KINETIC AND THERMODYNAMIC ADSORPTION STUDIES ON THE REMOVAL AND TREATMENT OF TEXTILES EFFLUENTS USING ACTIVATED CARBON DERIVED FROM *DIOSPYROS MESPILLIFORMIS* SEEDS.

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ABSTRACT

An agricultural waste *Diospyros mespiliformis* seeds were treated, and activated with 30% of 0.3M sodium hydroxide base, to obtain an activated carbon employed in an adsorption process. It was utilize to treat effluent textile water sample from African Textile Manufacturers Limited in Dala, Kano State, Nigeria. Various techniques, including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and proximate analysis were employed to investigate the adsorption process. The adsorbent was able to remove the dark red color to colorless found in textile effluents and shown a higher removal affinity for zinc (99.4%) and least affinity for nickel (0.11%), also Chromium (Cr) reduced by 39.4%, Copper (Cu) reduced by 20.9%, Iron (Fe) reduced by 91.9% , Manganese (Mg) reduced by 79.3%, are reduced significantly, the $_pH$ change from acidic $_pH$ 6.4 to neutral $_pH$ 7.1, turbidity decrease from 131 to 14 NTU , electrical conductivity change from 723 to 110 $\mu s \cdot cm^{-1}$.*Diospyros mespiliformis* seeds activated carbon was used for removal of congo red and malachite green from an aqueous solution. The effect of adsorbent dose, adsorbate concentration and contact time on the process of adsorption was investigated. The optimum dosage was found to be 0.5g had a percentage removal of 98.1% for congo red and 94.4% for malachite green. 10mg/l and 80minute was found to optimum concentration and optimum time in adsorption of congo red and malachite green. The equilibrium, kinetic and thermodynamic properties of the dyes removal were also investigated. The experimental data were modeled using linear regression method of analysis. The correlation coefficient was used as a criterion for model adequacy and acceptance. The pseudo second-order kinetic model was found to best correlate the experimental data with R^2 of 0.9523 for CR and 0.9297 for MG. The experimental data were investigated at three different temperature, 305k, 325k and 335k were found to follow the Langmuir model with R^2 of 0.9679, 0.9662 and 0.989 for CR and 0.9529, 0.9662 and 0.994 for MG. also were found to follow Temkinp model with with R^2 of 0.9549, 0.9318 and 0.9952for CR and 0.9885, 0.9443 and 0.9209 for MG. The negative free gribbs energy indicated that the adsorption processes were spontaneously feasible. The positive values of +31.66KJ/mol and +92.3KJ/mol on both CR and MG indicate that adsorption process has been found to be endothermic in nature. The removal of congo red was found to be more spontaneous and feasible than the removal of malachite green on the adsorbent. From the study, it was deduced that the *Diospyros mespiliformis* seeds activated with sodium hydroxide was found to be a good adsorbent for the treatment of textile wastewater containing Congo red and Malachite green.

Keywords

Thermodynamics, Kinetics, Adsorption, Congo Red, Isotherm, Malachite Green, *Diospyros mespiliformis* seed.

INTRODUCTION

Water is one of the essential commodities of life on earth but is most often contaminated by pollution due to industrial and other human activities. The first contaminant found in wastewater is color [1]. One of the world's most pressing environmental challenges today is water pollution caused by the discharge of colored effluents from textile dye manufacturing and dyeing mills [2]. The global textile industry consumes more than 107 tons of dyes per year. Malachite green (MG) is a cationic dye, whereas Congo red (CR) is an anionic dye derived from benzene [3]. Because they contain sulphonate (SO^3) groups, anionic dyes have a net negative charge in aqueous solutions, whereas cationic dyes have a net positive charge due to the presence of protonated amine or sulfur-containing groups. According to Onyechi (2014), many dyes can impair the kidneys, liver, brain, reproductive systems, and central nervous system, as well as cause allergic dermatitis and skin irritation. The toxicity of these dyes may also have an effect on the aquatic ecosystem by hindering sunlight from accessing water bodies. Many of them are naturally dangerous, and they can either directly damage something or inhibit the ability of some microorganisms to catalyze.

Water can become useless for a variety of purposes at extremely low dye concentrations [4]. Adsorption, nanofiltration, electrokinetic coagulation, coagulation and precipitation, advanced chemical oxidation, electrochemical oxidation, ozonation, supported liquid membrane, liquid-liquid extraction, and biological processes are just a few of the methods used to remove textile dyes from wastewater [5]. According to Prasad and Santhi (2012), adsorption is one of the most effective and widely utilized techniques for removing both inorganic and organic pollutants from contaminated water. A dye is often a chemical with a specific affinity for the surface on which it is applied. In aqueous solutions, it is commonly used. To reinforce its bond with the fibers, it requires a mordant. Because they absorb some light wavelengths more strongly than others, they seem colored. Chemical, refinery, textile, plastic, and food processing enterprises are only a handful of the businesses that emit wastewater [6].These wastewaters contain dye residues, which pose a variety of hazards. Such residual dyes are not biodegradable due to their complex chemical structures, which make them more persistent and harder to decompose [7]. They gravely harm the environment and pollute the water. These colored materials are not only ugly, but they also hinder sunlight from accessing water bodies, affecting the aquatic ecology [8]. Many of them are naturally dangerous, and they can either directly damage something or inhibit the ability of some microorganisms to catalyze [9]. Activated carbon can be created using either physical (steam) or chemical activation techniques. The physical activation method occurs in two stages: first, the

precursor is carbonized in an inert environment, and then the crude car is activated in the presence of a reactive gas such as carbon dioxide or steam at a high temperature of approximately 900ºC. This technology is used to manufacture the majority of the activated carbon utilized around the world, with coal as the primary supply material. In contrast, the chemical activation process needs only one step and employs a chemical agent (an acid or a base) prior to carbonization. The chemical agent acts as a dehydrating agent, reducing the amount of tar produced during the carbonizing process. Adsorption experiments on the removal of textile dyes have been conducted using several agro-based adsorbents, such as Formosa papaya seed powder [10], cow bone [11], mangrove bark [12], ginger waste [4], and peanut shells [13]. The goal of this research is to treat real textile wastewater on a small scale using an adsorption process and to evaluate the isotherm, kinetics, and thermodynamics of Congo red and malachite green removals utilizing plentiful waste in Northern Nigeria. The dye-removal efficiency of activated *Diospyros mespiliformis* seed will be compared under identical conditions.

MATERIALS AND METHODS

Preparation of the Adsorbent

The sample was taken from *a Diospyros Mepilliformis* tree in Azare, Bauchi State, northeast Nigeria. The *Diospyros Mepilliformis* seeds were thoroughly cleaned with deionized water to remove dirt. The *Diospyros* *Mepilliformis* seeds were smashed into little bits using a pestle and mortar. They were then dried in an oven (Gallenkamp Hotbox oven) at 70ºC until totally dry, weighing 300g. Chemical activation was used to prepare activated carbon from *Diospyros Mepilliformis* seeds. The impregnation ratio was calculated by dividing the volume of 0.3M NaOH by the weight of the dried seeds. *Diospyros Mepilliformis* seeds were impregnated with 30% 0.3M NaOH at a 1:4 ratio. 180ml of 0.3M NaOH was diluted in 420ml of distilled water and combined with 300g of dried *Diospyros Mepilliformis* seeds. The combination was permitted to sit for 24 hours at room temperature. The impregnated sample was then rinsed to neutral pH and dried in an oven at 100^0C for 6 hours. *Weighed Diospyros Mepilliformis* seeds were placed in a ceramic crucible and inserted into a muffle furnace (Kailaso Instrument). The sample was heated to 500ºC for two hours. The activated carbon was dried at 60˚C for 12 hours to remove any remaining moisture. Weighing the activated carbon yielded 115.4g and stored in air tight container for adsorption studies.

