

EFFECT OF PROCESS FACTORS ON DESORPTION OF SWISS BLUE DYE FROM SPENT MICROWAVE PREPARED ACTIVATED CARBON FROM HAMBURGAR SEED SHELL

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ABSTRACT

This work studied the effect of process factors on desorption of Swiss blue dye from spent microwave prepared activated carbon from 'hamburger seed shell'. The activated carbon was considered spent by saturating it with Swiss blue dye for twenty four hours. Effect of desorption time, temperature, spent carbon dosage and eluants on the desorptive capacity of the carbon was studied. Effect of five different eluants which are 0.1M HCl, 0.1M NaOH, chloroform, n-hexane, and ethyl acetate on the desorption efficiency of the spent carbon was studied and it was found that chloroform recorded the highest desorption efficiency. It was observed that the adsorptive capacity increased with increase in dosage of spent carbon. Adsorptive capacity decreased with increase in temperature and time at different initial solid phase concentrations. Desorption kinetic was found to fit pseudo second order, while isotherm data fitted well to Freundlich model. The thermodynamic studies showed that the process was endothermic in nature, spontaneous and feasible.

KEY WORDS: Chloroform, desorption, Eluants, spent carbon, Swiss blue dye, microwave oven,

1. INTRODUCTION

Activated carbon enjoys many uses because of its sorbent properties. Conventionally, activated carbon is packed in a column and the material to be purified is passed through it, though batch wise use of activated carbon is still carried on in many areas. When the activated carbon has lost its sorbent properties through use, it is replaced with fresh carbon. The spent carbon is then either disposed or regenerated. Disposal of spent carbon is wasteful and constitute environmental pollution, hence regeneration becomes necessary.

Regeneration is defined as the process followed by adsorption to remove the adsorbate from the adsorbent, either by raising the temperature or decreasing pressure or other

driving force such as vacuum (Wang, et. al. 2004). In general, regeneration is of two steps: desorption and drying (Nattkemper, 1997; Gu, et. al. 1999). Drying is a required step particularly in the case of steam regeneration, because there is a possibility of condensed water in the bed; then the condensed water can be removed by passing the dry air through the bed (Shivaji, 2012). The drying step could be neglected in the case of absence of moisture in the bed (Shivaji, 2012).

Swiss blue dye is a basic dye that is commonly known as Methylene blue dye. It is generally used for colouring and dyeing cotton, wool and silk (Cazetta et. al, 2011). This dye has been studied because of its known strong adsorption onto solids and it often serves as a model compound for removing organic

contaminants and coloured bodies from aqueous solution (Hameed et al, 2007).

This work studied the effect of process factors on Swiss blue dye desorption from activated carbon saturated with Swiss blue dye. The activated carbon was prepared from hamburger seed shell via microwave activation technique.

2. MATERIALS AND METHODS

2.1. Adsorbate:

Swiss blue dye is a basic dye with molecular weight of 319.9 and empirical formula of $C_{16}H_{18}N_3SCl$.

The chemical structure of Swiss blue dye is showed on figure 2.1:

