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OPTIMIZATION PROCESS INVOLVING CATEGORIC FACTOR FOR SWISS BLUE DYE ADSORPTION ONTO ACTIVATED CARBONS

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Abstract - The optimization of the process conditions for the removal of Swiss blue dye from aqueous solution was studied. Box Behnken Design (BBD) was employed as optimization tool .The process conditions involved four numeric factors of pH, dosage, initial dye concentration and temperature, while the categorical factor was the type of adsorbent. The adsorbents from hamburger seed shell and spent grain were prepared using microwave and conventional techniques giving four categorical levels. The levels are microwave prepared adsorbent from hamburger seed shell (MPAHS), microwave prepared adsorbent from spent grain (MPASG), conventionally prepared adsorbent from hamburger seed shell (CPAHS), and conventionally prepared adsorbent from spent grain (CPASG). Analysis of variance showed that all the factors significantly affected Swiss blue dye removal efficiency while temperature and dosage had quadratic effects. Microwave prepared adsorbents recorded highest removal efficiencies compared to the conventionally prepared ones, though all had efficiencies higher than 90%. Quadratic model was generated and validated with error less than 0.05% for all the adsorbents. The optimum conditions generated for all the prepared adsorbents are pH of 7.47, 8.57, 8.16, 7.98, temperatures (^oC) of 30.0, 29.96, 30.0, 30.90, initial dye concentrations (mg/l) of 50.15, 52.0, 50.05, 51.40, and dosages (g) of 0.09, 0.1, 0.1, 0.1, for MPAHS, MPASG, CPASG and CPAHS respectively.
Keywords: Adsorption, activation, microwave, optimization, Swiss blue dye

1. INTRODUCTION

Increase in industrial and human activities have given rise to generation of large scale waste waters that constitute grave environmental threats to human and aquatic lives. Major sources of these wastes are textile, leather and paper industries which when discharged into water bodies can be highly toxic to ecosystem and aquatic life. Swiss blue dye commonly known as Methylene blue dye is a basic 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 (Tan et al 2007). The presence of these dyes in water inhibits the penetration of light and photosynthesis activity of water plants (Robinson et al 2002; Kose 2008). This underscores the necessity to treat waste water containing dye for sustainable life and development (Safa 2011). For this purpose, some chemical and physical processes such as flocculation, chemical coagulation, precipitation, ozonation, and adsorption have been widely employed to treat waste waters containing some dyes (Pamesh et al 2006). These processes have been found to be efficient with reasonable range of adaptation.

However, treatment of dye waste waters by adsorption unto activated carbon has been found to be extraordinary in terms of its clearness of design and thorough adsorption of a wide range of adsorbates (Tan et al 2008). So many reasons have shown that commercial activated carbons are expensive for treatment of dye waste waters and these have ramped up the efforts of researchers at developing a cheaper, more effective and environmentally friendly activated carbon.

Activated carbon can be prepared from agricultural waste based materials using either microwave or conventional heating techniques. In this work, Response surface methodology was used to optimize the process conditions for adsorption of Swiss blue dye from its aqueous solution. The activated carbons were prepared from two precursors namely hamburger seed shell and brewers spent grain using microwave and conventional heating techniques.

Box Behnken Design (BBD) which is a type of RSM involving three levels (two factional points and one center point) was used to optimize the adsorption process. It involved four numeric factors of pH, dosage, temperature and initial concentration and one categoric factor which is the type of adsorbent. The categoric factor has four levels namely; conventionally prepared adsorbent carbon from hamburger seed shell (CPAHS), conventionally prepared adsorbent from spent grain (CPASG), microwave prepared adsorbent from hamburger seed shell (MPAHS) and microwave prepared adsorbent from spent grain (MPASG)

2. MATERIALS AND METHODS

Adsorbate

Swiss blue dye was chosen in this study because it has been known to attach firmly on solids. The chemical structure of Swiss blue dye is shows as follows:

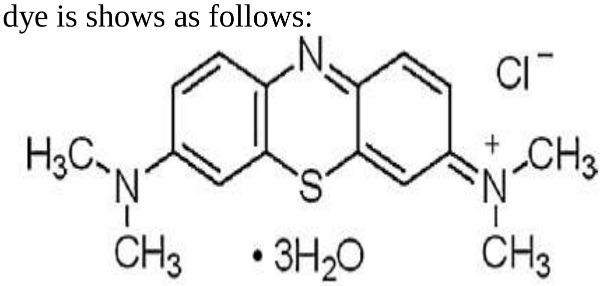

Fig. 2.1: Chemical structure of Swiss blue dye

Activated carbon precursors

The precursors used for the preparation of activated carbons were;

(1) Hamburger bean seed. The shells were collected from a local market at Abakpa, Enugu East Local Government Area of Enugu State Nigeria.

