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Kinetics, Isotherm And Thermodynamics Studies of Swiss Blue Dye Desorption from Spent Microwave Prepared 'Hamburgar' Seed Shell Activated Carbon

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ABSTRACT

Chloroform desorption of Swiss blue dye from saturated activated carbon prepared from hamburger seed shell via microwave technique has been studied and the kinetics, isotherm and thermodynamic data determined. Initial solid loading concentrations of the activated carbon after saturation were 123.72mg/g, 248.58mg/g, 373.28mg/g, and 498.11mg/g using 100mg/l, 200mg/l, 300mg/l, and 400mg/l initial concentration of Swiss blue dye respectively. The kinetic data were fitted to first order, second order, pseudo first order, pseudo second intraparticle diffusion, and Elovich models. The data fitted pseudo second order perfectly due to the high correlation coefficient. The isotherm data was fitted to Langmuir, Freundlich, Dublin-Radushkevich (D-R), Temkin, Flory-Huggins, Redlich-Peterson and Toth models. The data fitted well to Freundlich model. Activation energy for desorption process was calculated at different initial solid phase concentration. Arrhenius relationship was developed to represent the rate constant dependency on temperature at different initial solid phase concentrations. Thermodynamic parameters calculated confirmed the process as endothermic, feasible and spontaneous. The process had increased disorder as temperature was increased.

Keywords: *Activated carbon, Hamburger seed shell, Microwave, Saturation, Swiss blue dye.*

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I. INTRODUCTION

Textile industry use dyes and pigments to colour their product. There are more than 100,000 commercially available dyes with over 7×105 tonnes of dyestuff are produced annually [1]. Many industries discharge wastewaters such as textile, chemical, refineries, plastic and food-processing plants and these wastewaters include residual dyes which are not bio-degradable [2]. Generally, the dyes that are used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulphur dyes [2]. Swiss blue which is commonly known as methylene blue dye is the most commonly used for dying cotton, wood and silk. Although the dye is not regarded as a very toxic dye, MB can have various harmful effects on human being and animals. Once inhaled, it can cause heart rate increasing, nausea and vomiting. [3] Such residual dyes may cause water pollution and a serious threat to the environment [4], [5]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters. Among several chemical and physical methods of treatment, the adsorption onto activated carbon has been found to be superior compared to other techniques for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design [6]. For economic reasons, the use of activated carbon is limited. The cost of carbon for a single use may be so high that its use is unjustified. One procedure for reducing operation costs using activated carbon is to desorb the substances retained, thereby enabling the carbon to be reused. [7].

The different methods can be used to regenerate spent activated carbons. These methods can be divided into the groups [8]; thermal, extractive, chemical, electrochemical, and biological, as well as methods with utilization of X-ray radiation, ultrasound, and others. The thermal regeneration is most often used. Usually, high temperature regeneration (700–1000 ◦C) is not carried out in situ [8]. Chemical regeneration can be carried out by desorption of adsorbates using specific solvents or by decomposition of adsorbed species using oxidizing chemical agents [9]. Extraction with solvents requires further purification of the solvent and it is only recommended when a valuable product is recovered [10].

In general, the chemical regeneration is considered economically infeasible insofar as expensive organic solvents are used as regenerants. Therefore, the chemical regeneration process should be optimized with respect to its economics and a study on desorption kinetics of organic solvents from spent activated carbon would be an essential part of it [11].

In this work, kinetics, isotherm and equilibrium studies of chloroform desorption of Swiss blue dye from spent activated carbon prepared from hamburger seed shell via microwave techniques were studied.

II. MATERIALS AND METHODS

2.1 SWISS BLUE DYE

Swiss blue dye is a basic dye equally known as methylene blue dye with molecular weight of 319.9 and empirical formula of $C_{16}H_{18}N_3SCl$. It is the most commonly used substance for dying cotton, wood, leather and silk. It is a basic dye that is typically cationic or positively charged and reacts well with a material that is anionic or negatively charged. Swiss blue dye was chosen in this study because of its known strong adsorption onto solids. The chemical structure of Swiss blue dye is shows as follows (Fig. 1.)

Fig. 1: Chemical structure of Swiss blue dye

2.2 HAMBURGAR SEED SHELL

Hamburger seed (Mucuna Sloanei) shell. The seed belongs to legume family (fabaceal). The shells were collected from a local market at abakpa, Enugu, Enugu State Nigeria.

2.3 PREPARATION OF ACTIVATED CARBON

The method was in accordance with the work done by Hammed [12]. The sample was washed exhaustively with deionized water to remove adhering dirt particles from the surface. Dried sample was ground and screened to the desired mesh size of 1 – 2mm. The carbonization process was performed by loading a known quantity of the precursor into a vertical furnace, and the temperature was ramped from room temperature to the desired temperature of 800^oC. The char produced was soaked in 6M KOH solution with 1.5:1 impregnation ratio defined as the volume of activating agent to weight of char (KOH: Char). The mixture was then dehydrated in an oven for one hour to remove moisture.

Microwave heating was conducted in a 2450MHZ commercial microwave oven with modification. The oven has a power controller to select different power levels and a timer for various exposure times at a set microwave power levels. The reaction was performed in a glass reactor fixed in the chamber of microwave oven.

The resultant activated carbon was washed repeatedly with 0.1MHCl and distilled water until PH 6-7 was reached in the residual liquid.

2.4 EXPERIMENTAL SET- UP OF MICROWAVE OVEN WITH THE MODIFICATIONS

This work utilized a modified Sonik domestic microwave oven model SMW-90023 Japan, with a maximum power output of 900W delivered at a frequency of 2450MHz. As part of the modifications, the microwave casing was penetrated from the top to provide fittings to support the quartz glassware reactor. The reactor was opened from the top end to allow for the escape of the pyrolysis gases. The upper surface of the oven had a removable cover connected to a stainless steel pipe from which the volatiles exit. The volatiles were then transferred to a condensing system made up of large absorbing bottle. The quartz glassware which was mounted inside the microwave cavity consisted of 100mls round bottom flask into which the samples was loaded, and a quartz quick fit connection coller which joined the flask with the outlet connection. Quartz was selected as reactor of choice because is a good material to be used in microwave reactors, it resist temperatures, transparent to microwaves and can resist thermal shock much better than traditional laboratory glass such as pyrex [13]. However, the reactor was not completely invulnerable and was found to show signs of devitrification after extended use. Thus, periodic replacement of the reactor was done.