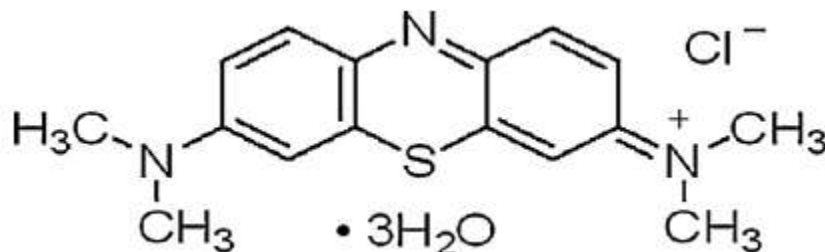


Fig. 2.1. Molecular structure of Swiss blue dye

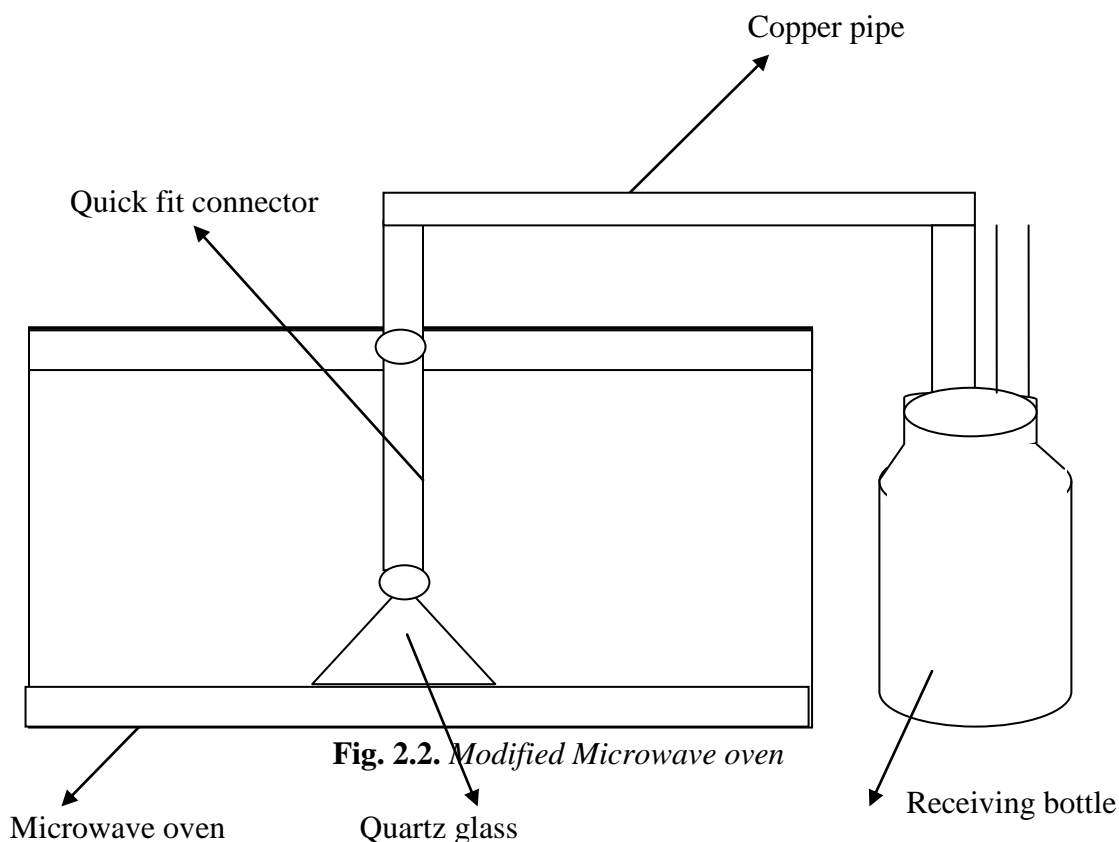
2.2. Adsorbent:

Activated carbon was prepared from Hamburger bean seed (*Mucuna Sloanei*) shell. The shells were collected from a local market at abakpa, Enugu East Local Government Area of Enugu State Nigeria.

2.3. Experimental Set-up of Modified Microwave Oven used for Activation Process.

This experimental set up was according to the work done by Ejikeme and Igbokwe 2016. It utilized a modified Sonik domestic microwave oven model SMW-90023 Japan, with a maximum power output of 900W delivered at a frequency of 2450MHz. The modified domestic oven used for the microwave activation is shown on Figure 2.2. 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 copper pipe from which the volatiles exit. The volatiles were then transferred to a condensing system made up of large receiving bottle. The quartz glassware which was mounted inside the microwave cavity consisted of 100mls flat bottom flask into which the samples were loaded, and a quartz quick fit connection collar 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 (Bradshaw et. al., 1998). However, the reactor was not completely invulnerable and was found to show signs of diversification after extended use. Thus, periodic replacement of the reactor was done.



2.4. Production of Activated Carbon Using Microwave Technique:

Detail method of preparation of the activated carbon has been discussed on our previous work on Kinetics, Isotherm and thermodynamics studies of Swiss blue dye desorption from spent microwave prepared ‘hamburger’ seed shell activated carbon (Ejikeme and Igbokwe 2016).