Characteristics of the Adsorbents

The proximate analysis parameters of the adsorbent (DMS) were assessed using the conventional procedures provided by [22]. The Fourier transform infrared (FTIR) spectrophotometer (Cary 630 FTIR) was used to detect the functional groups present in DMS adsorbent before and after adsorption of textile

effluent, with samples generated using the usual KBr disc method.

Scanning Electron Microscopy (Thermfisher phenon world prox G6 SEM USA) was used to determine the surface morphology of DMS absorbent before and after treatment.

Treatment of real textile wastewater

A plastic jerry can was used to collect waste water at African Textile Manufacturers Limited, Dala Local Government, in Kano State, Nigeria. Standard methods were followed to analyze samples of textile waste water. Temperature was monitored with a mercury-in-glass thermometer; turbidity, pH, electrical conductivity (EC), and color were determined before and after the adsorption procedure. 100 ml of textile wastewater was loaded into ten 250 ml conical flasks containing 1g of adsorbent, which were then placed on an orbital shaker at 250 rpm. And was shaken for 60 minutes. The concentrations of heavy metals present were evaluated using atomic adsorption spectroscopy (AAS) before and after the adsorption procedure.

Adsorption Studies

Batch investigations were carried out by contacting a specific amount of the adsorbent in 100 ml of the two dye solutions at a constant pH of 7.2. The samples were placed in an electric shaker and agitated at 250 rpm at a constant temperature. They were then removed from the shaker at the required time and ambient filtered through Whatman No. 1 filter paper. The filtrates were taken to a UV-visible spectrophotometer (Hamanatus Japan) to determine absorbance, from which the final concentration was calculated. The effects of contact time (10 to 100 minutes), adsorbent dosage (0.1 to 0.5 g), and starting dye concentration (10 to 50 ppm) on adsorption were studied. The amount of dye adsorbed per unit mass of activated carbon (mg/g) and the percentage adsorbed (%) were calculated as follows.

$$q_e = \frac{(C_0 - C_t)V}{W} \qquad (1)$$

q_e is the amount of CR or MG dye adsorbed onto the activated carbon at equilibrium , C_O and C_t are the concentrations of CR and MG dyes(mg/L) at t=0 and t=t respectively, W (g) is the mass of dry adsorbent used, and V (ml) is the volume of CR and MG dyes solution.

The dye removal percentage can be calculated as follows:

$$\%\text{Removal} = \frac{C_O - C_t}{C_O} \times 100 \qquad (2)$$

Where, C_O and C_t (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively.

Effect of temperature

To reach equilibrium, 100ml of CR and MG solutions were put into four 500ml beakers and swirled on a magnet stirrer (RPM=160) with 0.5g of activated carbon at various temperatures of 25oC, 350oC, and 45oC for 50 minutes. Every ten minutes, an aliquot was taken to determine the time at which equilibrium was reached.

RESULT AND DISCUSSION

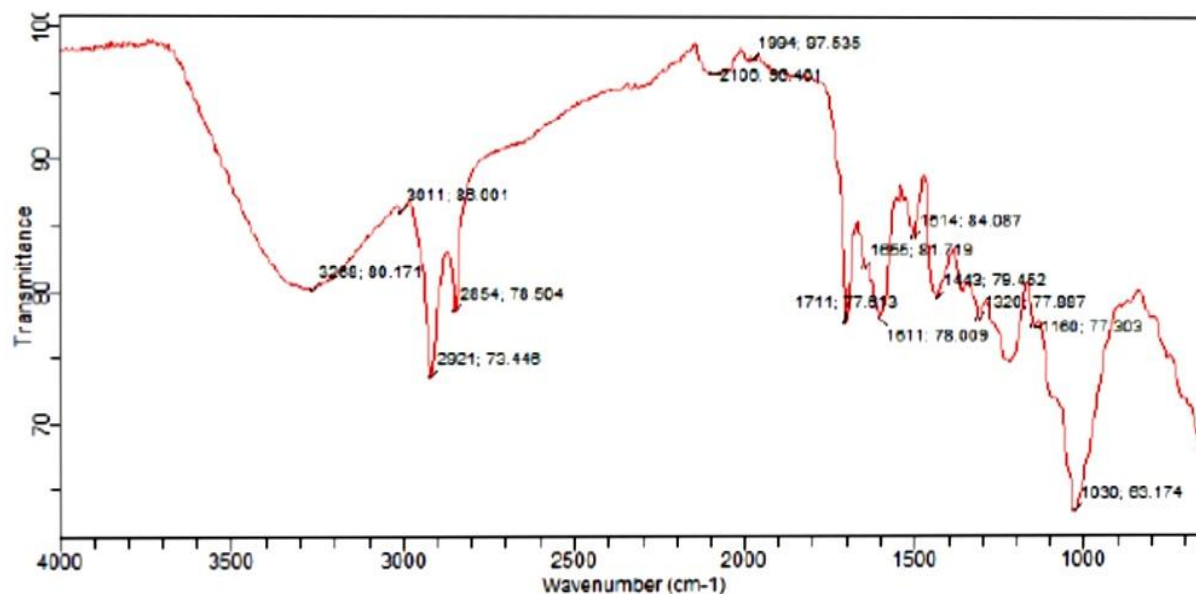*Characterization Analysis of Diospyros mespiliformis seeds (DMS) Activated Carbon*

Figure 1: FTIR spectrum of *Diospyros mespiliformis seeds* (DMS) Activated Carbon before adsorption
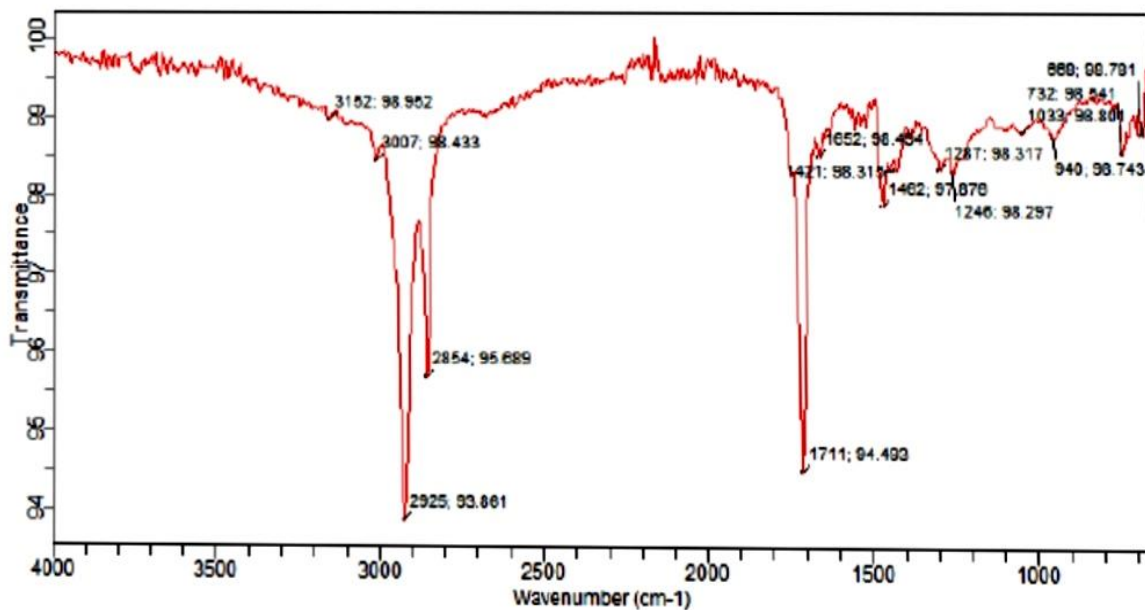

Figure 2: FTIR spectrum of *Diospyros mespiliformis seeds* (DMS) Activated Carbon After adsorption of textile water effluents