2.5 DESORPTION STUDY

Desorption studies were also conducted by batch mode similar to adsorption studies. Known initial concentrations (100-400mg/l) of the Swiss blue dye solution were used to equilibrate the adsorbent. The dye loaded activated carbon was immersed in the initial solution of the dye for 24hours to ensure that the active sites were fully saturated. After equilibrium, the saturated adsorbent was washed with distilled water in order to remove un- adsorbed traces of the dye adhering on the surface and dried over night. The initial solid loading concentration of Swiss blue dye on the saturated activated carbon qi (mg/g) was calculated using equation 1.

$$q_i\left(\frac{mg}{g}\right) = \left(\frac{C_o - C_e}{m}\right)V \qquad (1)$$

q_i is the initial solid phase dye concentration (mg/g) and can be calculated using equation 1, C_o is the initial dye concentration used in equilibrating the adsorbent (mg/l), m is the mass of the adsorbent (g), V is the volume of the eluent (L), C_e is the Swiss blue dye concentration in solution (mg/l) at equilibrium,

2.5.1 DESORPTION KINETICS FOR SWISS BLUE DYE REMOVAL FROM SPENT ACTIVATED CARBON

For the desorption kinetics, 25ml of chloroform solution was taken in 250ml of stopper corked conical flask. It was then heated in a temperature controlled water bath shaker to certain temperature range (303-323K) and 150rpm. After attaining the required experimental temperature, 0.02g of Swiss blue dye saturated activated carbon at different initial loading concentrations was put into the flask. The samples were withdrawn at specified time intervals (20-280mins) and were analysed by UV-Vis Spectrophotometer at maximum wavelength of 661nm. The amount of Swiss blue dye remaining on the adsorbent, qt (mg/g) was calculated using a mass balance equation;

$$q_t\left(\frac{mg}{g}\right) = q_i - \frac{V\,(C_t - C_i)}{m} \qquad (2)$$

Where C_i is the initial dye concentration on the eluant before desorption (mg/l), C_t is the Swiss blue dye concentration in solution (mg/l) at any time.

2.5.2 DESORPTION EQUILIBRIUM STUDIES FOR SWISS BLUE DYE REMOVAL FROM SPENT CARBON

For the desorption equilibrium, 25ml of chloroform solution was taken in 250ml of stopper corked conical flask. It was then heated in a temperature controlled water bath shaker to certain temperature range (303-323K) and 150rpm. After attaining the required experimental temperature, 0.02g of Swiss blue dye saturated activated carbon at different initial loading concentrations was put into the flask. The samples were withdrawn at the end of equilibrium time of five hours and were analysed by UV-Vis Spectrophotometer at maximum wavelength of 661nm. The amount of Swiss blue dye remaining on the adsorbent at equilibrium, qe (mg/g) was calculated using a mass balance equation;

$$q_e\left(\frac{mg}{g}\right) = q_i - \frac{V\,(C_e - C_i)}{m} \qquad (3)$$

Where C_e is the Swiss blue dye concentration in solution (mg/l) at equilibrium, C_i is the initial dye concentration on the eluant before desorption (mg/l), q_i is the initial solid phase concentration and can be calculated using equation 1.

III. RESULTS AND DISCUSSIONS

a. EFFECT OF INITIAL SWISS BLUE DYE CONCENTRATIONS ON THE SOLID LOAD CONCENTRATIONS OF SWISS BLUE DYE.

To study the desorption process of the spent activated carbon, it was saturated with Swiss blue dye at different initial concentrations of 100-400mg/l for 24 hours to make sure that the pores were fully saturated. After the saturation, the concentrations of the dye on the adsorbent were calculated as the initial solid load concentrations. These solid load concentrations were used to carry out desorption kinetics, isotherm and thermodynamic studies. Fig. 1 shows the results of initial solid load concentrations at various initial Swiss blue dye concentrations for the prepared activated carbon. It was observed that initial solid load increased with increase in initial Swiss blue dye concentrations. This can be attributed to the fact that increase in Swiss blue dye concentrations increased the mass transfer driving force necessary to favour the uptake of dye, thereby increasing the initial solid load concentrations.

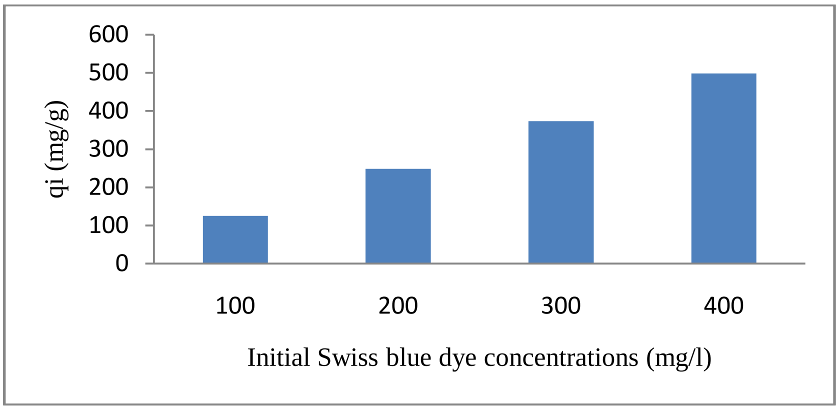


Figure 2. Initial solid phase concentration at various initial Swiss blue dye concentration

b. DESORPTION KINETICS OF SWISS BLUE DYE REMOVAL FROM SWISS BLUE DYE LOADED ACTIVATED CARBON

Desorption of Swiss blue dye from the activated carbon was described by mass transfer from the activated carbon to the solvent [14]. The kinetic data was obtained at different initial solid phase concentration, and was fitted to different kinetic models. The kinetic models verified were first order, pseudo first order, second order, pseudo second order and Elovich model. These models were based on the concentration of Swiss blue dye on the solvent (ct) and the amount of dye remaining on the activated carbon after desorption (qt).

The kinetic parameters of desorption of Swiss blue dye for the models are shown on Table 1.

The correlation coefficients (R^2) of different models showed that the data fitted well to pseudo second order model with correlation coefficient almost 1.0 for all the initial solid phase concentration used. The data equally fitted well to the intra particle diffusion model. This finding was in agreement with the works done by Sarici-Ozdemir [15] on desorption kinetics behaviour of methylene blue dye on to activated carbon and Kim and Kim [14] on the apparent adsorption kinetics of phenols in organic solvents from spent activated carbons saturated with phenol. This result was contrary to the work done by Tseng et. al., [16] on the kinetics and equilibrium of desorption of removal of copper from magnetic polymer adsorbent. They found out that pseudo first order fitted desorption data well.

The validity of pseudo second order was equally ascertained by the values of the predicted solid phase concentration (qed predicted). It was observed that the qed. predicted using pseudo second order equation were very close to the initial solid phase concentration used for the experiment (qe experiment) for all the initial solid phase concentrations.

Further examination of the values of desorption rate constants for pseudo second order model (K_{P2}) in Table 1, showed that K_{P2} decreased with increase in initial solid phase concentrations. This might be due to gradual increase in desorption resistance of the dye from activated carbon as the initial solid phase concentration increased [17].

The validity of pseudo second order model showed that driving force of desorption might be the difference between the equilibrium concentration in a solvent with the adsorbed amount of dye in activated carbons at a time and the bulk concentration of dye in solvent [14].