2.5. Saturation of Activated Carbons:

The saturation was according to the work done by Ejikeme and Igbokwe (2016). Known initial concentrations (100-400mg/l) of the 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 load concentrations of Swiss blue dye on the saturated activated carbon were calculated using equation 3.1.

$$q_i \left(\frac{mg}{g} \right) = \left(\frac{C_o - C_e}{m} \right) V \quad (3.1)$$

q_i is the initial solid phase dye concentration (mg/g), C_o is the initial dye concentration used in equilibrating the adsorbent (mg/l), C_e is the equilibrium concentration of the dye solution after equilibrium (mg/l), m is the mass of the adsorbent (g), V is the volume of the eluant (L), q_e is the the solid phase dye concentration after desorption (mg/l).

2.6. Desorption Studies:

Desorption studies were also conducted by batch mode. Firstly effect of types of eluants on desorption of dye was studied using 0.1M NaOH, 0.1M HCL, n-hexane, Chloroform and ethyl acetate as eluants. 0.02g of the saturated adsorbent was then treated with 25ml of eluant solution to desorbs the adsorbed dye solution.

At the end of 3hours, the dye remaining on the liquid phase was analyzed using UV-visible spectrophotometer at the maximum adsorbed wavelength of 661nm. The desorption efficiency, and adsorptive capacity were calculated using equations 3.2 and 3.3 respectively.

$$\text{Desorption efficiency (\%)} = \frac{q_i - q_e}{q_i} \times 100 \quad (3.2)$$

$$q_e \left(\frac{\text{mg}}{\text{g}} \right) = q_i - \frac{V(C_e - C_i)}{m} \quad (3.3)$$

Where C_i is the initial dye concentration on the eluent before desorption (mg/l), q_i is the initial solid phase dye concentration (mg/g), C_o is the initial dye concentration used in equilibrating the adsorbent (mg/l), C_e is the equilibrium concentration of the dye solution after equilibrium (mg/l), m is the mass of the adsorbent (g), V is the volume of the eluant (L), q_e is adsorptive capacity (mg/g).

2.7. Effect of Dosage of Saturated Activated Carbons on the Desorptive Capacity of the Activated Carbons:

Effect of dosage of saturated activated carbon on desorption capacity of the eluants was studied at dosage of 0.1, 0.2, 0.3, and 0.4g at different initial solid phase dye concentration. The known weight was added to 25ml of chloroform and was agitated for five hours. After, it was centrifuged and analysed for the residual dye concentration using aforementioned procedure. The desorption capacity; q_e (mg/g) was calculated using equation 3.3.

2.8. Kinetics and Equilibrium Studies:

Detail methods used for the kinetics, equilibrium and thermodynamic studies were given in our previous work done by Ejikeme

and Igbokwe 2016 on kinetics, equilibrium and thermodynamic studies of Swiss blue dye desorption from spent microwave prepared hamburger seed shell activated carbon.

3. RESULT AND DISCUSSIONS

3.1 Effect of Eluants on the Desorption

Efficiency of Spent Activated Carbon:

Eluants used were 0.1M NaOH, 0.1M HCL, n-hexane, ethyl acetate and chloroform. Figure 3.1 shows the desorption efficiency of spent activated carbon at different initial solid loading concentration. Sufnarski (1999) stated that two types of reagents are used for desorption, those with oxidizing ability and those with solubilizing ability, solubilising ability in the sense that the eluant will dissolve the adsorbate and oxidizing ability in the sense that the eluant has that power to open blocked pores.

Chloroform was found to be more efficient to recover the dye from the adsorbents compared to other eluants. This is because Swiss blue dye is soluble in chloroform. It was observed that desorption efficiencies decreased with increase in initial solid load concentration of dye. This can be attributed to the fact that increase in the concentration of Swiss blue dye increased desorption resistance of Swiss blue dye from the activated carbon to aqueous phase leading to decrease in Swiss blue dye desorption rate (Muhammed et. al., 2011).

