

Effect Of Microwave Activation On The Removal Efficiency Of Hamburger Seed Shell

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Abstract—In this study, hamburger seed shell (*Mucuna Sloanei*) was utilized as a precursor for preparation of activated carbon on the removal of Swiss blue dye. KOH chemical activation was achieved using modified microwave oven operating at 2.45GHZ with maximum power of 900KW. Effect of activating conditions on the removal efficiency and yield were studied. This study revealed that removal efficiency and yield were inversely proportional to each other. Removal efficiency was maximum at 81% power level, 7mins irradiation time and 6M KOH concentration, while yield was maximum at 3M KOH concentration, 18% power level and 5mins irradiation time. The kinetic data fitted well to the pseudo second order model, while the isotherm data fitted well to the Flory-Huggins model. The negative Gibb's free energy suggested the process to be spontaneous. The spontaneity increased with increase in temperature.

Keywords—*Adsorption; Flory-Huggins; Hamburger seed shell; KOH; Microwave*

I. INTRODUCTION

Adsorption technique has been proven to be effective and attractive for the treatment of dye bearing wastewater [1]. Adsorption has attracted interest in this context as an effective treatment process and has many advantages over other methods. This process is not only economic and feasible but also produces high quality of water [2], [3]. Activated carbon is the main adsorbent used in adsorption processes. Activated carbon can be prepared via two heating processes; conventional and microwave heating processes.

To overcome the apparent limitations of conventional heating methods, microwave heating methods have been developed. The mechanism of microwave heating is different from conventional heating in terms of its volumetric heating effect and the selective heating which results in a more efficient heating of material.

Unlike conventional heating methods, where materials is heated through heat flux, microwave heating is achieved throughout the volume of material by direct conversion of electro-magnetic waves energy to heat as waves penetrate the rate of heating is not limited by the thermal diffusivity of material and therefore more uniform heating is assumed to be achieved [4]. Also, microwave heating is referred to as selective heating, as electromagnetic wave energy is only dissipated as heat in materials with suitable dielectric properties and not necessarily everything in contact with them. By enabling high heating rates, utilizing microwave energy may lead to significant savings in total energy consumption and process time.

The volumetric heating and deep energy penetration reported for microwave heating is believed to produce more uniform heating inside materials [5],[4]. However, a successful treatment with microwave is strongly dependent upon several operational parameters such as power, radiation time and cavity design, in addition to the intrinsic dielectric properties of the materials. In fact, the realization of microwave heating advantages is only possible through correct control of these operational parameters [6],[7].

In this study, microwave heating technique was studied using a modified Panasonic domestic microwave oven model with a maximum power of 900KW, delivered at a frequency of 2.45GHZ. The operational parameters that were studied were activating agents, power level (%), radiation time (minutes) and the KOH concentration (M).

II. MATERIALS AND METHODS

A. Adsorbent precursor

Hamburger bean seed shell (*Mucuna Sloanei*). The seed belongs to legume family (fabaceal). Hamburger seed shell was procured from local Abakpa market in Enugu, Enugu State of Nigeria. The inner edible portion serves as thickener on native soaps.

B. Adsorbate

The adsorbate that was used is SWISS blue/Basic blue 9 with molecular weight of 319.9 and empirical formula of $C_{16}H_{18}N_3S$. It is the most commonly

used substance for dyeing 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.

C. Preparation of Swiss blue dye solution

Double distilled water supplied by Pymotech Research Center Abakpa Enugu State of Nigeria was used for the preparation of the solutions. A 1000mg/l stock solution was prepared and from there, necessary dilutions were made to obtain the desired concentrations.

D. Chemicals

The chemicals used in this study were procured from De Cliff integrated Ogbete main market Enugu, Enugu State Nigeria.

E. Experimental set up of microwave oven

This work utilized a modified Panasonic microwave oven with a maximum power of 900W delivered at a frequency of 2.45 GHz. As part of the modification, the microwave casing was penetrated from the top to provide fittings to support the quartz glass ware 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 glass ware which was mounted inside the microwave cavity consisted of 100mls round bottom flask into which the sample was loaded, and a quartz quick fit connection collar which joined the flask with the outlet connection.