Figure 1 shows the spectrum of DMS before adsorption. The broad band at 3260 cm⁻¹ was assigned to O-H stretching, which was caused by hydrogen bonding between the adsorbent's hydroxyl groups. The band at 2921 cm⁻¹ corresponded to C-H stretching vibrations. The characteristic peak at 1711 cm⁻¹ was linked to the adsorbent's C=O bond stretching. In the finger print, the band at 1030 cm⁻¹ was caused by C-O vibration. However, **Figure 2** shows the spectrum of DMS following adsorption. When compared to the spectra of the DMS adsorbent before adsorption, a new peak developed at 666 cm⁻¹, corresponding to the stretching vibrations of the bond (C - X) formed between the adsorbent and the dye molecule. The band for C-H was observed at 2925 cm-1, while the peak at 3152 cm⁻¹ was caused by the O-H band. In the finger print region, the band at 1039 cm⁻¹ corresponds to the stretching vibration of C-O.
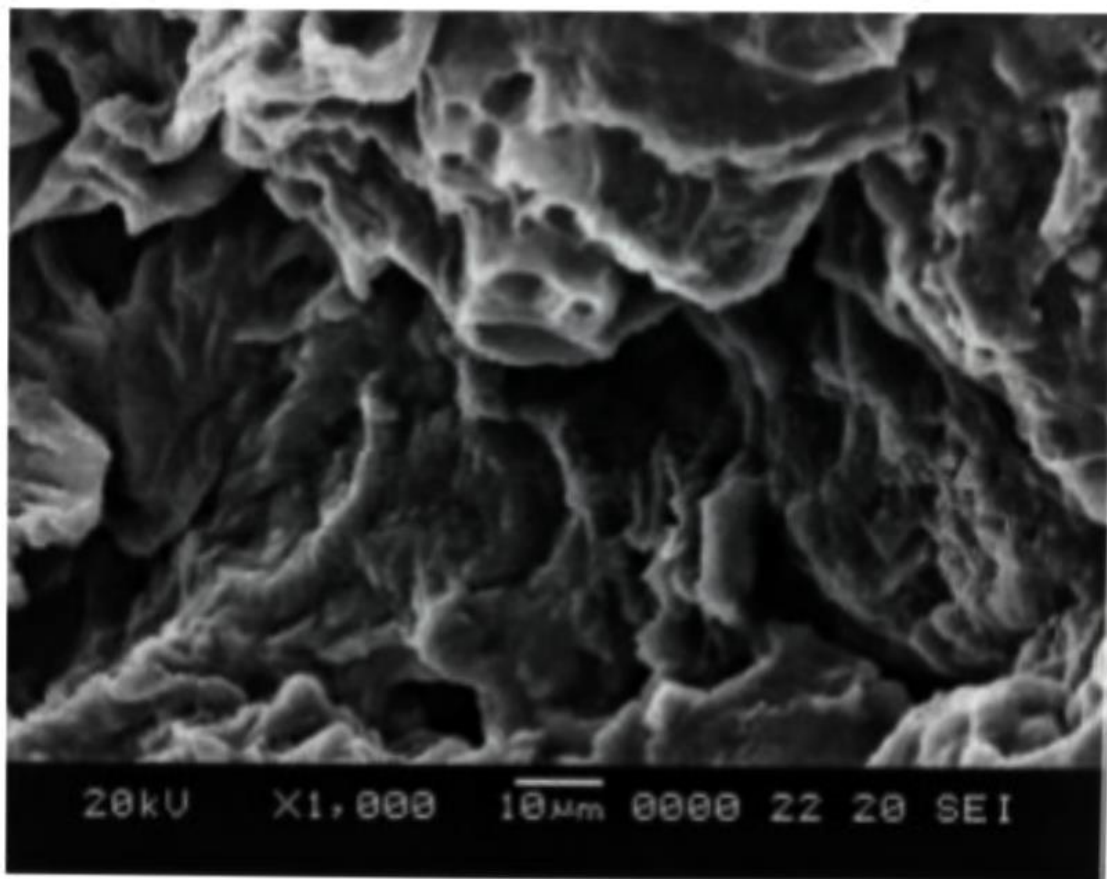

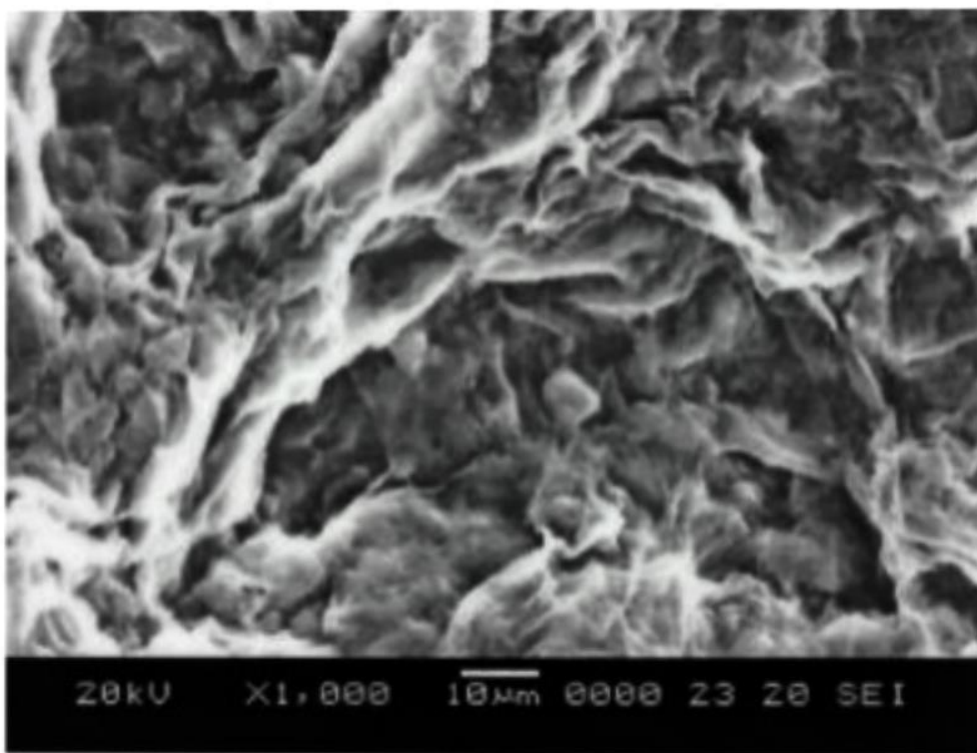**FIGURE 3   SEM image of *Diospyros mespiliformis seeds* (DMS) Activated Carbon before adsorption**

FIGURE 4   SEM image of *Diospyros mespiliformis seeds* (DMS) Activated Carbon After adsorption of   textile water effluents.

Figures 3 and 4 show SEM images of *Diospyros mespiliformis* seeds (DMS) activated carbon samples before and after textile water effluent adsorption. The *Diospyros mespiliformis* seeds (DMS) Activated Carbon sample previously contained a large number of holes for the adsorption of water effluents. The pores within the DMS particles are heterogeneous prior to the adsorption of textile water effluents, as seen in image **figure 3**. Adsorption of textile water effluents on *Diospyros mespiliformis* seeds (DMS) activated carbon results in a considerable change in surface topography of the activated carbon. The original *Diospyros mespiliformis* seeds (DMS) Activated Carbon before adsorption has a very porous structure, whereas *Diospyros mespiliformis* seeds (DMS) Activated Carbon after adsorption has a partially covered surface by textile water effluents compounds.