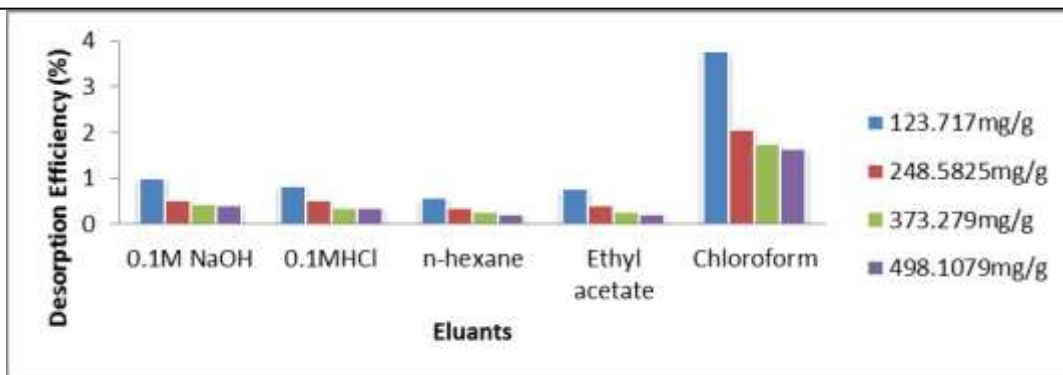
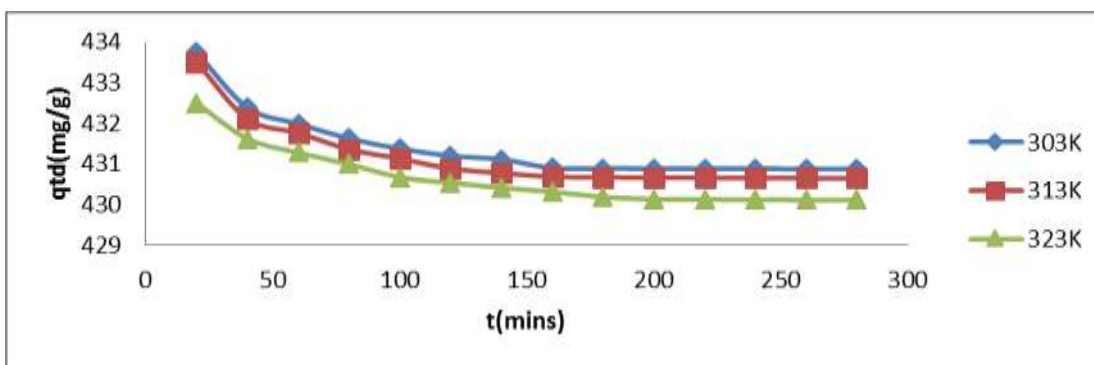


Fig. 3.1. Effect of Eluant on the desorption capacity

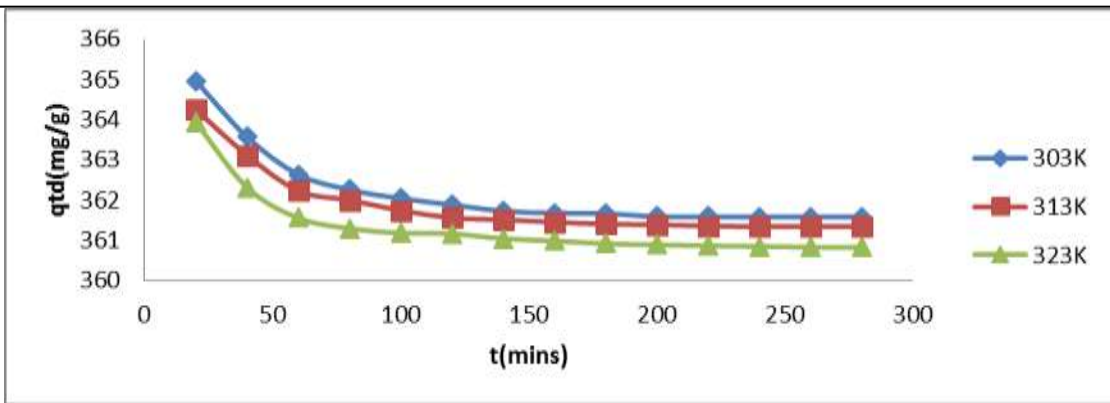
3.2. Effect of Contact Time on the Desorption Capacity of Spent Activated Carbon:

The extent of Swiss blue dye desorption from the loaded activated carbon using Chloroform was studied as a function of time under different initial solid phase concentrations and temperatures. Figure 3.2 shows the effect of desorption time on desorption capacity of chloroform at various temperatures for different initial loading concentrations. It was observed that the desorption capacity (which is the amount of Swiss blue dye in (mg/g) remaining on the activated carbons after desorption) under different initial solid loading concentration decreased with an increase in time and finally reached