Quartz is an extremely good material to be used in the microwave reactors, as they are resistant to high temperatures and transparent to microwaves and resist thermal shock much better than traditional laboratory glass such as pyrex (boro silicate). However, the reactors are not completely invulnerable and were found to show sign of devitrification after extended use. This was also reported in other studies using quartz reactors in microwave processing of carbon material [6]. Thus, periodic replacement of the reactor was done.

F. Production of activated carbon

Hamburger seed shell 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 800°C. The char produced was soaked in 6N KOH solution with impregnation ratio of (1.5: 1) defined as the volume of activating agent solution per weight of char. The mixture was then dehydrated in an oven for one hour to remove moisture.

For the activation, Microwave heating was conducted in a 2450MHZ commercial microwave oven with suitable 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 0.1M HCl and distilled water until PH 6-7 was reached in the residual liquid. The carbon yield was defined as the weight of Activated carbon per weight of char utilized for activation.

G. Adsorption Isotherm

Batch isotherm studies were carried out in 250ml conical flask at different temperature of 303K, 313K, 323K, 343K on an Isothermal shaker for 3hours to ensure equilibrium. 0.02g of the adsorbent was mixed with 50ml of 30mg/l, 50mg/l, 80mg/l and 110mg/l of the Swiss blue dye solution. At the end of equilibrium time, the reaction mixture was centrifuged and the residual Swiss blue dye concentration analysed. The amount of Swiss blue dye on the adsorbent at equilibrium q_e (mg/g) was calculated from the following equation (1).

$$q_e = \left(\frac{C_o - C_e}{W} \right) V \quad (1)$$

Where q_e is the adsorption capacity (mg/g) at equilibrium, C_o is the initial concentration of the swiss blue dye, C_e is the equilibrium concentration of the swiss blue dye, W is the weight of the activated carbon and V is the volume of the adsorbate used. The equilibrium data was fitted to Flory- Huggins isotherm model

H. Adsorption Kinetic Model

The kinetic experiments were performed using a procedure similar to the equilibrium studies. 50mls of known concentration of the swiss blue dye solution was mixed with 0.02g of the adsorbent in a flask.

Then, the flask was agitated in a shaker incubator for a contact time varied in the range 0- 240mins at a speed of 200rpm under room temperature. The adsorbent was separated from the solution by centrifugation and the filtrate was analyzed by the same procedure as batch equilibrium studies. The amount of Swiss blue dye adsorbed at each time interval per unit mass of the adsorbent, q_t (mg/g), was calculated by equation 2:

$$q_t = \left(\frac{C_o - C_t}{W} \right) V \quad (2)$$

The kinetic data was fitted to pseudo second order model.

III. RESULTS AND DISCUSSIONS

A. Effect of microwave power level on the Swiss blue dye removal efficiency and carbon yield.

Effect of microwave power levels was studied at 7M KOH and radiation time of 7minutes. The power level

shows the percentage of the total power of the microwave used for a particular study. From fig.1, it can be seen that Swiss blue removal efficiency increased with increase in power level up to a point that further increase in power level resulted to decrease in the removal efficiency.

Heating the carbon precursors without chemical impregnation is very difficult, and the activation agents act as the primary microwave absorber at the beginning of radiation in the activation stage [8], with the further development of pore structure, the activated carbon itself can absorb microwave energy [9]. As suggested by the result, at low power of 18% and 36%, the pore structure was not adequately developed, and their removal efficiencies were low, indicating no continual reaction between the char and the activating agent. At higher power levels of 58% and 81%, the pore width was successively broadened and new micropores-mesopores were formed in the original pore walls, giving a sustaining increase in removal efficiency. High microwave power improves the development of the pore structures of activated carbon which indicates that microwave power is important in the activation stage. However, the removal efficiency decreased when the power level was increased to 100% due to decrease in the formation rate of new pores and beginning of pore destruction. According to Deng et al [10], the decrease in removal efficiency with further increase in power might be due to the sintering effect at high power, followed by shrinkage of the char and realignment of the carbon structure which resulted to reduced pore areas as well as volume. Over gasification might occur causing destruction of pore structures, thus decrease in the removal efficiency.