It was equally observed that the kinetic data equally fitted well to intra particle diffusion model. The intra particle diffusion was equally used to identify the mechanism of desorption and the rate controlling step. The linear plots at various initial solid phase concentrations do not pass through the origin, which shows that the intra particle diffusion was not the only rate controlling step and the boundary layer diffusion controlled the he desorption to some extent. The value of the intercept (C) which related to the boundary layer resistance increased with increase in initial solid phase concentration. These values were close to the initial solid phase concentration and showed that thickness of the boundary layer increased as the initial solid phase concentration increased. This showed that as the initial solid phase concentration increased, the contribution of the boundary layer in the rate limiting step increased [15].

Table 1. Kinetics parameters for desorption of Swiss blue dye from spent Microwave prepared activated carbon from hamburger seed shell

Initial dye conc. (mg/l)	100.00	200.00	300.00	400.00
Initial solid phase conc. qe exp mg/g	123.72	248.58	373.28	498.11

First Order Model

C_{AO} (mg/l)	2.442	3.196	4.577	5.551
K_1 (min^{-1})	0.002	0.001	0.00	0.00
R^2	0.669	0.642	0.715	0.888

Pseudo First Order Model

qe calc (mg/g)	0.0645	0.0704	0.1144	0.0425
Kp_1 (min^{-1})	-0.033	-0.037	-0.032	-0.822
R^2	0.808	0.892	0.794	0.822

Second Order Model

C_{AO} (mg/l)	2.415	3.175	4.762	5.587
K_2 (min^{-1})	0.002	0.001	0.0004	0.0001
R^2	0.669	0.62	0.715	0.888

Pseudo Second Order Model

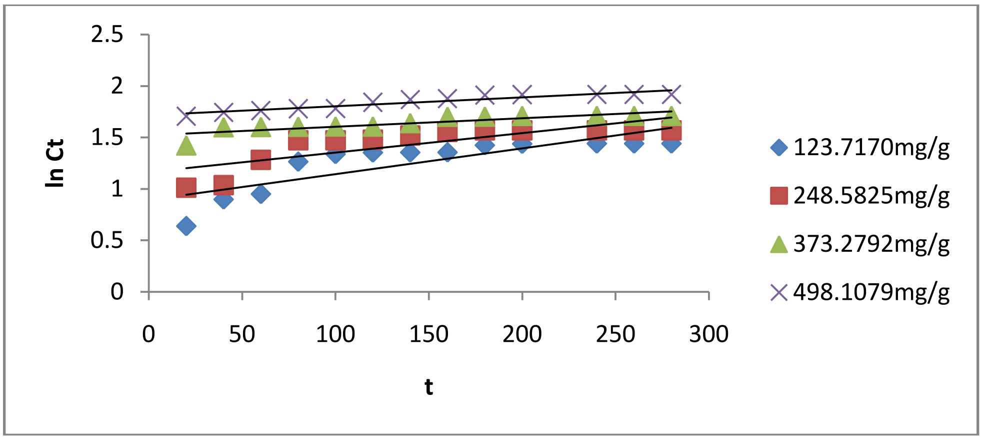
qe calc (mg/g)	125.0	250.0	400.0	500.0
$-Kp_2$ (min^{-1})	0.009	0.006	0.004	0.003
R^2	1.0	1.0	1.0	1.0

Intra particle Diffusion

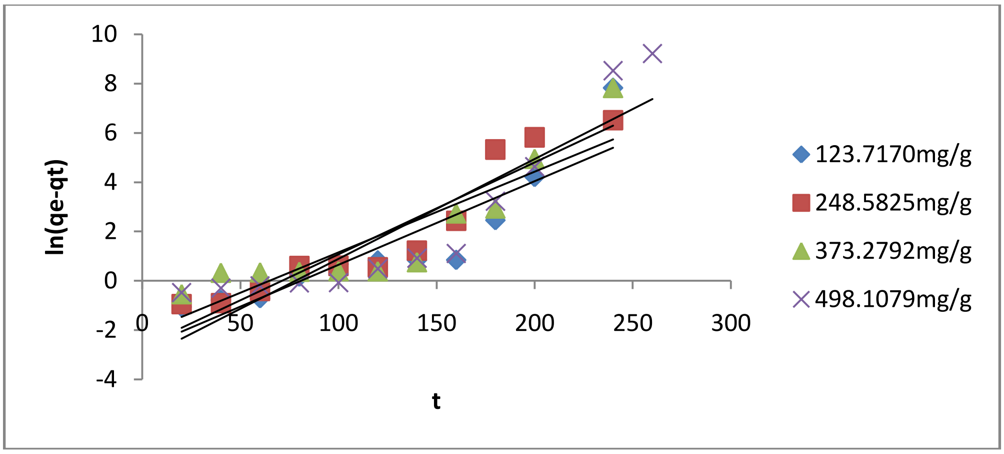
C(g/mg)	125.6	249.4	347.7	400.3
K_d ($mg/m.min^{-1}$)	-0.531	-0.342	-0.452	-0.532
R^2	0.918	0.884	0.928	0.952

Elovich Model

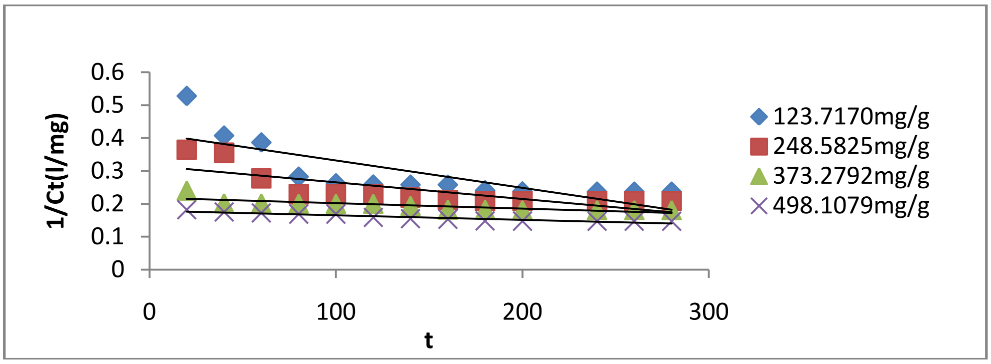
B(g/mg)	-0.835	-0.894	-1.675	-1.370
R^2	0.926	0.897	0.876	0.910



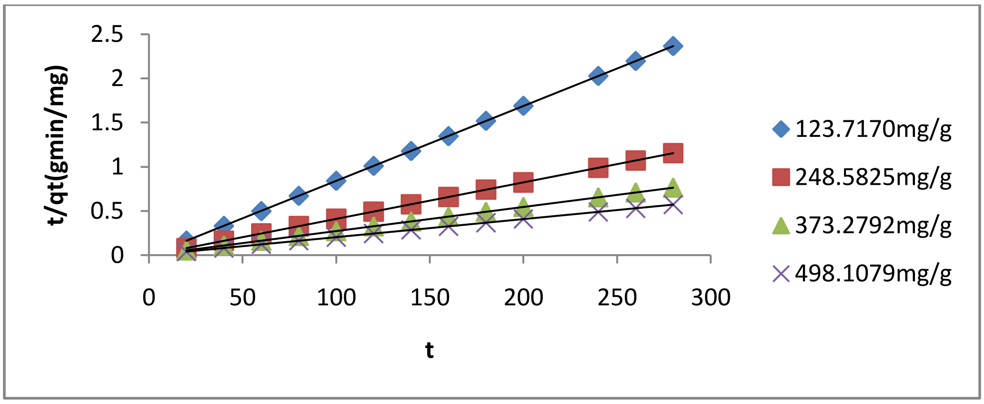
(a)