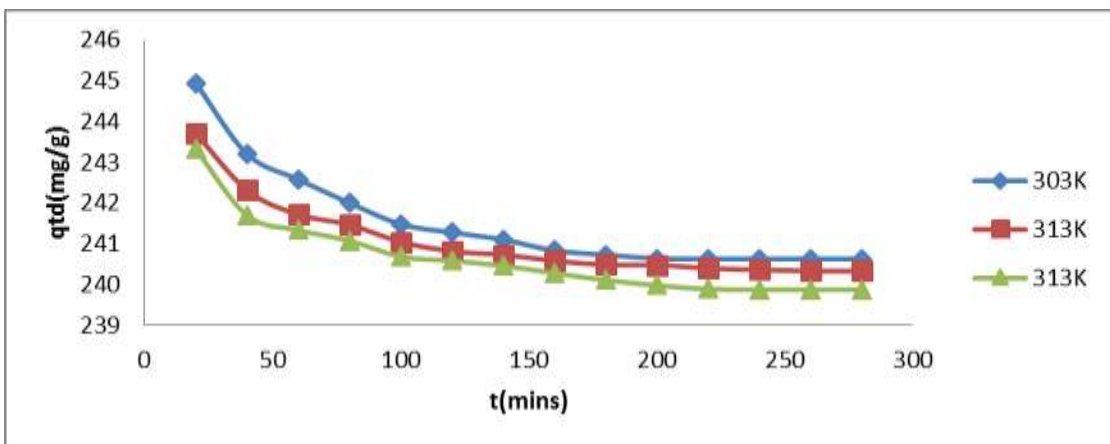
equilibrium. The studies showed rapid desorption phase initially becoming slower as it proceeds towards equilibrium. Desorption capacity decreased with increase in temperature, meaning that increase in temperature favoured desorption process. The desorption capacity (mg/g) increased with increase in initial solid phase concentration, implying that the amount desorbed decreased with initial solid phase concentration. As the concentration of Swiss blue dye gradually increased, it increased desorption resistance of Swiss blue dye from the activated carbons to aqueous phase leading to decrease in Swiss blue dye desorption rate (Muhammad et. al., 2011).



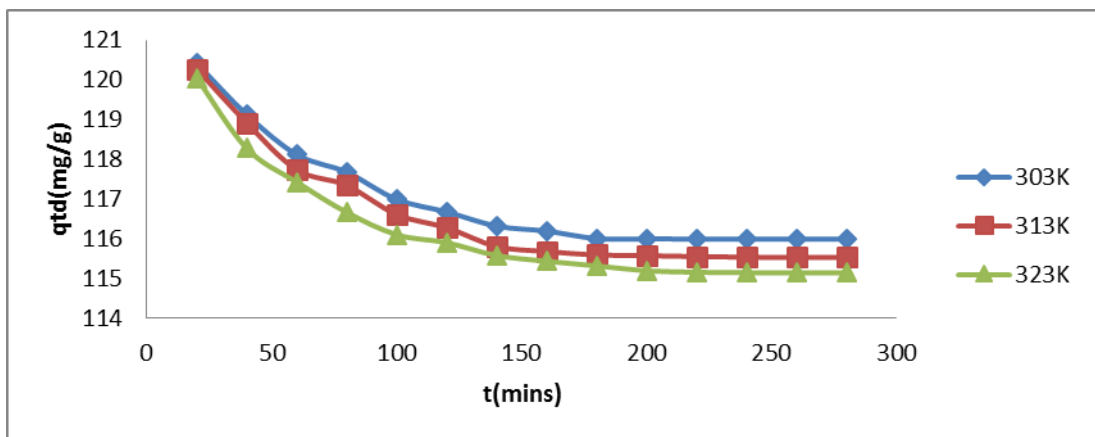
(a)



(b)



(c)



(d)

Fig. 3.2. Effect of time on desorption capacity (a) 498.1079mg/g, (b) 373.279mg/g, (c) 248.58mg/g, (d) 123.72mg/g