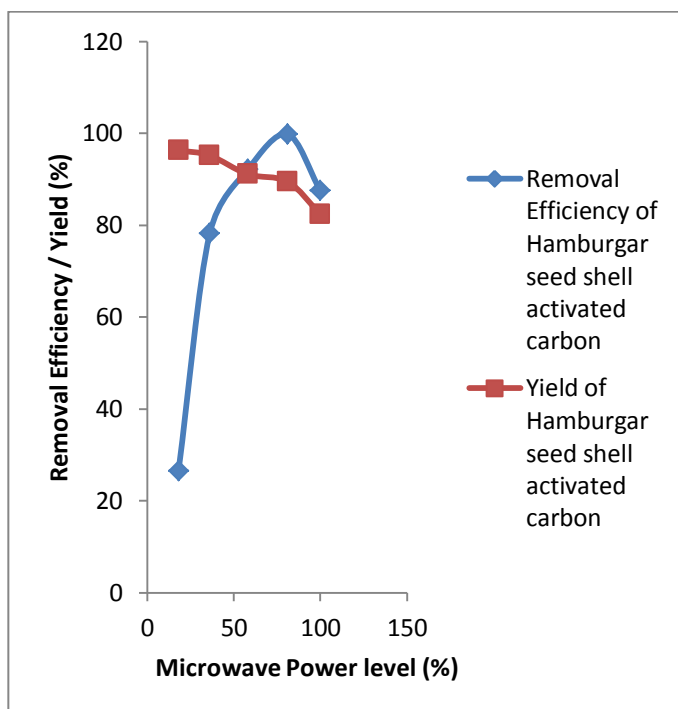


Fig. 1: Effect of microwave power level on the removal efficiency and carbon yield of hamburger seed shell

Effect of microwave radiation power on the carbon yield was equally studied. From the result, it was ascertained that carbon yield decrease with increase in power levels. At high microwave power levels, absorbed microwave energy exceeded a certain level which led the plentiful energy to cause excessive destruction of pore structures, and a progressive decrease in carbon yield was observed. The weight loss of carbon increased proportional to the microwave power level, mainly due to the fierce reaction at higher thermal recitation which intensified devolatilization, dehydration and decomposition [11].

B. Effect of radiation time on the swiss blue dye removal efficiency and carbon yield

Microwave radiation time is another key parameter affecting the removal efficiency and carbon yield. Fig. 2 revealed that prolonging the radiation exhibited an enhancement of removal efficiency. This phenomenon implied that prolonging exposure time promotes an acceleration of temperature, which in turn increases reaction rates thus developing porosity [11]. A slight drop was observed at 9mins. However as the radiation time arrives at its optimum values, absorption and reflection of energy tends to balance and the activated carbon achieved its maximum removal efficiency. As activation proceeds, temperature increased dramatically and led to opening of microspores and mesopores which resulted in enlargement of the average diameter.

The drop in removal efficiency is probably due to a sintering effect, which largely destroyed the pore walls between adjacent pores. Moreover, high temperature might produce local hotspots, leading to external ablation and collapse of the carbon framework, resulting in reduced accessibility of carbon active sites. Higher pyrolytic temperatures could induce C-KOH, C-K₂CO₃, C-K, C-K₂O, C-CO and C-CO₂ reactions facilitating breaking of the C-O-C and C-C bonds thus decreasing removal efficiency and carbon yield. This was why there was decrease in carbon yield as the radiation time increased.