(b)


1/Ct(l/mg)
0.6
0.5
0.4
0.3
0.2
0.1
0
0
100
200
300
t
123.7170mg/g
248.5825mg/g
373.2792mg/g
498.1079mg/g

(c)


t/qt(gmin/mg)
2.5
2
1.5
1
0.5
0
0
50
100
150
200
250
300
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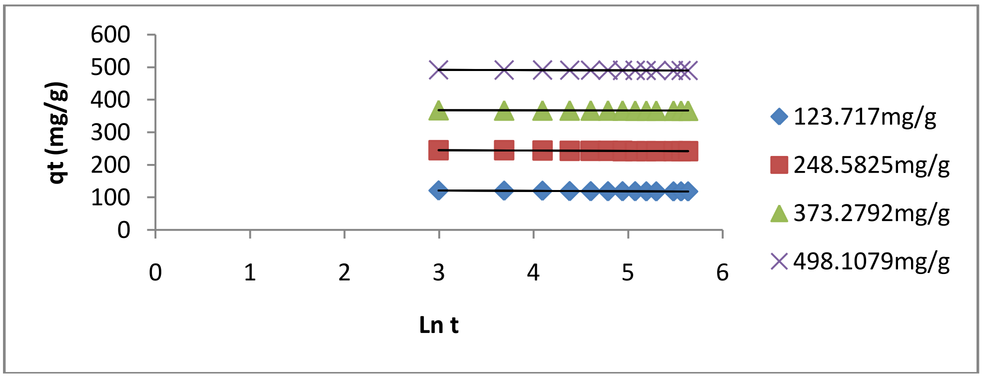
373.2792mg/g
498.1079mg/g

(d)


qt (mg/g)
600
500
400
300
200
100
0
0
1
2
3
4
5
6
Ln t
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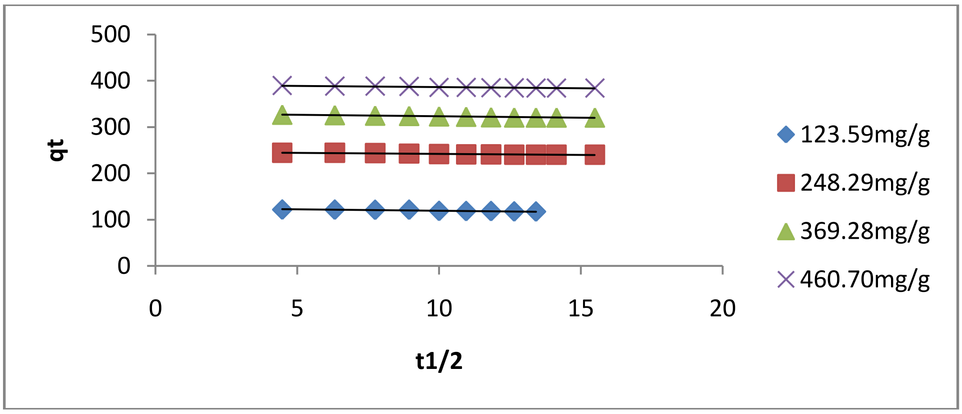
373.2792mg/g
498.1079mg/g

(e)


qt
500
400
300
200
100
0
0
5
10
15
20
t1/2
123.59mg/g
248.29mg/g
369.28mg/g
460.70mg/g

(f)

Figure 2. Kinetic plots of Swiss blue dye desorption from spent activated carbon (a) First order, (b) Pseudo first order, (c) Second order, (d) Pseudo second order, (e) Elovich, (f) Intra particle diffusion

3.3 Desorption Kinetics Of Swiss Blue Dye At Different Temperatures

In order to obtain the activation energy and frequency factor for the desorption process, the kinetic data were obtained at different temperatures of 303K, 313K and 323K. The data were fitted to pseudo second order model that was considered the best kinetic model. The plots of the pseudo second model at different temperature are shown in Figures 3. It was observed from the pseudo second order kinetic parameters on table 2 that the rate constant and correlation coefficients for the model increased with increase in temperature. This suggested that increase in temperature favoured the desorption process. The correlation coefficients (R^2) were unity for all the initial solid loading concentrations. The rate constants that allowed the best fit to experimental kinetic data (for pseudo second order) of Swiss blue dye concentration in chloroform were applied to Arrhenius equation to determine the activation energy and frequency factor. The relationship between the rate constants and solution temperature was expressed by Arrhenius equation 4 [14], [19], [20].

$$Kd = Ad \exp\left(\frac{-Edes}{RT}\right) \qquad (4)$$

Where Ad is the frequency factor or temperature independent factor (min^{-})

E_{des} is the activation energy (J/mol) for desorption process, R is the gas constant (8.314J/mol.K) and T is the solution temperature (K).

The activation energy measures the magnitude of the forces required to overcome during desorption process [17]. It determines the chance of the adsorbent dye molecules overcoming the potential barrier to desorption.

Transformation of the equation into linear form gave

$$InKd = InAd - \frac{Eds}{RT} \qquad (5)$$

Plot of InKd Vs 1/T gave slope of $\frac{-Edes}{R}$ and intercept of InAd. The properness of the Arrhenius equation was checked by a plot of InK_d vs. 1/T on Figure 4. The squares of the linear correlation coefficients (R^2) for all the initial solid phase concentration were greater than 0.9. Therefore, the Arrheius relationship could be justifiable for representing the temperature dependency expression of K_d [14]. Furthermore, the excellent temperature dependency expression of K_d might indirectly support the properness of K_d values as well as that of the desorption pseudo second order model. The activation energy, frequency factors and the correlation coefficients of Arrhenius plot is showed in table 3.