Table 1 proximate analysis of activated carbon prepared from *Diospyros mespiliformis seeds* (DMS)

PROXINMATE ANALYSIS	RESULT%
Moisture content	4
Ash content	6.95
Volatile matter	14.25
Carbon content	74.8

Proximate analysis was performed on activated carbon to determine its various properties and carbon content. **Table 1** demonstrates that the moisture content (4%) is relatively low, as are the volatile matter (14.5) and ash amounts (6.95). If the ash content is significant, it interferes with pore structure development, resulting in reduced adsorption [14]. *Diospyros mespiliformis* seeds (DMS) have a reasonable carbon content, making them a useful low-cost adsorbent. The proportion of inorganic components in carbon precursors has been observed to significantly influence carbon porosity by blocking pore entrances during the activation process [15]. Thus, the ash content, which is the inorganic residue left after the organic matter has been burned away, should be very low in order to achieve a high yield of the carbonaceous result of carbonization. The fixed carbon is the amount of solid carbon present in the carbonaceous product. Decomposition occurred because volatile molecules could not maintain their stability at high temperatures; the volatile stuff was totally eliminated during carbonization, leaving just a part of stable carbon as residues. To produce extremely porous carbon, a precursor for activated carbon must contain a high proportion of fixed carbon as well as a high volatile matter content.

The wastewater solution had a dark red color due to the presence of dyes and suspended solids. After treatment, the color changed from dark red to colorless, as shown in **Table 2**. **Table 2** also shows that the effluent has a pH of around 6.4 and does not require any neutralization. At 27°C, the conductivity was around 723 $\mu s \cdot cm^{-1}$ due to the high presence of ions. Result **Table 2** indicates a drop in turbidity from 131 to 14 NTU. Examining the results in Table 2, we can see that heavy metals were reduced in comparison to the untreated effluent. So Nikel (Ni) reduced by 0.011%, Chromium (Cr) reduced by 39.4%, Copper (Cu) reduced by 20.9%, Iron (Fe) reduced by 91.9%, Manganese (Mg) reduced by 79.3%, and Zinc (Zn) reduced by 99.4% are greatly reduced.

Table 2 Physicochemical characteristics of untreated textile wastewater and treated textile wastewater

S/N	Parameters	untreated textile wastewater	treated textile wastewater
1	Temprature (ºC)	27	25.2
2	$_pH$	6.4	7.1
3	Colour	Dark red	Colorless
4	Condutivity (μs·cm^{-1})	723	110
5	Turbidity (NTU)	131	14
6	Copper (Co) (mg·L^{-1})	1.095	0.866
7	Chromium (Cr) (mg·L^{-1})	0.581	0.352
8	Nickel (Ni) (mg·L^{-1})	0.963	0.952
9	Iron (Fe) (mg·L^{-1})	1.231	0.100
10	Zinc (Zn) (mg·L^{-1})	0.909	0.005
11	Manganese (Mg) (mg·L^{-1})	1.602	0.332

Batch Adsorption Studies

Effect of Adsorbate Concentration

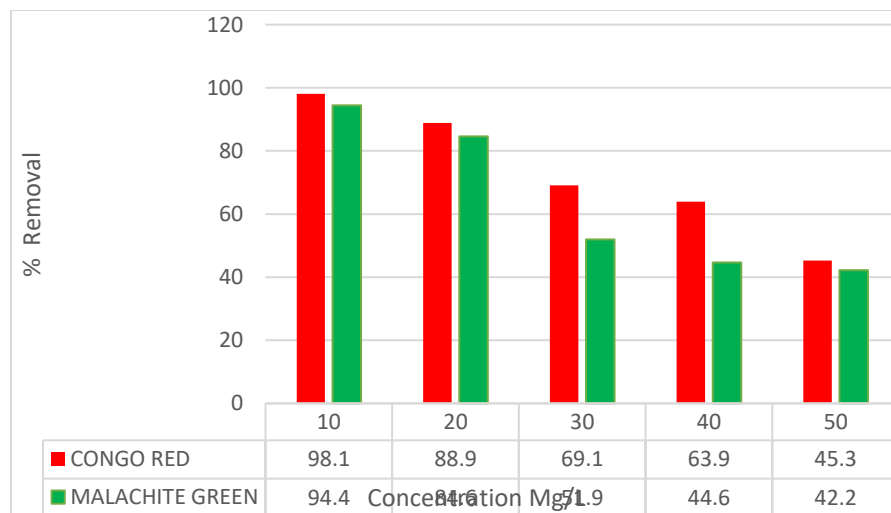|	10	20	30	40	50
CONGO RED	98.1	88.9	69.1	63.9	45.3
MALACHITE GREEN	94.4	84.6	51.9	44.6	42.2

Figure 5: Effect of adsorbate concentration. Dosage = 0.5 g, Time = 50 min, Temperature = 305k

Figure 5 shows that the dye's initial concentration appears to influence its exclusion from the aqueous phase. The effect of congo red and malachite green dye concentration on adsorption performance was also investigated in the starting concentration range of 10-50 mg/L, as illustrated in **figure 5**.At equilibrium, the adsorption capacity of DMS absorbent appears to decrease as the initial dye concentration increases.This trend could be attributed to the fact that because of the high concentration of the dye, the driving force for mass transfer is also relatively high. Additionally, if the concentration of dye in the solution is higher, the active sites are enclosed by more dye molecules which leads to more efficient adsorption. Both coir pith and bagasse fly ash showed similar trends however the trend in coir pith didn't flat line and continued to rise up for higher subsequent values of adsorbent mass taken [16].

The effects of adsorbent, i.e. DMS sample dose, on the quantity of CR and MG dye removed expressed as a percentage at an initial concentration of 10mg/l at 305K, were tested for varied dosages of 0.1g, 0.2g, 0.3g, 0.4g, and 0.5g in a 100mL solution. **Figure 6** shows that the percentage of dyes removed grows as the adsorbent dosage increases until the amount of colorant removed does not increase any further.

Effect of Asorbent Dosage

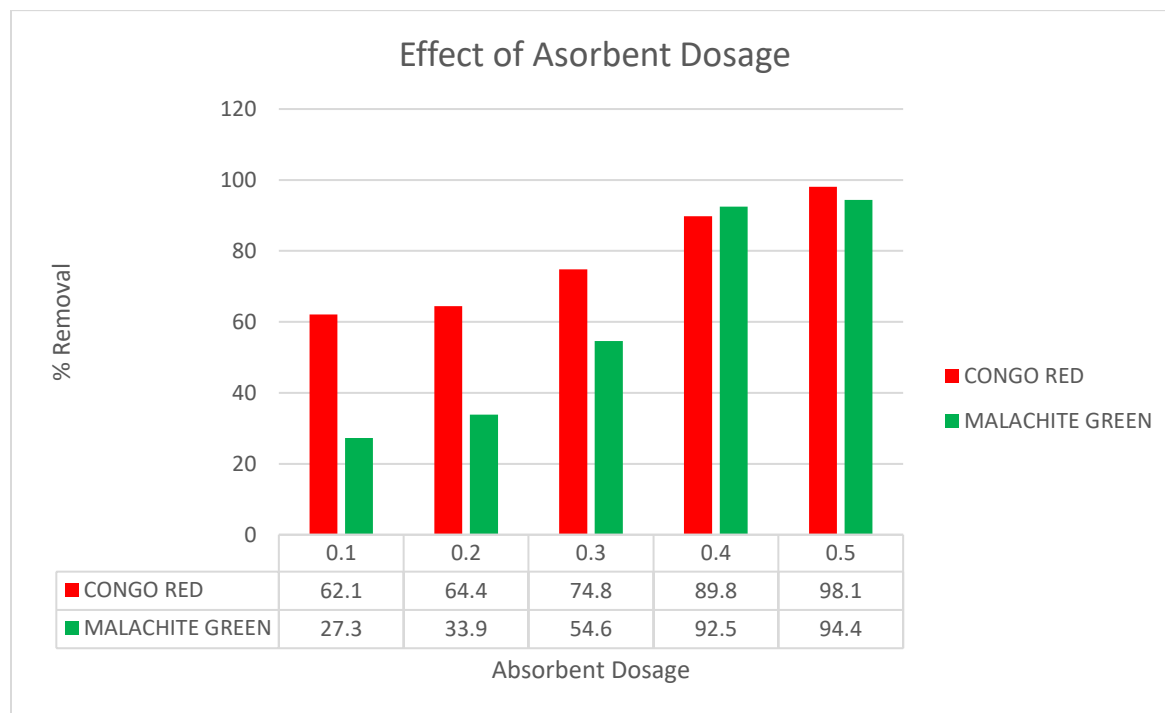|	0.1	0.2	0.3	0.4	0.5
CONGO RED	62.1	64.4	74.8	89.8	98.1
MALACHITE GREEN	27.3	33.9	54.6	92.5	94.4