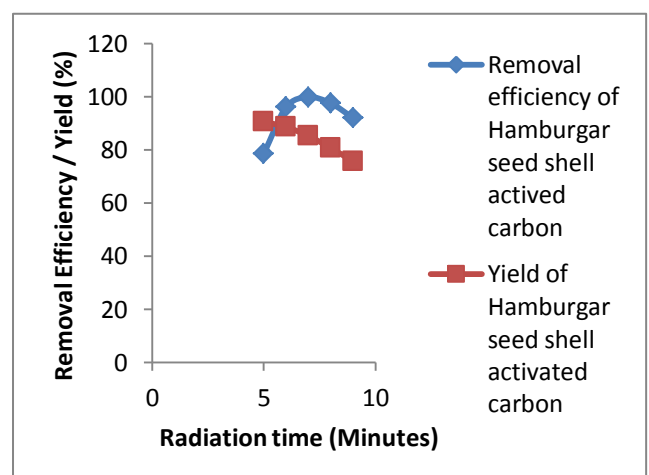
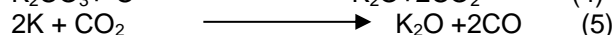
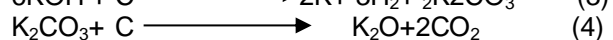


Fig. 2: Effect of microwave irradiation time on the removal efficiency and carbon yield of hamburger seed shell

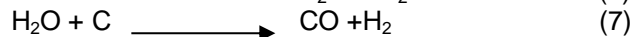
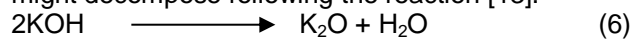
The decrease in carbon yield as radiation time was increased can equally be attributed to rapid evolution of volatile material to form stable compound.

C. Effect of KOH concentration on Swiss blue dye removal efficiency and carbon yield

Effect of KOH concentration on the Swiss blue dye removal efficiency and carbon yield was studied at the microwave input power of 81% and irradiation time of 7mins at 1:1.5 carbon to KOH ratio. From fig.3, it shows that augmenting KOH concentration from 2M to 6M showed an increase in Swiss blue dye removal efficiency and carbon yield. Beyond 6M a further increase in KOH concentration illustrated a gradual decrease in Swiss blue dye removal efficiency and carbon yield. KOH activation involves the redox reduction and carbon oxidation to generate porosity. It can be deduced that the pore enlargement related to KOH activation is associated to the redox reduction and oxidative modification responsible for the development of micro and mesoporosity. During the reaction of CO, CO₂ and H₂ constituents, and additional reactions between the active Intermediates with the carbon surfaces are possible [12].



Concurrently, the alkaline and carbonate metal formed during the activation stage are Intercalated to the carbon matrix and are responsible for both stabilization and widening of pores between the carbon atomic layers. Therefore, by increasing the KOH concentration, the activation process was accelerated and correspondingly, the removal efficiency was further enhanced [11]. Beyond the optimum value, the excessive KOH would promote vigorous gasification reaction, which destroys the carbon frame work leading to a drastic decrease of accessible areas besides, excessive KOH molecules might decompose following the reaction [13].



Therefore, the catalytic oxidation entailed widening of mesoporous structures and carbon burn off.

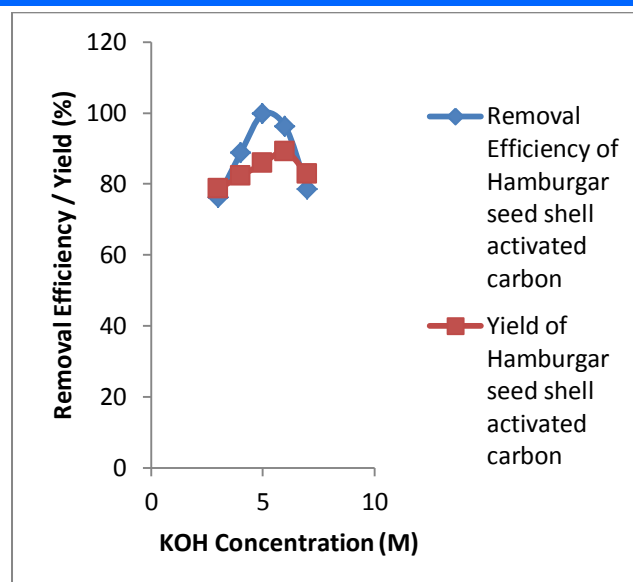


Fig. 3: Effect of KOH Concentration on the removal efficiency and carbon yield of hamburger seed shell.