When Kd values of Swiss blue dye were expressed as an experimental function of temperature, the equation at different initial Swiss blue dye concentration used for saturation becomes;

100mg/l;

$$Kd(min^{-1}) = 14355.67 \exp\left(\frac{-1463.5}{T}\right) \qquad (6)$$

200mg/l;

$$Kd(min^{-1}) = 185164.52 \exp\left(\frac{-2350.1}{T}\right) \qquad (7)$$

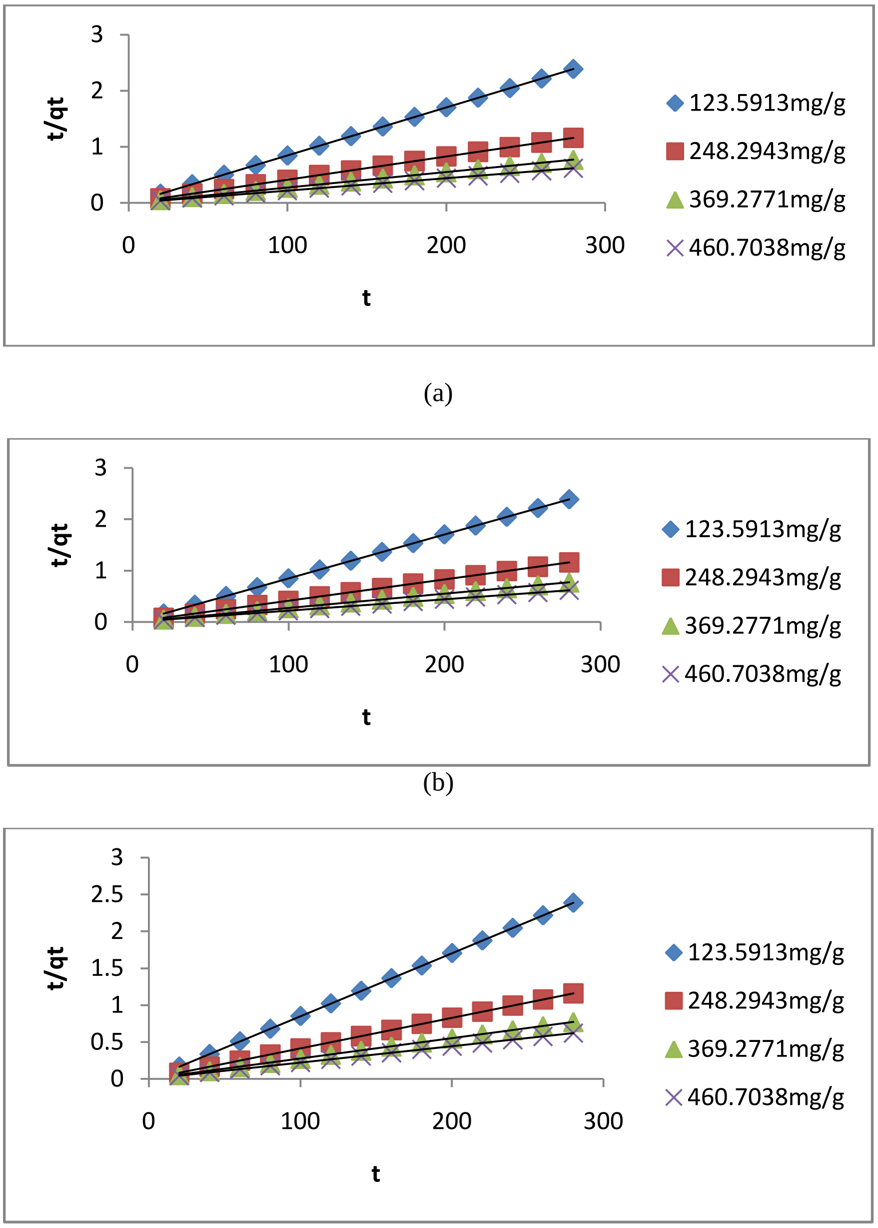
300mg/l;

$$Kd(min^{-1}) = 790167.3 \exp\left(\frac{-2832.5}{T}\right) \qquad (8)$$

400mg/l;

$$Kd(min^{-1}) = 115844.03 \exp\left(\frac{-2304}{T}\right) \qquad (9)$$

As a result of using equations (6-9), the desorption kinetics of Swiss blue dye removal from spent activated carbons using chloroform would be predicted at certain temperatures.



(a)

(b)

(c)

Figure 3. Pseudo second order model plots for Swiss blue dye desorption at different temperatures (a) 303K, (b) 313K, (c) 323K.

Table 2. Pseudo second order parameters at different temperature

	303K			
qe (exp)(mg/g)	123.59	248.29	369.28	460.70
qe (calc.)(mg/g)	114.942	238.1	333.33	434.78
$-K_d$ x10^{-4}(min^{-1})	86.0	126.0	143.0	177.0
R^2	1.0	1.0	1.0	1.0
	313K			
qe (exp)(mg/g)	123.59	248.29	369.28	460.70
qe (calc.)(mg/g)	114.942	238.1	333.33	434.78
$-K_d$ x10^{-4}(min^{-1})	757.0	882.0	110.0	128.0
R^2	1.0	1.0	1.0	1.0
	323K			
qe (exp)(mg/g)	123.59	248.29	369.28	460.70
qe (calc.)(mg/g)	114.942	238.1	333.33	434.78
$-K_d$ x10^{-4}(min^{-1})	64.0	78.0	80.0	111.0
R^2	1.0	1.0	1.0	1.0

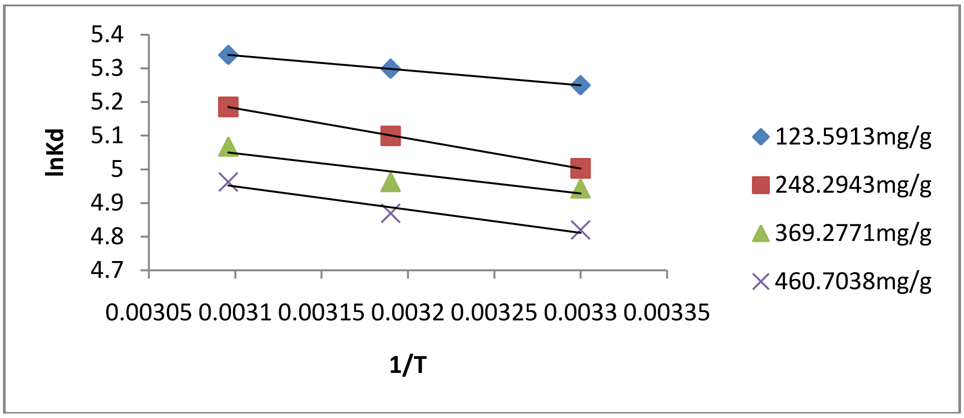


Figure 4. Arrhenius plots for desorption of Swiss blue dye from spent activated carbon

Table 3. Arrhenius parameters for desorption of Swiss blue dye from spent microwave prepared activated carbon from hamburger seed shell

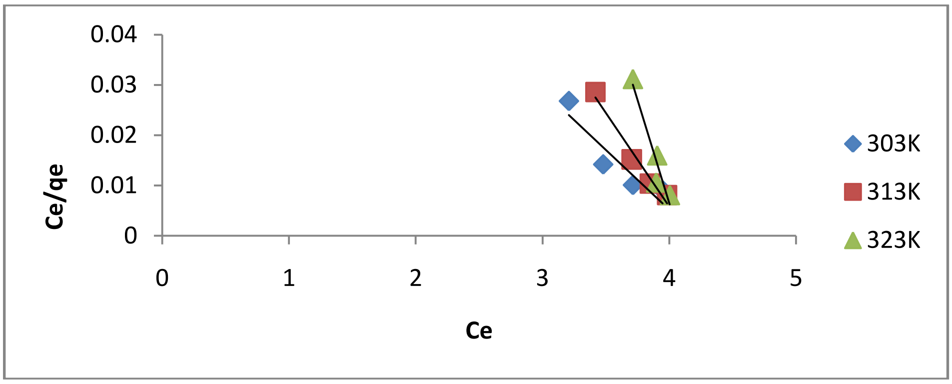
Initial solid phase conc. (mg/g)	123.72	248.58	373.28	498.11
Ad (min^{-1})	8112.0	2833.87	989.20	1198.23
E_{des} (J/mol)	3652.67	7425.4	4959.72	5737.57
R^2	1.0	0.9998	0.929	0.9526