(2) Brewer's spent grain is the main by-product of brewing industry, representing approximately 85% of total by-product generated (Aliyu and Bala 2011). The brewers' spent grain was collected from Nigerian brewery Ninth mile corner Enugu, Enugu State Nigeria. It was obtained immediately it was generated.

2.1. Experiment design for optimization processes

In the first step of RSM, a suitable approximation is introduced to find true relationship between the dependent variable and the set of independent variables, that is, the single-response model using the RSM corresponding to independent variables. Then a mathematical model in the form of a second-order polynomial is formed to predict the response as a function of independent variables involving their interactions. Generally the behaviour of the system is explained by the following quadratic equation 2.1.

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} biix_{ii}^2 + \sum bijxixj \quad \textbf{(2.1)}$$

where Y is the predicted response, b_0 the offset term, bi the linear effect, bii the squared effect, bij the interaction effect and xi and xj represent the coded independent variables.

Optimization of adsorption conditions was done with Box Behnken Design (BBD) involving three levels (two factorial points and one center point). BBD is more economical and efficient in terms of number of required runs than central component design (CCD). It is useful in avoiding experiments that would be performed under conditions for which unsatisfactory results might occur.

The optimization of adsorption conditions involved four numeric factors of pH, dosage, temperature and initial concentrations and one categoric factor which is the type of adsorbent with four levels namely; conventionally prepared adsorbent from hamburger seed shell (CPAHS), conventionally prepared adsorbent from spent grain (CPASG), microwave prepared adsorbent from hamburger seed shell (MPAHS), and microwave prepared adsorbent from spent grain (MPASG). The number of levels of the categoric factor multiplied the number of experiments (29) giving one hundred and sixteen (116) experiments for the process. The dependent variable which is the response is the Swiss blue dye removal

Efficiency. The factors and levels used for the optimization process are shown on table 2.1

Table 2.1. Factors and levels for the adsorption conditions using BBD

Factors	Units	Levels		
		-1	0	+1
Temp.	^{O}C	30	35	40
pH	-	3.0	6.0	9.0
Dosage	g	0.05	0.075	0.10
Initial Concentration	mgl	50.0	100.0	150.0
Adsorbents types				
CPASG				
CPAHS				
MPAHS				
MPASG				

2.2. Production of activated carbons

Hamburger seed shell and spent grain were washed exhaustively with deionized water to remove adhering dirty particles from the surface. They were dried and ground. The ground samples were sieved to the target mesh size of 1 – 2mm. The carbonization process was achieved using electric furnace at a temperature of 800^{o}C. 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 (6MKOH: Char). The mixture was dried in an oven for one hour. For the conventional activation, the dried samples were charged into an electric furnace to a temperature of 850^{o}C and time of one hour.

Microwave heating was achieved using modified domestic microwave oven. It operates at 2450MHZ frequency with maximum power output of 900W. The control panel consists of two function operators; one is a timer knob, while the other is a power knob. The activation was carried out inside a Pyrex flask fixed inside the chamber of the oven. The resultant activated carbon was washed repeatedly with 0.1MHCl and distilled water to neutral pH.

2.3. Batch adsorption Studies

The batch adsorption studies were performed by mixing 20ml of 30mg/l initial concentration of dye with 0.02g of the adsorbent in a flask.

Then, the flask was agitated in a shaker incubator for one hour at a speed of 200rpm under room temperature. The adsorbent was separated from the solution by centrifugation and the filtrate was analyzed. The removal efficiency was calculated using equation 2.2.

$$\%Removal = \frac{C_o - C_t}{C_o} \times \frac{100}{1} \qquad \textbf{(2.2)}$$

Where C_o (mg/L) is initial dye concentration, C_t (mg/L) is final dye concentration.