Effect of KOH Concentration on carbon yield was equally studied. It was observed that carbon yield increased with initial increase in KOH Concentration and decreased with further increase in KOH concentration beyond the optimal value. The increase in yield at low KOH concentration was as a result of intercalation of potassium metals on the carbon matrix which resulted to increase in weight. A additionally, a further increase in KOH Concentration beyond the optimal value would intensify a vigorous activation reaction, which leads to carbon burn off and transition of microspores - mesopores into macropores lowering the carbon yield.

D. Pseudo Second order Equation

The pseudo second order adsorption kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2 \quad (8)$$

Integrating for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$

$$\frac{t}{q_t} = \frac{1}{K_p q_e^2} + \frac{1}{q_e} (t) \quad (9)$$

$$h = K_p q_e^2 \quad (10)$$

Where K_p is the rate constant of the pseudo second order equation (1/min), q_e and q_t were the sorption capacity at equilibrium and time t (mg/g). h is the initial sorption rate. A plot of t/q_t versus t gives $1/q_e$ and $1/K_p q_e^2$ as slope and intercept.

The values of q_e and K_p were obtained from the slope and intercept. The values of the rate constant, correlation coefficients, the experimental and calculated values are shown in table 1.

It can be seen that the correlation coefficients for the linear plot of the pseudo second order was 1.0.

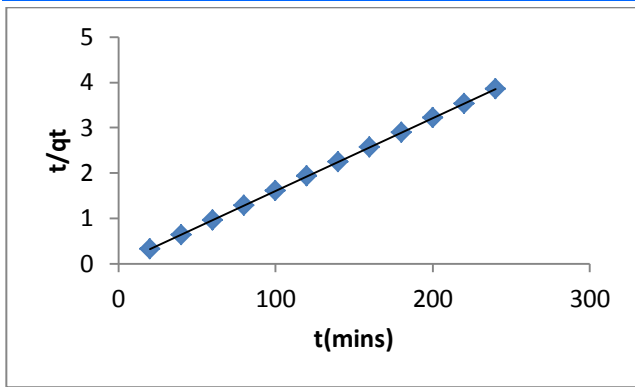


Fig. 4: Pseudo second order kinetic model for microwaved hamburger seed shell activated carbon

Also, there was a good agreement between the experimental q_e values and the calculated q_e values.

Table 1: Pseudo second order kinetics data for microwaved hamburger seed shell activated carbon

C_o (mg/l)	K (h^{-1})	h	q_e (cal)	q_e (exp)	R^2
50.0	0.1707	666.8	62.5	62.3	1.0

This indicates that the adsorption kinetic was better represented by the pseudo-second order model. This was in agreement with the work done by some researchers, work done by Dalis et al on basic dye adsorption using Kenaf fiber char [14], Gil et al on dye removal using pillsed clay [15], Emmanuel I. et al on MB adsorption on defalted carica papaya seeds [16],

Mehmet Ulas et al on Methylene blue adsorption on activated carbon from posindonia oceanic dead leaves [15], Andre Cazetta et al on methylene blue adsorption on NaOH-activated carbon from coconut shell [17], M. Auta and B. Hameed on MB removal using modified mesoporous clay [18] and so many others.

The high initial sorption rate, h , obtained showed that the adsorption was rapid. The rapid adsorption of Swiss blue dye by this adsorbent is probably due to the abundant availability of active sites on the biomass, and the perceived porous and mesh structure of the adsorbent which provides ready access and large surface area for the adsorption of Swiss blue dye on the binding sites [19], [20].