Figure 6: Effect of adsorbent dose on percentage adsorbed. , Concentration = 10 mg/l, Time = 50 min, Temperature = 305k

Inter particle attraction or a loss in free surface area due to overpopulation can be assigned as the cause. Coir pith was applied in extravagant amounts to remove Congo red [17]. This resulted in a higher percentage of removal than in our previous studies; however, because we have established that there are issues with disposing of the spent adsorbent and that regeneration of the adsorbent or dye recovery is critical, we can conclude that our process will generate less waste.

Effect of Contact Time

Figure 7 data table:

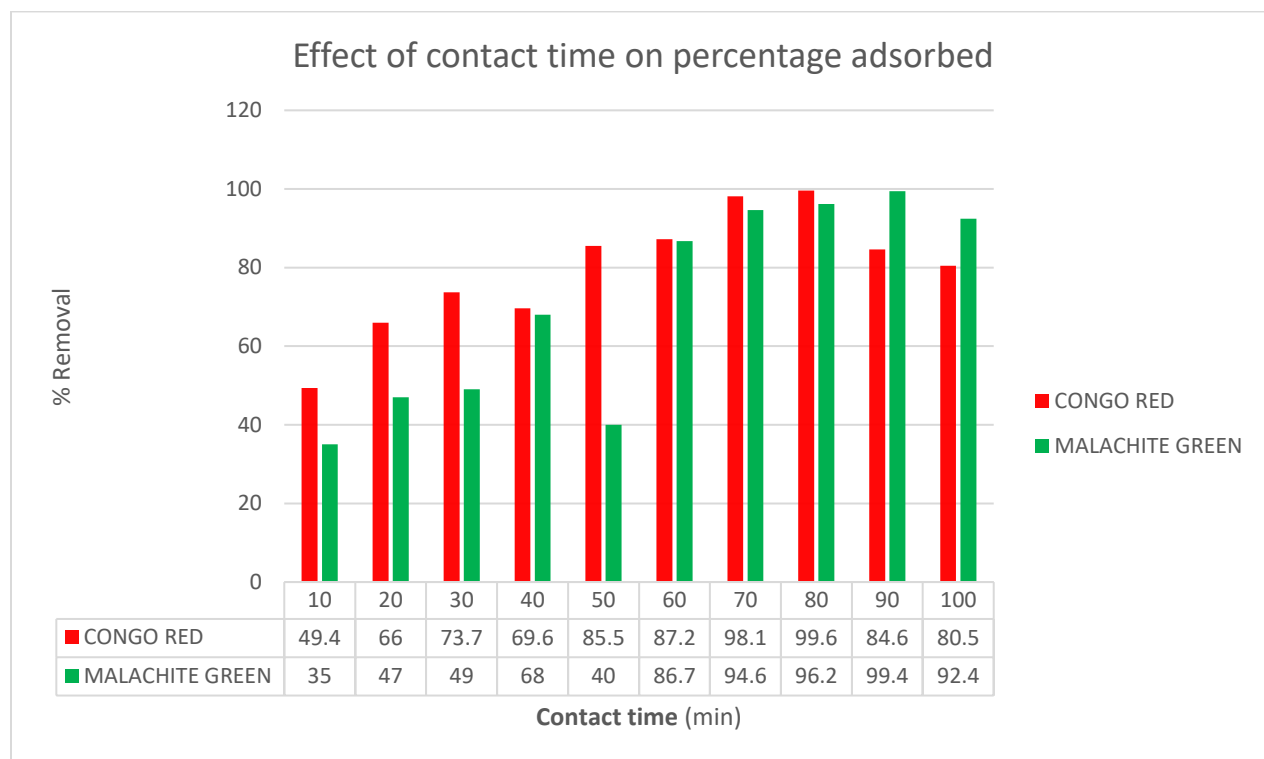|	10	20	30	40	50	60	70	80	90	100
CONGO RED	49.4	66	73.7	69.6	85.5	87.2	98.1	99.6	84.6	80.5
MALACHITE GREEN	35	47	49	68	40	86.7	94.6	96.2	99.4	92.4

Figure 7. Effect of contact time on percentage adsorbed. Dosage = 0.5, Concentration = 10 mg/l, Temperature = 305K

The impact of contact time on adsorption of Congo red and malachite green dye can be seen from **Figure 7** .It is clearly depicted in the figure that the rate of adsorption is very high initially it is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed. The final dye concentration did not vary significantly after 80minute from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 80 (min) both on Adsorption of CR and MG. It is basically due to saturation of the active site which do not allow further adsorption to take place [18]. But at later stages, the rate of adsorption decreases. The concentration of dye nearly remains constant after 70 minutes. This sets the

equilibrium time for adsorption as 100 minutes. It is chiefly because of the saturation of these active sites on the DMS which do not permit furthermore adsorption to occur. This can be explained by the fact that initially, the quantity of sites on the surface are very large which allows adsorption to take place very easily. But with the passage of time, the active sites get saturated thereby reducing the rate at which adsorption occurs. It was observed that CR adsorbed faster than MG at different time interval this is because due to surface charges on the produced absorbent from DMS.

Adsorption Isotherm

The equilibrium isotherm relationship between the concentration of the dyes in the liquid phase and the dyes in the adsorbent (DMS) at a given temperature was studied. The results were analyzed using the Langmuir, Freundlich and Tempkin isotherm.

Langmuir Isotherm

The linear form of Langmuir's isotherm model is given by the following equation [19].

$$\frac{C_e}{q_e} = \frac{1}{b \times Q_O} + \left(\frac{1}{Q_O}\right)c_e \qquad (3)$$

Where Ce is the equilibrium concentration of the adsorbate, qe the amount of adsorbate adsorbed per unit mass of adsorbate (mgg^{-1}), and Qo and b are Langmuir constants related to adsorption capacity and rate of adsorption, 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 [20].

$$R_L = \frac{1}{(1+bC_O)} \qquad (4)$$

Where b is a Langmuir constant. R_L value implies the adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$)

From **Table 3.**When Ce/qe was plotted against Ce, straight line with slope 1/Qo was obtained, indicating that the adsorption of adsorbate on activated carbon prepared from *disopryros melliformis* seed at different temperature follows the Langmuir isotherm. The Langmuir constants 'b' and 'Qo' obtained from the graph.The plot of Ce/qe against Ce is shown. The correlation coefficients (R^2) at three different temperature of 0.9679, 0.9662 and 0.989 for CR and 0.9529, 0.9662 and 0.994 for MG on DMS respectively showed that the adsorption conformed to the Langmuir model. The separation factors, R_L at three different temperature were obtained to be 0.118, 0.070 and 0.04 for CR and 0.35, 0.074 and 0.02 on DMS respectively were found to be less than one indicating favorable adsorption (Table3)

Table 3. Calculated Lagmuir isotherm parameters for the adsorption of CR and MG dye on DMS at three different Temperature

CONGO RED			
Parameters	305k	325k	335k
Q_o	1.23	1.06	0.90
(b)	0.75	1.32	2.39
R_L	0.118	0.070	0.04
R^2	0.9679	0.9662	0.989
MALACHITE GREEN			
Parameters	305k	325k	335k
Q_o	2.11	1.07	0.75
(b)	0.20	1.26	5.61
R_L	0.35	0.074	0.02
R^2	0.9529	0.9662	0.994

Freundlich Adsorption Isotherm

According to Taha *et al*. The Freundlich adsorption model assumes that adsorption takes place on heterogeneous surfaces. Its linear form can be written as:

$$logq_e = \log k_f + 1/n \, logc_e \tag{5}$$

Where, K_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicates the capacity and intensity of the adsorption, respectively.