3. RESULTS AND DISCUSSION

3.1.1. Analysis of variance for the adsorption process

From analysis of variance (ANOVA) (table 3.1), the model F-value of 292.39 implied the model was significant. There was only a 0.01% chance that a model F-value this large could occur due to noise. Values of “Prob > F” less than 0.0500 indicated model terms were significant. In this case, the linear effect of pH, temperature, initial dye concentration, dosage and adsorbent types were significant. The interaction effect of pH and temperature (AB), interaction effect of pH and initial dye concentration (AC), interaction effect of pH and dosage (AD), interaction effect of temperature and initial dye concentration (BC) and interaction effect of initial concentration and dosage (CD) were significant. Quadratic effect of temperature (B^2) and quadratic effect of dosage (D^2) were significant. Values greater than 0.100 indicated the model terms were not significant. The “lack of fit F-value” of 0.70 implied the lack of fit was not significant relative to the pure error. There was 84.87% chance that a lack of fit “F-value” this large could occur due to noise.

The predicted R-squared of 0.9684 was in agreement with the “Adj R-squared of 0.9726. R-squared of 0.9759 showed that 97.95% of the variation on the response can be explained by the model.

Table 3.1. Analysis of variance table for Swiss blue dye adsorption process

Source	Sum of squares	Df	Mean Square	F value	P – value Prob > F
Model	21190.77	14	1513.63	292.39	<0.0001
A – pH	2674.56	1	2674.56	516.66	<0.0001
B – Temp	1346.20	1	1346.20	260.05	<0.0001
C – Initial Conc.	5963.24	1	5963.24	1151.94	<0.0001
D – Dosage	2832.24	1	2832.23	547.11	<0.0001
E – Type of adsorbent	5664.54	3	1888.18	364.75	<0.0001
AB	105.06	1	105.06	20.30	<0.0001
AC	40.01	1	40.01	7.73	0.0065
AD	89.30	1	89.30	17.25	<0.0001
BC	46.24	1	46.24	8.93	0.0035
CD	312.32	1	312.32	60.33	<0.0001
B^2	1861.73	1	1861.73	359.64	<0.0001
D^2	98.13	1	98.13	18.96	<0.0001
Residual	522.84	101	5.18		
Lack of fit	412.47	85	4.85	0.7	0.8487
Pure Error	110.37	16	6.90		
Cor Total	21716.62	115			

3.1.2. Model equation involving categoric factors

Categoric factor levels are represented by indicator “dummy” variables in regression, the values of the dummy variables are “0” if that type is not present in that treatment/run, and “1” it is present, therefore the four adsorbent type levels were represented by 100, 010, 001 and -1-1-1 respectively as shown on table 3.2 below.

Table. 3.2. Factors and levels for the categoric factors’ levels

S/N	Names	E(1)	E(2)	E(3)
1	CPASG	1	0	0
2	MPASG	0	1	0
3	MPAHS	0	0	1
4	CPAHS	-1	-1	-1

Alphabet “E” means categoric factor with three treatments (1), (2) and (3). Treatment (1) involves only CPASG (100), treatment (2) involved only MPASG (010), treatment (3) involved only MPAHS (0010). Adsorbent type CPAHS (-1-1-1) served as the reference level in which all the adsorbent types were excluded. The model equation involving categoric factors can be seen as four model equations. One comprising E (1) with all its interactions, two, comprising E (2) with all its interactions, three, comprising E (3) with all its interactions. The fourth equation was a reference equation that is the equation with all the E terms and their interactions eliminated. The model equation in coded form is shown as follows;

Removal efficiency (%) = $+68.64 + 7.46A + 5.30B - 11.15C + 7.68D + 1.15E[1] - 6.75E[2] + 10.95E[3] - 2.56AB + 1.58AC + 2.36AD - 1.70BC - 4.42CD + 8.21B^2 - 1.89D^2$ **(2)**

The model equation can be split into four equations as follows;

Conventional prepared activated carbon from spent grain (CPASG);

Removal efficiency (%) = $+68.64 + 7.46A + 5.30B - 11.15C + 7.68D + 1.15E[1] - 2.56AB + 1.58AC + 2.36AD - 1.70BC - 4.42CD + 8.21B^2 - 1.89D^2$. **(3)**

Microwave prepared activated carbon from spent grain (MPASG);

Removal efficiency (%) = $68.48 + 7.46A + 5.30B - 11.15C + 7.68D - 6.75E[2] - 2.56AB + 1.58AC + 2.36AD - 1.70BC - 4.42CD + 8.21B^2 - 1.89D^2$. **(4)**

Microwave prepared activated carbon from hamburger seed shell (MPAHS);