3.4 Desorption Isotherm Of Swiss Blue Dye From Spent Activated Carbon

When the spent activated carbons were desorbed using chloroform, it was observed that the concentration of Swiss blue dye in the solvent increased with time, whereas the amount of Swiss blue dye on the adsorbents decreased with time. The equilibrium state at which the concentration of Swiss blue dye in the solvent remained constant with time shortly varied at different initial solid phase concentration and temperatures. At equilibrium, the relationship between the concentration of Swiss blue dye in the chloroform (Ce) and the remaining amount on the adsorbents (qe) was expressed like the Lagmuir, Freundlich, Dublin-Radushkevich (D-R), Temkin, Flory-Huggins, Redlich-Peterson (S- P) and Toth-isotherm equations. Desorption data were applied to the linear plots of these isotherm models to describe desorption of Swiss blue dye from the spent adsorbents. The desorption parameters obtained from the model plots (Figure 5) is listed in table 4.

The regression coefficients (R^2) value for Freundlich model were comparatively higher suggesting that desorption of Swiss blue dye from the spent activated carbons were well described by Freundlich model. The applicability of Freundlich model confirmed that heterogeneous sites were actively involved for the adsorption process. This indicates that the adsorption sites on the surface of the adsorbents may possess different potential energies to form surface complex [16]. These results were in agreement with the previous study on adsorption of Swiss blue dye on the adsorbents.

These results were in agreement with the work done by Tseng et. al.,[16] on the kinetics and equilibrium desorption for removal of copper from magnetic polymer adsorbent, Kim and Kim [14] on apparent desorption kinetics of phenol in organic solvents from spent activated carbon saturated with phenol, and Chu et. al. [21] on desorption of vitamin E from silica based adsorbent. Contrary to these results, Muhammad et. al., [19] reported the applicability of Lagmuir model for desorption of β-carotene from mesoporus carbon coated monolith. Sip and Redlich-Peterson isotherm models equally recorded high correlation coefficients (R^2). These models were three parameters obtained from Freundlich isotherm constant that recorded high correlation coefficients (R^2). The applicability of Freundlich model for the desorption process showed that at equilibrium, the concentration of Swiss blue dye in the chloroform (Ce) is directly proportional to the remaining Swiss blue dye on the adsorbents (qe). It was equally observed from the results that the equilibrium constants for Freundlich isotherm decreased with increase in temperature. This shows that increase in temperature favoured the desorption process, thus the amount of Swiss blue dye remaining on the adsorbents decreased with increase in temperature.


Ce/qe
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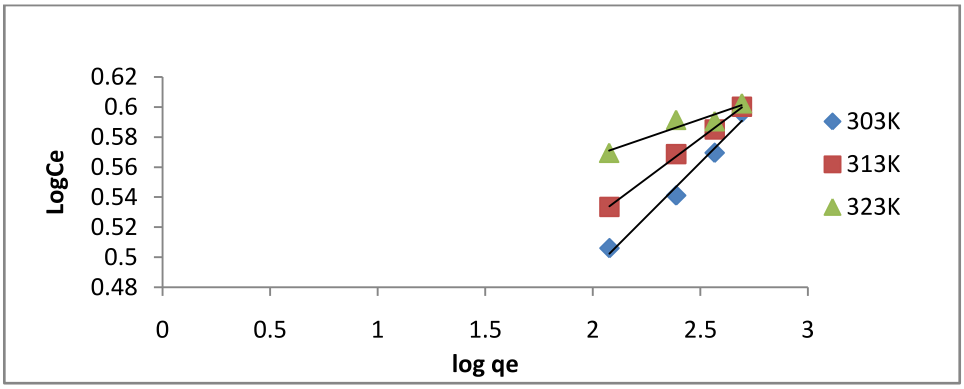
0.03
0.02
0.01
0
0
1
2
3
4
5
Ce
303K
313K
323K

(a)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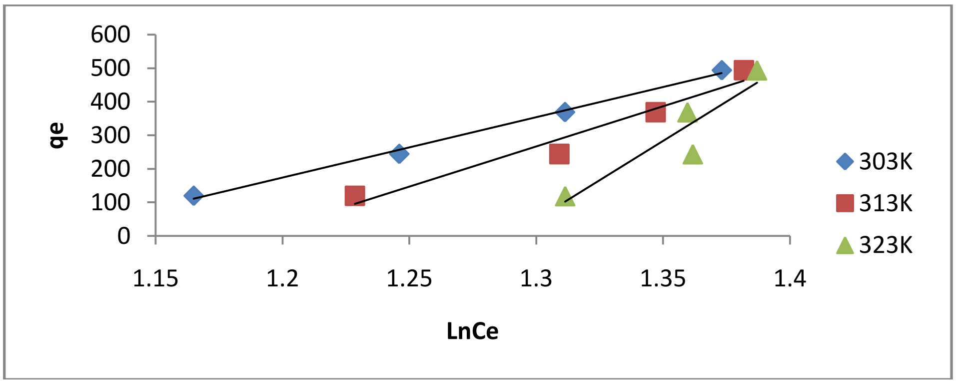
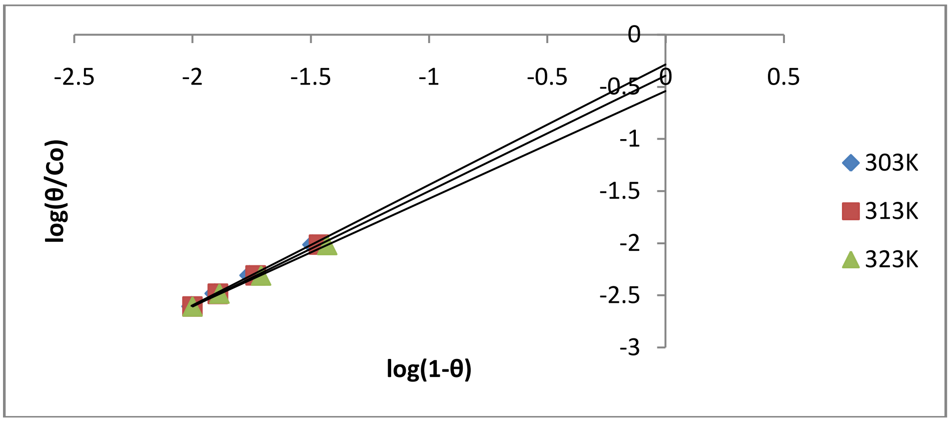
0.56
0.54
0.52
0.5
0.48
0
0.5
1
1.5
2
2.5
3
log qe
303K
313K
323K