Table 4. Calculated Freundlich isotherm parameters for CR and MG adsorption on DMS at three different Temperature.

CONGO RED			
Parameters	305k	325k	335k
n	-0.459	-0.385	-0.375
K_f (l/g)	5.52	6.13	6.55
R^2	0.9018	0.9634	0.9888
MALACHITE GREEN			
Parameters	305k	325k	335k
n	-0.92	-0.494	-0.189
K_f (l//g)	4.73	5.54	21.16
R^2	0.9561	0.9561	0.8654

The respective Freundlich constants, n and K_F, **Table 4** were calculated from the slopes and intercepts of the linear plots of logqe versus logCe . The values of K_F (measure of adsorption) increased with increasing temperature. The R^2 values at three different temperature, 0.9018, 0.9634 and 0.988 for CR and 0.9561, 0.9561 and 0.8654 for MG on DMS respectively obtained shows that the adsorption on DMS conformed to the Freundlich isotherm generally

Temkin Adsorption Isotherm

The Temkin isotherm model is based on the fact that the heat of adsorption of all the molecules in a layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and also that the adsorption is characterized by a uniform distribution of the bonding energies, up to some maximum binding energy [21]. The Temkin isotherm is given as:

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \qquad (6)$$

q_e is the amount adsorbed at equilibrium in mg/g; . The constants b_T which is related to the heat of adsorption and K_T which is the equilibrium binding constant corresponding to the maximum binding energy were determined from the plot of q_e versus in C_e. Maximum binding energy were determined from the plot of qe versus inCe . The constants are presented in **Table 5**. The values of b_T at three different temperatures of -1489, -1309 and -1344 J/mg for CR and -2325, -1140 and -803 for MG on DSM respectively indicate that the interaction between the adsorbate and the adsorbent was strong. The correlation coefficients, R^2 value of 0.9549, 0.9318 and 0.9952 for CR and 0.9885, 0.9443 and 0.9209 for MG on DMS respectively indicate that the isotherm model fitted well to the equilibrium adsorption experimental data.

Table 5. Calculated Temkin isotherm parameters for CR and MG adsorption on DMS at three different Temperature .

CONGO RED			
Parameters	**305k**	**325k**	**335k**
b_T	-1489	-1309	-1344
K_T (j/mg)	0.136	0.153	0.148
R^2	0.9549	0.9318	0.9952
MALACHITE GREEN			
Parameters	**305k**	**325k**	**335k**
b_T	-2325	-1140	-803
K_T(j/mg)	0.087	0.171	0.308
R^2	0.9885	0.9443	0.9209

Kinetics Of Adsorption

The adsorption kinetics was studied in order to study the mechanism of the process of adsorption

Pseudo First-Order Kinetic Model

Pseudo-first-order kinetic model is given by [21]

$$\ln(qe - qt) = \ln qe - k1t \qquad (7)$$

Where q_e and q_t are the amounts of dye adsorbed (mg/g) at equilibrium and at time t respectively. K_1 is the pseudo first order rate constants.

K_1 and q_e were calculated using the slope and intercept of the plot of $\ln(q_e - q_t)$ vs t shown in (**Figure 8**). **Table 6** shows the pseudo first-order rate constants, K_1. The correlation coefficients (R^2) of 0.1355 and 0.4239 for CR and MG, respectively, suggest that the removal of CR on DMS did not follow the pseudo first-order kinetic model, as did the removal of MG on DMS.
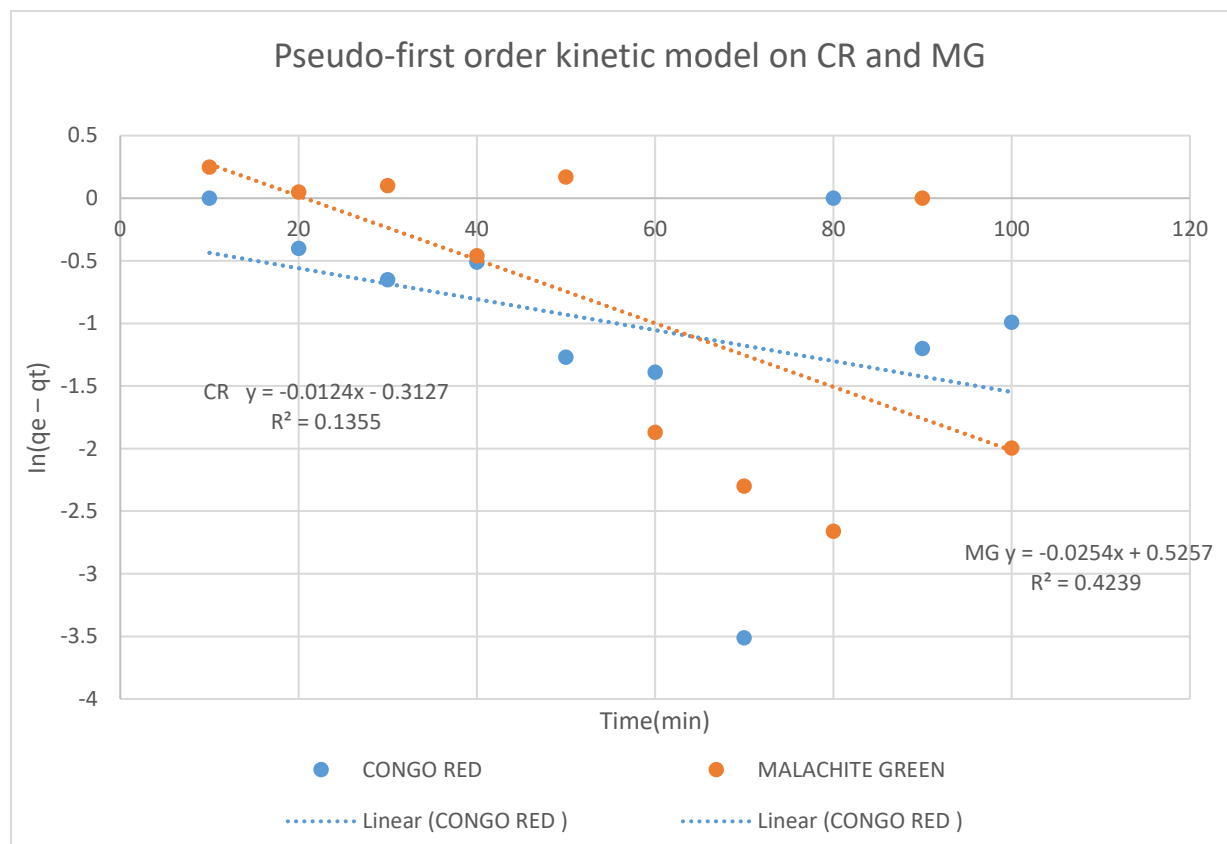