E. Flory- Huggins isotherm model

An adsorption isotherm describes the relationship between the amount of adsorbate uptaken by the adsorbent and the adsorbate concentration remained in the solution. Flory-Huggins model derives the degree of surface coverage characteristics of adsorbate onto adsorbents. It equally expresses the feasibility and spontaneous nature of an adsorption process. The model can be represented as below[21].

$$\frac{\theta}{C_o} = K_{FH}(1 - \theta)^{n_{FH}} \quad (11)$$

$$\text{Log}\left(\frac{\theta}{C_o}\right) = \log(K_{FH}) + n_{FH} \log(1 - \theta) \quad (12)$$

Plot of $\log\left(\frac{\theta}{C_o}\right)$ vs. $\log(1 - \theta)$ gives slope of n_{FH} and intercept of $\log(K_{FH})$.

Where K_{FH} is Flory-Huggins equilibrium constant that can be used for the calculation of spontaneity free Gibbs energy, θ is the degree of surface coverage.

$$\Delta G = -RT \ln(K_{FH}) \quad (13)$$

$$\theta = 1 - \frac{C_e}{C_o} \quad (14)$$

n_{FH} is the number of dye occupying adsorption site, C_e is the equilibrium concentration and C_o is the initial concentration of the Swiss blue dye.

The results of the isotherm parameter obtained at different temperatures are shown on table 2.

The negative values of ΔG° indicated the feasibility of the process and the spontaneous nature of the adsorption. The value of ΔG° became more negative with increasing temperature. The values indicated that the adsorption process was more spontaneous at higher temperature of 50°C.

This was confirmed by the high correlation coefficient (1.0) and high negative value of the Gibb's free energy at the said temperature. This suggested that the process is endothermic in nature, that increase in temperature favoured the adsorption of the dye on the adsorbent.

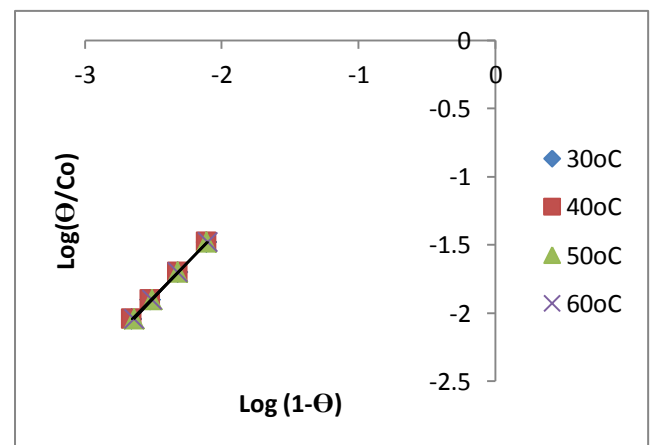


Fig. 5: Flory – Huggins isotherm model for microwaved hamburger seed shell activated carbon

Table 2: Flory-Huggins isotherm parameters

Temp(K)	n_{FH}	K_{FH} (L/mol)	ΔG (KJ/mol)	R^2
303	1.0199	4.65	-3871.59	0.999
313	1.0194	4.64	-3993.76	0.999
323	1.0603	5.70	-4673.89	1.0
333	1.0497	5.36	-4648.32	0.999

IV. CONCLUSION

The results confirmed the viability of preparing activated carbon from hamburger seed shell by microwave induced KOH activation. The prepared activated carbon could be effectively used for removal of Swiss blue dye from aqueous solutions. Effect of microwave power levels revealed that removal efficiency increased with increase in power level to 81% at which further increase resulted to decrease in removal efficiency. Effect of irradiation time equally revealed the same trend that removal efficiency increased to 7mins at which further increase in irradiation time decreased the removal efficiency. Effect of KOH concentration showed that removal efficiency increased to 6M at which further increase in KOH concentration decreased the removal efficiency. The observed removal efficiencies were inversely proportional to the yield of activated carbon at various activation conditions.

The kinetic data fitted well to the pseudo second order model, while the isotherm data fitted well to Flory-Huggins model.

The negative value of the Gibb's free energy calculated from the Flory-Huggins model showed that the process was spontaneous.

The spontaneity increased with increase in temperature.

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