Removal efficiency (%) = $68.48 + 7.46A + 5.30B - 11.15C + 7.68D + 10.95E[3] -$

2.56AB + 1.58AC + 2.36AD – 1.70BC – 4.42CD + 8.21B^2 – 1.89D^2. **(5)**

Conventional prepared activated carbon from hamburger seed shell (CPAHS);

Removal Efficiency (%) = 68.48 + 7.46A + 5.30B – 11.15C + 7.68D – 2.56AB + 1.58AC + 2.36AD – 1.70BC – 4.42CD + 8.21B^2–1.89D^2. **(6)**

3.2. Optimal Conditions for the adsorption process

The optimum conditions were generated with the aim of maximizing the Swiss blue dye removal efficiency. Tables (3.3 and 3.4) show the optimum conditions and the validated conditions respectively for the Swiss blue dye adsorption process.

Table 3.3. Optimal conditions for adsorption of Swiss blue dye

pH	Temperature (^{o}C)	Initial dye conc. (mg/l)	Dosage (g)	Adsorbent Types	Predicted Values (%)
7.47	30.0	50.15	0.09	MPAHS	99.90
8.57	29.96	52.00	0.1	MPASG	99.79
8.16	30.00	50.05	0.1	CPASG	99.68
7.98	30.90	51.40	0.1	CPAHS	99.61

Table. 3.4. Model validation for the Adsorption of Swiss Blue Dye

pH	Temp.(^{o}C)	Initial dye conc. (mg/l)	Dosage (g)	Adsorbent types	Removal Efficiency (%)		Error (%)
					Experimental values	Predicted values	
7.47	30.0	50.15	0.09	MPAHS	99.90	99.87	0.03
8.57	29.96	52.00	0.1	MPASG	99.79	99.8	0.01
8.16	30.00	50.05	0.1	CPASG	99.68	99.7	0.02
7.98	30.90	51.40	0.1	CPAHS	99.61	99.66	0.05

As seen from the model validation table 3.4, the errors obtained were less than 0.1%. This showed the experimental values were very close to the predicted values, thus the model equation generated was effective in predicting the removal efficiency of Swiss blue dye.

3.2.1. Effect of activation methods on the removal efficiency of Swiss blue dye

In order to analyze the effect of different methods of activation used in this study (conventional and microwave) on the removal efficiency of Swiss blue dye solution, the adsorption was done using 0.02g of each activated carbon prepared using the optimal conditions obtained. The adsorption process was done for 1hr in a mechanical shaker using 20ml of 30mg/l of Swiss blue dye solution. As can be seen from the results in Fig. 3.1, all the activated carbons prepared from the two precursors had removal efficiency above 90$^o/_o$. Microwave prepared activated carbon from hamburger seed shell (MPAHS) showed highest removal efficiency, followed by microwave prepared activated carbon from spent grain (MPASG), followed by conventionally prepared activated carbon from hamburger seed shell (CPAHG) and lastly conventional prepared activated carbon from spent grain (CPASG).