Figure 8. Pseudo-first order kinetic model on CR and MG adsorption on DMS
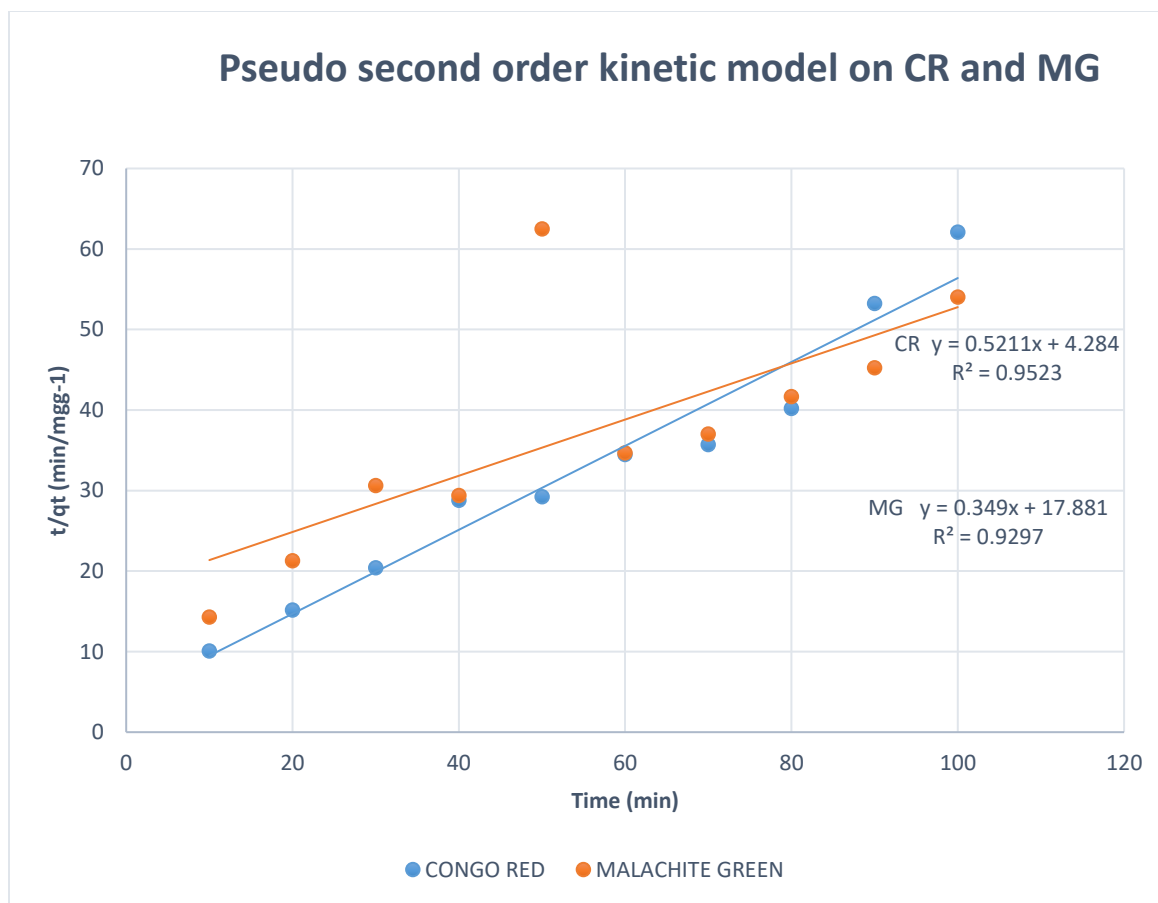
Figure 9. Pseudo-second order kinetic model on CR and MG adsorption on DMS

Table 6. Kinetic parameters and correlation coefficients obtained for the adsorption of CR and MG on DMS at 305K

Kinetic Model	Congo Red (CR)	Malachite Green (MG)
Pseudo first-order		
K_1 (min−1)	0.0124	0.0254
q_e (mg/g)	0.73	1.69
R^2	0.1355	0.4239
Pseudo second – order		
K_2 (g/mg/min)	0.063	0.0068
q_e (mg/g)	1.92	1.87
R^2	0.9523	0.9297

Pseudo Second-Order Kinetic Model

The pseudo second – order adsorption kinetic equation is expressed as [23]

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{q_e} \qquad (8)$$

K_2 is the rate constant for pseudo second order adsorption (g/mg/min). The values of K_2 and q_e (**Table 8**) were computed using the graphs of t/qt vs t shown in **Figure 9**. The R^2 values close to unity (0.999) reveal that the adsorption of CR and MG on DMS is best represented by the pseudo second-order mechanism, indicating that the rate-limiting phase is a chemical adsorption [24].

Thermodynamic Adsorption Studies

Adsorption thermodynamics is the study of the effect of temperature on the process of adsorption. ΔG^0 and ΔH^0 were used to evaluate the spontaneity and nature of the adsorption process respectively (Al-Ghouti *et.al* ., 2005). In this present work, the effect of temperature on adsorption was studied at three temperatures(305k, 325k and 335K) on two textiles dye solution i.e Congo red and malachite green. The thermodynamic parameters free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined as follows [25].

$$\ln b = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (9)$$

$$DG^o = \text{-RT } \ln(b) \qquad (10)$$

Where,

ΔG^o = Gribb free energy

ΔH^o = change in the enthalpy

ΔS^o = change in entropy

T= absoluteTemprature

b = Langmuir isotherm constant

R = is the universal gas constant (8.314×10^{-3} kJ/mol K)

ΔH^o and ΔS^o was calculated from the slope and intercept of the linear plot of ln(b) vs. 1/T according to Eq. (9),i.e. the van't Hoff equation. ΔG^o can be calculated using Eq. (10)

The activation energy was evaluated from the pseudo second-order kinetic rate constants obtained from adsorptive removals performed at 305, 325 and 335K. The Arrhenius equation is given as [26].