3.3. Effect of Dosage of the Swiss Blue dye Loaded Activated Carbon on the Desorption Capacity:

The effect of the dosage of the Swiss blue dye loaded activated carbon on the desorptive

capacity was equally studied. Figure 3.3 shows the effect of dosage on the desorption capacity (mg/g) of Swiss blue dye at different initial solid phase concentration. It was observed from the result that desorption

capacity increased with increase in the dosage of the Swiss blue dye loaded activated carbon at different initial solid phase concentration. The increase on desorption capacity recorded as the dosage was increased can be attributed to the effect it had on the physical characteristics of the solid-liquid suspension. The increase in dosage increased the viscosity of the eluant thereby inhibiting the diffusion of the dye molecules to the eluant phase. At low dosage of the loaded activated carbon, the viscosity was low, and the eluant was able to interact effectively with the adsorbed dye

molecules thereby facilitating desorption (Qing-Zhu et. al., 2009).

It was equally observed that the desorptive capacity increased as the initial solid phase concentration was increased. The increase inhibited desorption efficiency because the eluant binding sites have been saturated at high initial solid phase concentration (Qing-Zhu et. al., 2009). Since the volume of the eluant was fixed, it was unable to interact with high initial dye loading concentration thereby increasing the desorption capacity.

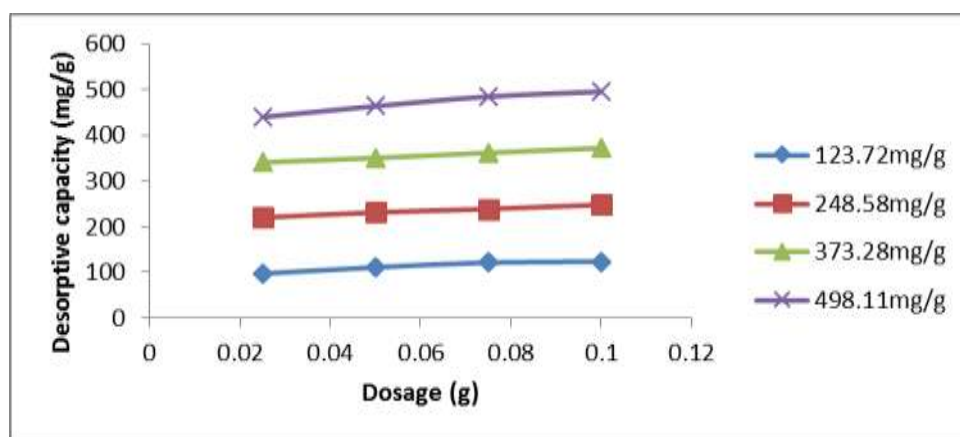


Fig. 3.3.: Effect of dosage on the desorption capacity

3.4. Effect of Temperature on the Desorptive Capacity of Swiss Blue dye:

The effect of temperatures on desorption of Swiss blue dye from the loaded activated carbon was evaluated at different initial solid phase concentrations. Desorption study was examined at only 303K, 313K and 323K because of the volatility of chloroform used for desorption. It was observed that at higher temperature, there was tendency of the eluant to vaporize thereby jeopardizing the desorption study. From Figure 3.4, it was observed that the desorptive capacity decreased with increase in temperature from 303K to 323K at various initial solid loading concentrations. This indicated that desorption of Swiss blue dye

from the loaded activated carbon was an endothermic process. Because the dye molecules were held to the activated carbon by physical bonds, higher temperature was sufficient to break the bonds and free the adsorbed dye. On the other hand, the desorption capacity increased with increase in initial solid loading concentrations. This implied that at higher solid loading, desorption of Swiss blue dye from the activated carbon decreased. As the concentration of the Swiss blue dye increased, it increased the desorption resistance of the dye from the activated carbon to the eluant phase, leading to decrease in the desorption rate.