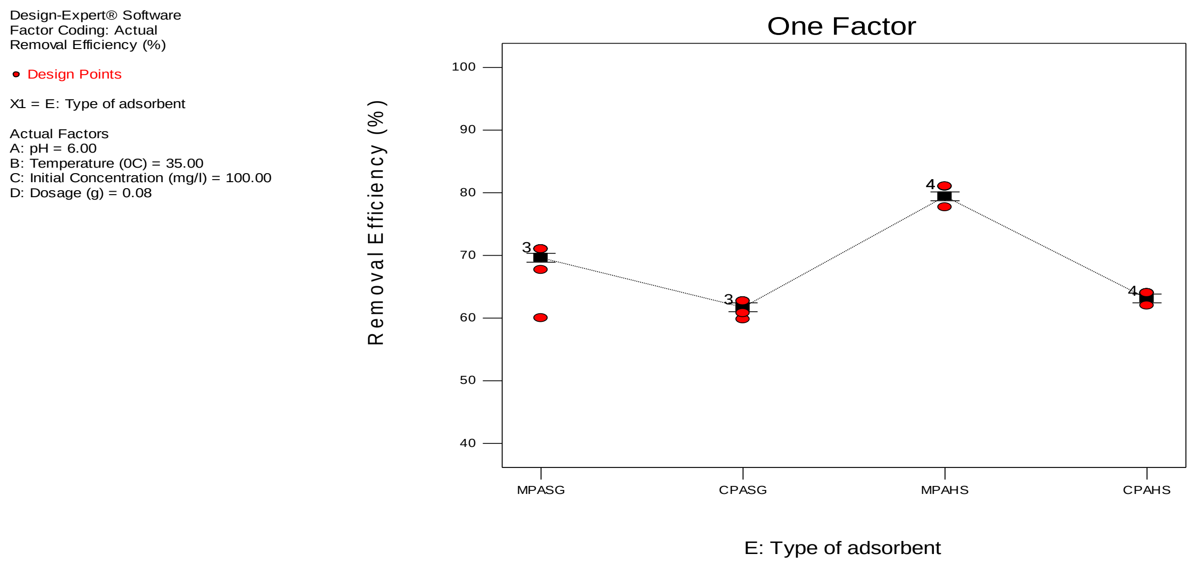

Fig. 3.1: Effect of type of adsorbent on Swiss blue dye removal Efficiency

High removal efficiency experienced by microwave activated carbons was as a result of mechanism of microwave heating. The mechanism of microwave heating is different from conventional heating methods. Microwave heating affects entire workload as the radiation perforates through the sample. Because of this, the mode of heating is not affected by the thermal dissemination of the sample. As a result, constant heating is assumed (Foo and Hameed 2012). The mechanism of microwave heating can be said to be selective in the sense that the microwave energy can only be converted to heat by that material with negligible electrical and thermal conductivity and not anything in contact with it.

In conventional heating, the mechanism of heat transfer is by conduction. There is always a graded change on the magnitude of heat from the surface to the centre of the sample which makes the temperature of the sample always lower than that of the furnace and in some cases the sample may not reach the marked temperature (Fernandez 2011). Even when the temperature of the surface is controlled, the rate with which heat is transferred depends on the physical and thermal properties of the sample. In addition, when large sample mass is involved, longer time will be needed for the sample to be heated. This is always very hard and not homogenous when thick sample is involved (Foo and Hameed 2012).

Moreover, when samples are heated conventionally, a graded change in the magnitude of heat will always result in the sense that the hottest part will be close to the outward. The principal volatile matter escaping from the core of the sample has to pass through the high temperature region where indirect reaction takes place before reaching the outward surface. This reaction always results to disintegration of the volatiles and deposition of huge amount of shapeless carbon on the activated carbon thereby blocking the pores (Miura et al 2004).

Contrarily to the conventional heating, microwave heating occurs throughout entire sample surface. Because of this, the sample is always hotter than the outside. This allows the volatiles released from the center of the sample to escape without decomposition. This development produces activated carbon with clear pores.

Properties of activated carbons prepared in this study are shown on table 3.5

Table 3.5. Properties of adsorbents used in the Study

Parameters	Units	MPASG	MPAHS	CPASG	CPAHS
Surface Area	m^2/g	596.3	621.7	556.0	548.6
Iodine Number	mgI_2/g	1100.3	1295.2	1068.0	1009.3
Moisture Content	%	4.31	4.1	3.5	3.6
Ash	%	2.0	2.1	3.4	3.2
Volatile Matter	%	8.9	6.5	3.8	3.5
Fixed carbon	%	84.8	87.3	89.3	89.7
pH	-	6.8	6.8	6.5	6.8
pHpzc	-	6.3	6.4	6.2	6.3
Bulk Density	g/ml	0.482	0.51	0.49	0.50
Basic Sites	mmol/g	0.98	0.75	0.99	0.82
Acidic Sites	mmol/g	3.2	3.6	3.5	3.5

4. CONCLUSION

Box Behnken design (BBD) was used to optimize Swiss blue dye removal efficiency at various adsorption conditions involving four numeric factors which were pH, temperature, initial dye concentration, dosage and one categoric factor which was type of adsorbent. Through analysis of variance, all the factors were found to have significant effect on Swiss blue dye removal, though temperature and dosage had quadratic effects. Activated carbons were produced from hamburger seed shell and spent grain using microwave and conventional heating techniques. It was observed that activated carbons prepared from microwave technique recorded highest removal efficiency compared to that prepared from conventional technique. Carbon from hamburger seed shell activated by microwave recorded highest removal efficiency. This was followed by carbon from spent grain activated by microwave. Carbon from spent grain activated by the conventional method placed third and lastly conventional prepared activated carbon from hamburger seed shell. The optimum conditions generated were validated with little errors of less than 0.05%.

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