483	0.03E-05	0.9999	0.0214		-0.004
0.9974							
	308	1.0000	0.0000	1.0000	0.0000		-0.1E-05
0.0000							

Table 3.15: Langmuir and Freundlich Isotherm Constants for Methylene Blue on Cotton Fibre at Different Temperatures

3.3. Adsorption Isotherms

The experimental results were compared with two isothermal theoretical models of Langmuir and Freundlich , from table 3.26 it is seen that the values of the coefficient R^2 Langmuir and Freundlich for unprocessed cotton are lesser than 0.95 except at 298K (1.0000) and 308K (1.0000) for Langmuir and 298K (1.0000) for Freundlich. This shows that these models are not applicable for explaining the adsorption of methylene on unprocessed cotton fibre. It was also seen from Table 3.26 that the values of the coefficient R^2 Langmuir & Freundlich for processed cotton are greater than 0.95 except at for 288K (0.035) and 308K (0.0000). This shows that Langmuir model are applicable for explaining the adsorption of methylene blue on processed cotton fibre and it also indicated a very good mathematical fit. The Langmuir isotherm fits the experimental data very well maybe due to the homogenous distribution of active sites on processed cotton fibre, while the Freundlich model

shows the adsorbent has a surface heterogeneity. The values of K_f for unprocessed cotton with methylene blue at 288 298 and 308K are in the order of -0.429,0.022 and -1.576 and for processed cotton are 0.019, 0.021and 0.0000 respectively.
The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is defined by the following relationship

$$R_L = 1/(1 + bC_i)$$

According to the value of R_L the isotherm shape may be interpreted as follows:
R_L > 1.0 unfavourable
1.0 > R_L > 0 unfavourable
R_L = 1.0 Linear
R_L = 0 irreversible
The result given in table 3.26 show that the adsorption of methylene blue on cotton (unprocessed & processed) is linear but favourable for processed cotton at 288K and 298K.

4. Discussion

4.1. Adsorption kinetics

The applicability of the pseudo-first-order and pseudo-second-order model were tested for the adsorption of methylene blue on processed and unprocessed cotton fibre. The best fit model were selected based on the linear regression correlation coefficient R^2 values are shown in Table 3.25, it was observed that the rate constant increases from 208K to 308K in unprocessed cotton but increases from 288K – 298K and decreases from 298K to 308K in processed cotton. It was also observed that correlation coefficients were lower for all temperatures for both cottons (processed and unprocessed). This shows no applicability of the pseudo-first – order model in predicting the kinetics of the methylene blue adsorption on both processed and unprocessed cotton.

The kinetic data were further analysed using pseudo-second –order kinetics is applicable to the adsorption of methylene blue on both cotton fibre (processed and unprocessed) because the plot of t/qt vs.t shows a linear relationship. This is similar to the report from (Yasemin & Haluk 2006). The calculated k_2, qe and R_2^2 values for both processed and unprocessed cotton are summarized in Table 3.35. The correlation coefficient for second-order kinetic model R_2^2 are greater than 0.99, thus indicating the applicability of this kinetic and the second-order nature of adsorption process of methylene blue on cotton (unprocessed & processed cotton). This study shows similar result with the adsorption of methylene blue on wheat shells (Yasemin &Haluk,2006).

4.2. Adsorption Thermodynamic

The negative values of the standard Gibbs energy (ΔG°) for adsorption of methylene blue adsorption on cotton (unprocessed & processed) indicate that the adsorption is possible and thermodynamically spontaneous ,the decrease in ΔG° with increasing temperature may be explained by the fact that adsorption become easier or more efficient thus indicating the presence of a high drive strength.

The value of the standard enthalpy (ΔH°) is negative for unprocessed cotton which shows that the adsorption of methylene blue with processed cotton is exothermic but positive for unprocessed cotton which shows that the adsorption of methylene blue is endothermic.

The positive value of standard entropy ΔG° shows decreasing appearance at the solid/liquid interface during adsorption of methylene blue on cotton fibre (processed & unprocessed). In other words, it reflects the affinity of cotton fibre (processed & unprocessed) for methylene blue.

5. Conclusion and Recommendation

5.1. Conclusion

This present study shows that cotton processed or unprocessed an agro – based biomaterial can be used as an adsorbent for the adsorption of methylene.
The amount of methylene uptake (mg/g) for both cotton (processed and unprocessed) was found to vary with time, pH and temperature.

The amount of methylene blue adsorbed (mg/g) was found not to be affected with increase in time but increased as temperature increases with time.
The amounts of methylene blue adsorbed were almost constant with pH for processed cotton, and decreases with pH for unprocessed cotton.

The amount of methylene blue adsorbed (mg/g) increases as temperature increases and decreases at highest temperature (308 K) for processed cotton and increases at highest temperature (308K) for unprocessed cotton.
The rate of adsorption was found to conform to pseudo – second order kinetics with good correlation for both cotton (processed and unprocessed).

Equilibrium data fitted very well in the Langmuir isotherm equation for both cotton (processed and unprocessed).
The dimensionless separation factor (R_L) showed that cotton (processed and unprocessed) can be used for adsorption of methylene blue.

The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as $\Delta G°$, $\Delta H°$ and $\Delta S°$ of adsorption. The results indicate that methylene blue adsorption onto cotton fibre (processed and unprocessed) was spontaneous and physical in nature.
Cotton fibre is an inexpensive and easily available material, can be an alternative for more costly adsorbent used for adsorption.

5.2. Recommendation

More work should be done on the adsorption of dyes (different dyes) with cotton and also for the removal of dye from wastewater since cotton is a cheap adsorbent and agro based biomaterial it will help in the treatment of waste water and thus reduce the use of radiation.
Researchers should use low cost and efficient alternative and innovative treatment techniques for dye adsorption.
Also, further work should be done on the kinetic and thermodynamic studies of the adsorption dye with cotton fibre with different parameters and also using different models to interpret the result.

6. References

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APPENDIX

The chemical and reagents used for this research work were prepared using deionized water.
The materials are thermometer, pH meter (Jenway model), analytical weighing balance, water – bath, spectrophotometer (721 COLE spectrophotometer),sample bottles, spatula volumetric flasks , beakers measuring cylinder and magnetic stirrer.
The reagents used include Hydrochloric Acid, Sodium Hydroxide, Di hydrogen Potassium Phosphate, Methylene Blue and Aro (indigo).
Adsorbent used: Cotton (processed and unprocessed).