$$\ln K_2 = \ln A - \frac{E_a}{RT} \qquad (11)$$

Ea was obtained from the slope Where K_2 is the rate constant obtained from the pseudo second-order kinetic model (g/mgmin^{-1}), Ea is the Arrhenius activation energy of adsorption (kJ/mol) and A is the Arrhenius factor. In K_2 was plotted against 1/T and $\ln K_2$.
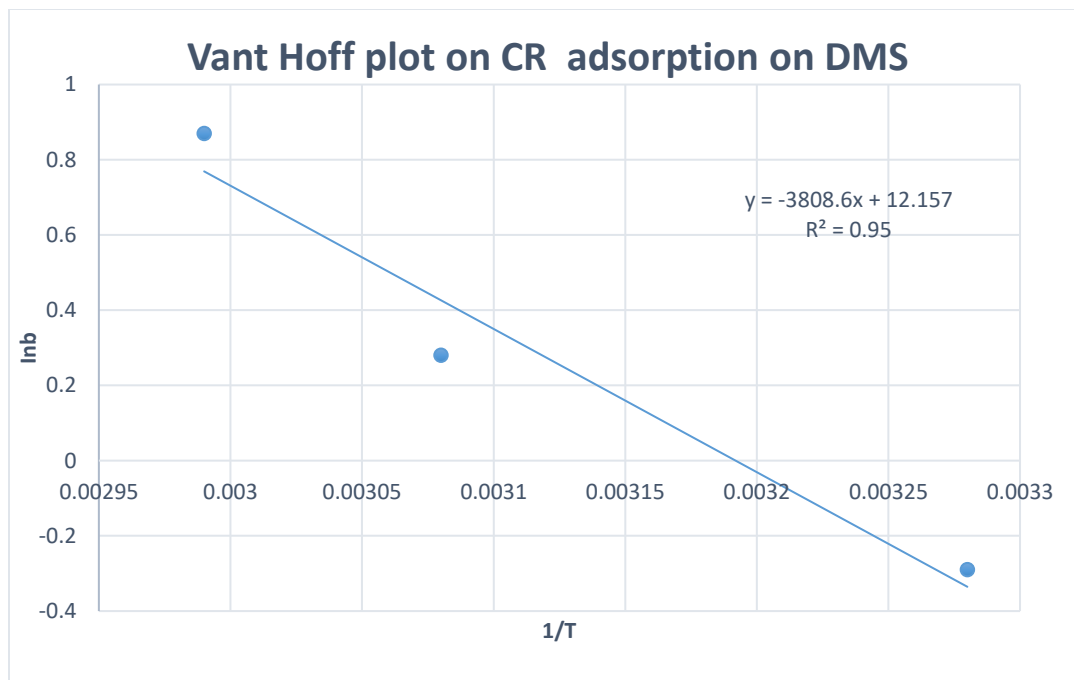
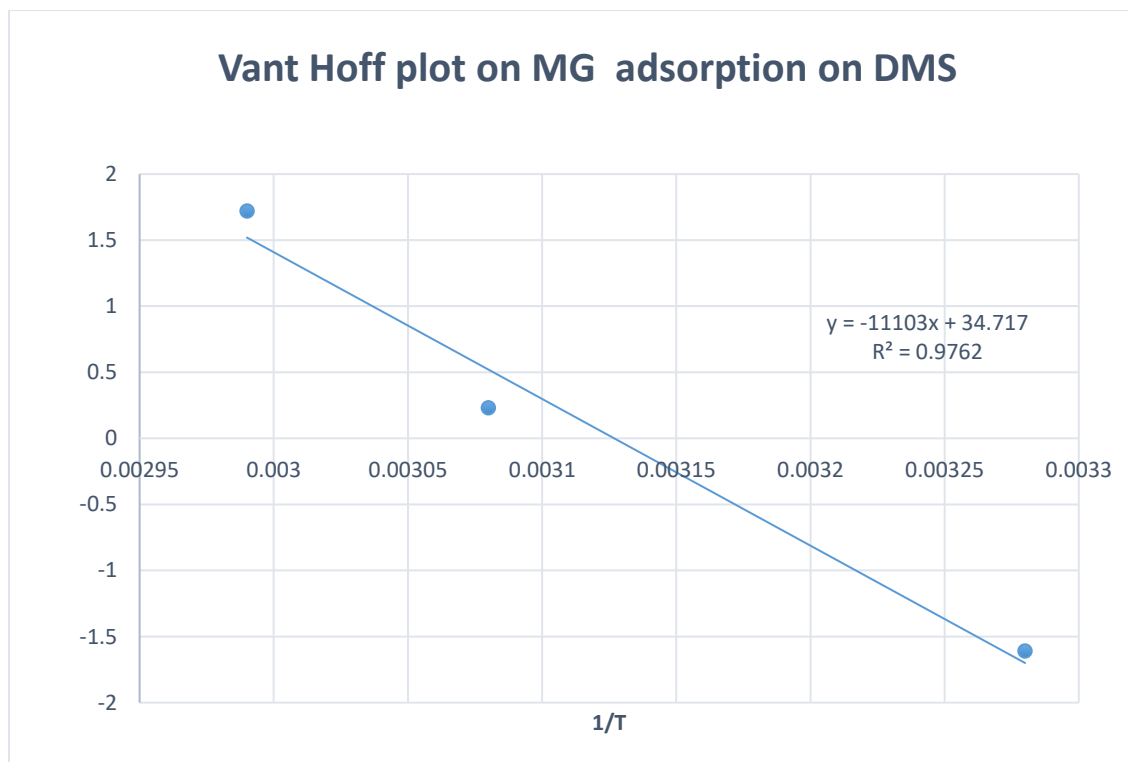**FIGURE 10 : Vant Hoff plot on CR Adsorption on DMS**

FIGURE 11: Vant Hoff plot on MG Adsorption on DMS

TABLE 7: Thermodynamic parameters for the adsorption of CR and MG dye on DMS

	Congo Red			
T (K)	E_a (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/K/mol)	ΔG^0 (KJ/mol)
305	10.19	31.66	0.101	0.73
325	10.19	31.66	0.101	-0.75s
335	10.19	31.66	0.101	-2.43
	Malachite Green			
305	56.44	92.3	0.289	4.08
325	56.44	92.3	0.289	-6.24
335	56.44	92.3	0.289	-4.80

The activation energies of CR adsorption on DMS are 10.19 KJ/mol, implying that the rate-limiting step may be a physically controlled process because it is less than 40 KJ/mol, and MG adsorption on DMS is 56.44 K/Jmol, which is greater than 40 KJ/mol and may be a chemically controlled process [27]. The negative values of ΔG^0 reduced with increasing temperature, indicating that adsorption was more favorable and spontaneous at higher temperatures (**Table 7**). The positive value of ΔH^0 implies that the process is endothermic.Positive ΔS^0 values suggest increased unpredictability at the solid/solution interface due to energy redistribution between dyes and adsorbents [24].

The elimination of CR was discovered to be more spontaneous than the removal of MG on DMS. Chemical activation was employed to remove Congo red and Malachite Green (textile dyes) from aqueous solution. The removal efficiency of NaOH activated carbon (DMS) on CR and MG was evaluated. The batch adsorption investigations revealed that the proportion adsorbed varied with temperature, adsorbent dosage, contact time, and adsorbate concentration. The adsorption of DMS on CR and MG was discovered to follow the Langmuir, Freundlich, and Tempkin isotherms.

The pseudo second order kinetic model was found to best correlate with the experimental data collected. The process is feasible and

spontaneous, as indicated by its negative free energy change (ΔG^0) and positive entropy (ΔS^0). The removal of CR was discovered to be more spontaneous and practical than the removal of MG from DMS. DMS was found to be a more effective adsorbent for CR removal than MG. The thermodynamic and kinetic data can then be utilized to build a large-scale facility for treating industrial wastewater including Congo red and Malachite green.

CONCLUSION

Diospyros mespiliformis seeds adsorbent have been used and proved effectiveness to remove dyes and heavy metals from real textile wastewater samples of Kano city Nigeria. Advantage of using these adsorbent is the possibility of removing different types of dyes compounds and heavy metals having an attractive potential on the surface of the adsorbents. It would be interesting to continue testing on real wastewater not only batch processes but also column processes in pilot scale. Activated carbon prepared from *Diospyros mespiliformis seeds* (abundantly available agricultural waste) using chemical activation was used for the removal of Congo red and Malachite green (textile dyes) from aqueous solution. The removal efficiencies of using 0.3M NaOH activated carbon (DMS) on CR and MG were compared. The batch adsorption studies indicated that the percentage adsorbed depended on adsorbent dose, pH, and contact time and adsorbate concentration. The adsorption of DMS on CR and MG was found to

follow the Langmuir, Freundlich and Tempkin isotherms. The pseudo second order kinetic was found to best correlate the experimental data obtained. The negative free energy change (ΔG^0) and positive value of entropy (ΔS^0) indicate the feasible and spontaneous nature of the process whereas the positive values of ΔH^0 indicate the endothermic nature. The removal of CR was found to be more spontaneous and feasible than the removal of MG on DMS. DMS was found to be a better adsorbent for CR removal than for MG. The thermodynamic and kinetics data can be further used for the design of a plant for treatment of industrial wastewater containing congo red and malachite green on large scale.

Nomenclature

q_t Adsorption capacity (mg/g)

q_e Adsorption capacity at equilibrium (mg/g)

C_o initial metal concentration (mg/L)

C_e metal concentration at equilibrium (mg/L)

C_t metal concentration at t time (mg/L)

V volume of the metal solution (L)

W weight of the adsorbent (g)

Qo Adsorption capacity from Langmuir model (mg/g)

b Langmuir isotherm constant (L/mg)

R_L separation factor (dimensionless)

K_F Freundlich isotherm constant $(mg/g) (L/mg)^{1/n}$

n_F Freundlich exponent (dimensionless)

DMS   *Diospyros mespiliformis seeds*

CR Congo red

MG Malachite green

T Temperature (K)

ΔG^o Gribb free energy

ΔH^o change in the enthalpy

ΔS^o change in entropy

R is the universal gas constant $(8.314 \times 10^{-3}$ kJ/mol K

Ea Activation energy

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