(b)


qe
600
500
400
300
200
100
0
1.15
1.2
1.25
1.3
1.35
1.4
LnCe
303K
313K
323K

(c)


log(θ/Co)
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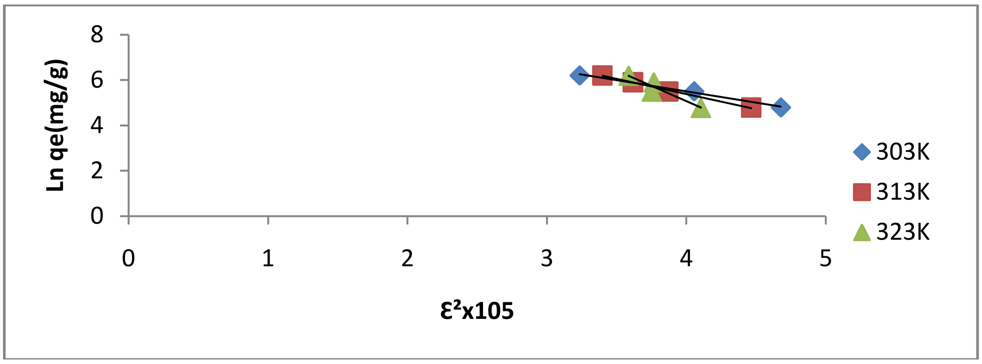
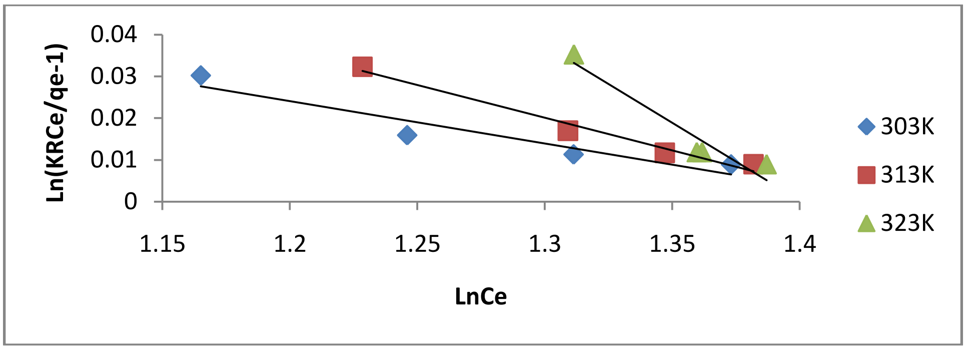
-2.5
-2
-1.5
-1
-0.5
0
0.5
-0.5
-1
-1.5
-2
-2.5
-3
log(1-θ)
303K
313K
323K

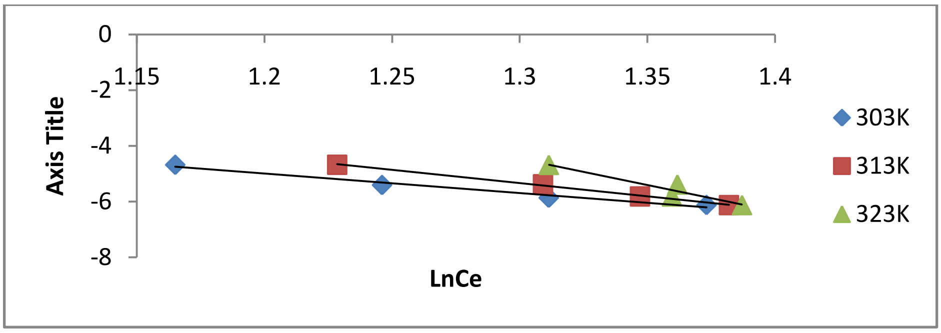
(d)



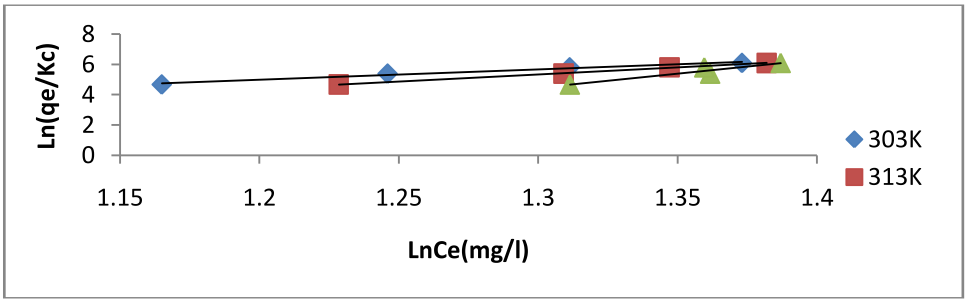
(e)



(f)



(g)



(h)

Fig. 4.40. Isotherm plots of Swiss blue dye desorption from spent Microwave prepared activated carbon from hamburger seed shell (a) Langmuir, (b) Freundlich, (c) Temkin, (d) Flory-Huggins, (e) D-R, (f) Redlich – Peterson, (g) Sip, (h) Toth

Table 4. Isotherm parameters for desorption of Swiss blue dye from Microwave prepared activated carbon from Hamburgar seed shell

Temperature (K)	303	313	323
Langmuir Model			
-b(mg/g)	43.4783	27.0270	12.3450
-K_L(L/mg)	0.23	0.24	0.24
R^2	0.857	0.968	0.914
Freundlich Model			
N	6.993	9.434	20.408
K_f(mg/g) (mgl^{-1})-1/n_F	0.751	0.657	0.582
R^2	0.950	0.998	0.910
Dublin-Radushkevich (D-R) Model			
B_D	0.987	1.334	2.705
E(J/mol)	0.712	0.612	0.430
R^2	0.992	0.996	0.910
Temkin Model			
A(L/mol)	0.3320	0.1264	0.2760
B	1.401	1.091	0.573
R^2	0.995	0.953	0.843
Flory-Huggins Model			
K_{FH}(L/mol)	0.518	0.406	0.287
nF_H	1.153	1.106	1.031
R^2	0.999	1.0	0.999
Redlich-Peterson Model			
K_R(mg/g)(mg/L)-1/n_F	0.751	0.657	0.582
R^2	0.901	0.975	0.916
Sip Model			
Ks(mg/g)(mg/l)	0.751	0.657	0.582
B(L/mg)	6.998	9.468	18.820
αs(L/mg)	29.93	10.63	4.85
R^2	0.977	0.977	0.906
Toth Model			
-K_T(l/mg)	0.23	0.24	0.24
a_T	0.665	0.5180	2.7350
T	0.1280	0.0968	0.0510
R^2	0.950	0.998	0.910

3.5 Thermodynamics Study For Desorption Of Swiss Blue Dye From Spent Activated Carbons

The thermodynamic parameters (ΔHdes, ΔSdes and ΔGdes) were obtained from the combination of Arrhenius equation [19], [14], [20] and Freundlich equilibrium constant (Ke) expressed as an exponential function of temperature [14], [22], [23].