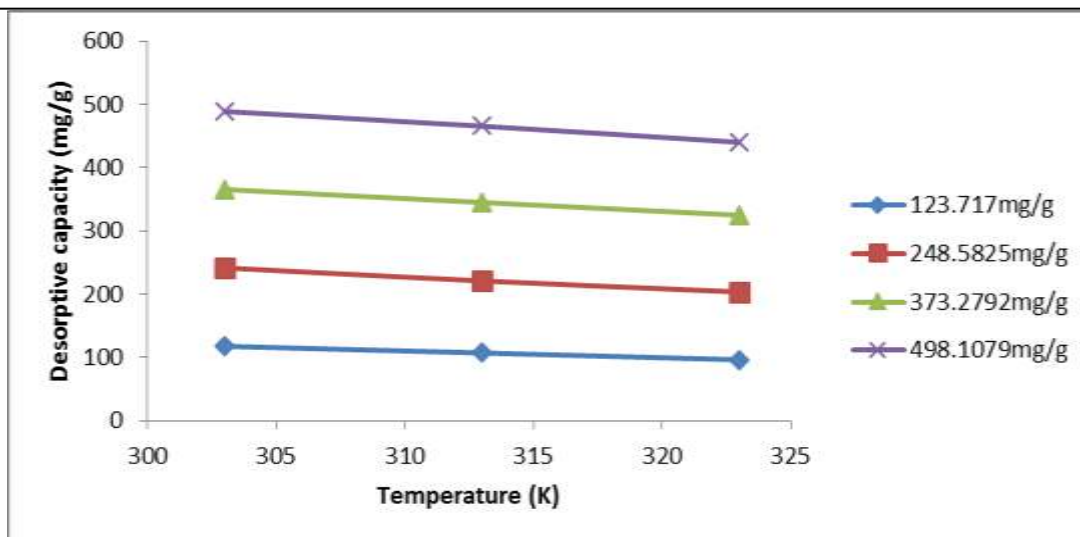


Figure 3.4.: Effect of temperature on the desorption capacity of Swiss blue dye

3.5. Kinetics and Equilibrium Studies for the Desorption Process

Tables 3.1-3.3 show the kinetics, isotherm and thermodynamics parameters for the desorption process. It was observed that the kinetics data fitted well to pseudo second order model, while the isotherm data fitted well to Freundlich model. 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 (Bradshaw et. al 1998). The applicability of Freundlich model for the desorption process showed that at equilibrium, the concentration of Swiss blue dye in the chloroform (C_e) is directly proportional to the remaining Swiss blue dye on the adsorbents (q_e). It was observed that the enthalpy change was positive which confirmed the process as endothermic in nature, and the negative value of Gibbs free energy at various initial solid load concentrations suggested the process to be feasible and spontaneous in nature.

Table 3.1. Kinetic parameters for the desorption of Swiss blue dye loaded activated carbon

Initial dye conc. (mg/l)	100.00	200.00	300.00	400.00
Initial solid phase conc. q_e exp mg/l	123.72	248.58	373.28	498.11
Pseudo Second Order Model				
q_e calc (mg/g)	125.0	250.0	400.0	500.0
$-K_p2$ (min^{-1})	0.009	0.006	0.004	0.0038
γ (mins)	111.11	166.667	250	263.15
R^2	1.0	1.0	1.0	1.0

Table 3.2. Isotherm parameters for the desorption of Swiss blue dye from spent activated carbon

Temperature (K)	303	313	323
Freundlich Model			
N	0.5	0.5618	0.6061
$K_f(\text{mg/g}) (\text{mg/l}^{-1})^{-1/n_F}$	15.985	20.511	23.471
R^2	0.950	0.998	0.910

Table 3.3. Thermodynamic parameters for desorption of Swiss blue dye from spent activated carbon.

Initial solid phase conc. (mg/g)	ΔH_{des} (KJ/mol)	ΔS_{des} (J/mol.K)			$-\Delta G_{des}$ (KJ/mol)		
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

4. CONCLUSION

Activated carbon was prepared from ‘hamburger’ seed shell using microwave activation method. It was considered spent by saturation with Swiss blue dye. Effect of temperature, dosage, time and eluants on desorption of the spent carbon was studied. It was observed that out of the eluants used, chloroform recorded highest desorption efficiency and was used throughout the study. It was observed that increase in temperature decreased the desorptive capacity of the eluant, while increase in dosage increased the desorptive capacity. It was equally observed that increase in time decreased the desorptive capacity at various initial solid phase concentrations. Desorption data was found to fit pseudo second order, and Freundlich models. Thermodynamic parameters showed that the process was endothermic, spontaneous and feasible in nature.

Acknowledgements:

The authors wish to thank PYMOTEC RESEARCH CENTRE AND LABORATORIES ENUGU, ENUGU STATE NIGERIA for all their facilities used throughout the research work.

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