When rate constant K_d is described by the Arrhenius equation, we have it that [14], [19], [20];

$$Kd = Ad \exp\left(\frac{-Edes}{RT}\right) \qquad (10)$$

Equally, at equilibrium, the relationship between the concentration of the Swiss blue dye in chloroform (Ce) and the adsorbed amount on the activated (qe) might be expressed like the Freundlich isotherm equation.

$$qe = Ke(Ce)^n \qquad (11)$$

Ke was expressed as an exponential function of temperature as

$$Ke(T) = K_O \exp\left(\frac{\gamma}{T}\right) \qquad (12)$$

Linearization of equation 4.41 gives

$$InKe = InK_O + \gamma\left(\frac{1}{T}\right) \qquad (13)$$

γ(K) and K_O(mg/g)(mg/l)$^{-n}$ are constants in eqn. (13), Ke is Freundlich isotherm constant (mg/g)(mg/l)$^{-n}$ and T is temperature (K).

Plot of InKe against 1/T in equation 13 gave InK_o as intercept and γ as slope. Table 5 show the parameters obtained from plot of InKe against 1/T while Fig. 6 shows the plots.

It was observed that correlation coefficients (R^2) were approximately 1.0. This proved the validity of equation 13.

To further understand the nature of the desorption process, Schroeder and Gottfried (2002) [19] stated that differences between activation energy (ΔEdes) and enthalpy change (ΔHdes) are in practice often negligible. Therefore, they assumed that ΔEdes = ΔHdes. They equally stated that the frequency factor (Ad) in the Arrhnius equation can be equated to the entropy term as follows ;

$$Ad = \frac{K_d T}{\gamma} \exp\left(\frac{\Delta\text{Sdes}}{R}\right) \qquad (14)$$

Entropy of desorption can be extracted from the frequency factor (Ad) above as;

$\Delta \mathrm{Sdes} = \mathrm{R}.\frac{InAd.\gamma}{K_d T})$ (15)

Where R is the universal gas constant (J/mol.K), γ is constant from equation (13) (K), T is the temperature (K), and K_d is the pseudo second order rate constant (1/min).

Change in the standard free energy (ΔG_{des}) can be calculated from the enthalpy (ΔS_{des}) using the following relation [24];

$\Delta \mathrm{Gdes} = \Delta \mathrm{Hdes} - \mathrm{T}\Delta \mathrm{Sdes}$ (16)

The thermodynamic parameters obtained at different initial solid phase concentration and temperatures are shown in table 6.

It was observed from the results that the enthalpy change for desorption process at different temperatures were positive, indicating endothermic reaction. This means that increase in temperature favoured the desorption process. Desorption process consumed energy from the surrounding in overcoming the activation barrier needed before desorption takes place. Positive entropy (ΔS) observed at different initial solid phase concentration suggested that the desorption process had disorder at various conditions studied. The entropy values increased as reaction temperature was increased with exception of few. This suggested that the reaction gets more disorder as temperature was increased confirming the endothermic nature of the reaction. The negative Gibbs free energy (ΔG) observed on the entire initial solid phase concentration at various temperatures confirmed the process to be spontaneous and feasible. Increase in temperature increased the Gibbs free energy (ΔG) with exception of few. This showed that the desorption process becomes more spontaneous as the temperature was increased.

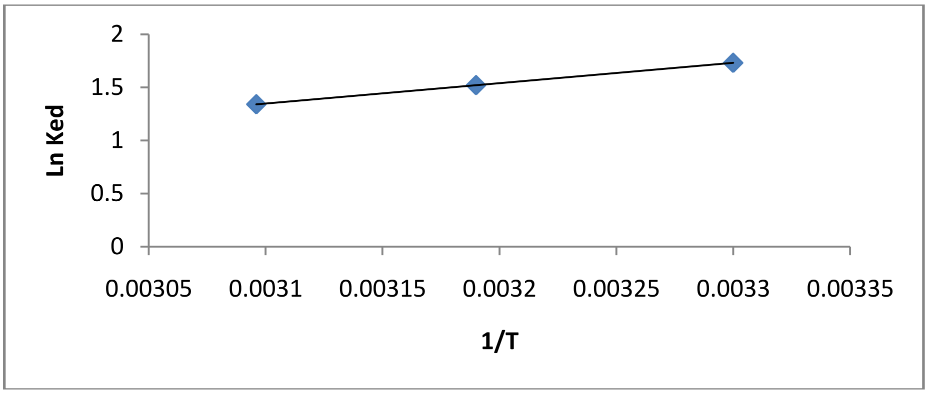


Figure 6. Freundlich constant against reciprocal of temperature for Swiss blue dye desorption from spent activated carbon.

Table 5. Parameters of Freundlich equilibrium constant (Ke) expressed as an exponential function of temperature for desorption of spent activated carbon

Parameters	MPAHS
K_O((mg/g)(mg/l)$^{-n}$)	0.0103
γ(K)	1911.7
R^2	1.0

Table 6. Thermodynamic parameters for desorption of Swiss blue dye from spent microwave prepared activated carbon from hamburgar seed shell.

Initial solid phase conc. (mg/g)	ΔH_{des} (KJ/mol)	ΔS_{des} (J/mol.K)			- ΔG_{des}(KJ/mol)		
		303K	313K	323K	303K	313K	323K
123.5913	3.652	133.99	134.12	134.20	36.95	36.99	37.01
248.2943	7.425	123.22	123.73	124.18	29.91	30.06	30.20
369.2771	4.959	113.95	113.83	114.45	29.57	29.53	29.72
460.7038	5.737	114.51	114.66	115.16	28.96	29.00	29.16

IV. CONCLUSION

This work has studied the chemical desorption of Swiss blue dye loaded activated carbon prepared from hamburger seed shell via microwave technique. Microwave heating method had proved its effectiveness in activating hamburger seed shell. The activated carbon was saturated with 100mg/l, 200mg/l, 300mg/l and 400mg/l of Swiss blue dye concentrations. It was observed that increase in Swiss blue dye concentrations increased the initial solid phase concentration of the adsorbent. The chemical desorption was achieved using chloroform. The kinetic data obtained at different initial solid phase concentrations was fitted to first order, second order, pseudo first order, pseudo second order, intraparticle diffusion, and Elovich models, and pseudo second order was found to fit the data more appropriately. Based on the high correlation coefficient obtained, Arrhenius relationship was justified to represent the rate constant dependency on temperature. Isotherm data was fitted to Langmuir, Freundlich, Temkin, Flory-Huggins, D-R, R-P, and Toth models, and was observed that the data fitted well to Freundlich model. Thermodynamic parameters calculated suggested the desorption to be feasible, spontaneous and exothermic in nature.

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