Statistical Analysis for Malachite Green Removal Using Palm-Kernel-Shell-Activated Carbon

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Abstract— **Malaysia is a country with luxurious agricultural resources. However, without proper management, the waste resulted from processing activities of these agricultural process will lead to a major waste problem. This study involved the utilization of the palm kernel shell (PKS) activated carbon by performing the decolorisation of malachite green color. The adsorption study was done using shake flask investigation. The result obtained showed that the best product of activated carbon, produced at 750°C at 90 minutes impregnated with K_2CO_3 weight ratio of 1.0. This product was chosen because of cost factor and the percentage removal of MG was high 99.2%. From this study, the best candidate for adsorption of MG gives 121.416 mg/g adsorption rate. It is recommended for future study that detailed should be conducted on production of activated carbon to produce a larger surface area, this study should be extended on the method of application of Potassium Carbonate in enhancing the pore size of activated carbon, and this study should be** continued for removal of other colors especially colors that are high toxicity.

Keywords- PKS; activated carbon; ANOVA; MG

XLIX. INTRODUCTION

Malaysia, the largest palm oil producer in the world, about two million tonnes (dry weight) of extracted fibres are generated annually [1]. They were used as boiler fuels or building materials. To make better use of these cheap and abundant wastes, it is proposed to make them into effective adsorbents or activated carbons. Preliminary characterization has shown it feasible to prepare char with sufficient densities and high porosity from oil palm fruit wastes [2].

Many industries which used dyes and pigments generated wastewater, characteristically high in colour and organic content. Presently, it was estimated about 10,000 of different commercial dyes and pigments exist and over 7 x 105 tonnes are produced annually world-wide [1]. Dyes are widely used in industries such as textile, rubber, paper, plastic, and cosmetics. Among these various industries, textile ranks first in usage of dyes for coloration of fibre.

Colour is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies. Residual dyes are the major contributors to colour in wastewaters generated from textile and dye manufacturing industries, etc. [3]. Colour impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which result in micro-toxicity to fish and other organisms [4], [5]. It should be noted that the contamination of drinking water by dyes at even a concentration of 1.0 mg l could impart significant colour, making it unfit for human consumption. Most of the used dyes are stable to photodegradation, bio-degradation and oxidizing agents [6].

Currently, several physical or chemical processes are used to treat dye-laden wastewaters. However, these processes are costly and cannot effectively be used to treat the wide range of dye wastewater. The convectional wastewater treatment, which rely on aerobic biodegradation have low removal efficiency for reactive and other anionic soluble dyes. Due to low biodegradation of dyes, a convectional biological treatment process is not very effective in treating a dyes wastewater. It is usually treated with either physical or chemical processes. However, these processes are very expensive and cannot effectively be used to treat the wide range of dyes waste[7][8].

The adsorption process is one of the effective methods for removal dyes from the waste effluent. The process of adsorption has an edge over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution. Activated carbon (powdered or granular) is the most widely used adsorbents because it has excellent adsorption efficiency for the organic compound. But, commercially available activated carbon is very expensive.

L. MATERIALS AND METHODS

A. Sample Collection

The sample collection of the raw material of palm kernel shell was obtained from palm oil mill of FELDA Serting Hilir, Negeri Sembilan. The samples were stored at temperature of 4°C to maintain its moisture content.

B. Sample Pretreatment

The PKS samples are dried at 100 °C for 24 hours in an oven to remove moisture content. Then, samples were stored at room temperature in closed box to avoid it from exposed to high humidity and to maintain its constant weight.

C. Production of Activated Carbon

For the production of activated carbon, it undergoes heat treatment process. Firstly, the raw materials of palm kernel shell are weighed and then inserted into crucibles and closed with a lid. The crucibles are inserted into a furnace at 400°C for 2 hours to undergo the carbonization process. The purpose

of this carbonization process is to remove excess of volatile matters. After that, the carbonized material will be cooled and weight to calculate the total dried weight. Then, the carbonized material is proceed to activation process. In the activation process, three temperatures (600°C, 750°C, and 1000°C) and three different activation time (60 min, 90 min, and 120 min) was used. From this conditions, we will be producing five different AC according to table 1.

TABLE 1. CONDITIONS FOR THERMAL ACTIVATION

Temperature/ ˚C (A)	heating period/ minute (B)
600 (-1)	60 (-1)
750 (0)	90 (0)
1000 (1)	120 (1)

LI. RESULTS AND DISCUSSION

A. Production of Activated Carbon

5 different samples of PKSAC were heated at various temperatures for different heating time. The results are tabulated to show the percentage of yield of activated carbon. The initial mass of the raw material and the final mass (m_f) of the product were taken to get the percentage of yield.

TABLE 2. PERCENTAGE OF YIELD

Condition	m_0 (g)	m_f (g)	m_f (g)	% Yield
600˚C, 60min	50.0020	18.6508	31.3512	37.30
600˚C, 120min	50.0103	18.8541	30.1562	37.70
750˚C, 90min	50.0005	16.5002	33.5003	33.00
1000˚C, 60min	50.0045	15.4014	34.6031	30.80
1000˚C, 120min	50.0029	15.2509	34.7520	30.50

B. Screening

The purpose of screening is to obtain the best product of PKSAC for further adsorption test. The screening was done by taking 2 hours as contact time, 150 mg/L initial concentration, 3 g of adsorbent dosage, initial pH of 4, and agitation speed at 150 rpm. The best product was obtained by determining the colour removal and adsorption capacity and the values was run using MINITAB software to get the optimum condition. Table 3 and 4 showed the % of colour removal and adsorption capacity.

TABLE 3. PERCENTAGE OF COLOUR REMOVAL

Sample	OD reading (Optical Density)	Colour removal (%)
600˚C, 60 min	0.359	85.5
600˚C, 120 min	0.104	95.8
750˚C, 90 min	0.002	99.9
1000˚C, 60 min	0.000	100.0
1000˚C, 120 min	0.004	99.8

TABLE 4. ADSORPTION CAPACITY OF MB

Sample	Initial concentration (g/l)	Final concentration (g/l)	Adsorption capacity
600˚C, 60min	0.1	0.0145	85.5
600˚C, 120min	0.1	0.0042	95.8
750˚C, 90min	0.1	0.0001	99.9
1000˚C, 60 min	0.1	0.0000	100.0
1000˚C, 120 min	0.1	0.0002	99.8

From Table 3, the maximum percentage removal is 100% during the activation temperature of 1000˚C and time of 60 min. However, there is not much difference in the percentage of colour removal from activation temperature of 750˚C at 90 min to 1000˚C where the percentages are above 99%. Therefore, the best product selected is PKSAC at 750˚C at 90 min as it has a lower temperature and the cost determining factor is taken into account. The coefficient of determination, R^2 obtained from the regression analysis is 91.5%. The adjusted R^2 obtained is 88.7%. The polynomial regression model relating the adsorption capacity with independent variables of x1, x2 is

Adsorption capacity = 80.4 + 0.506 X1 - 0.00313 x1*x1

Where; x_1 is variable of temperature, x_2 is the variable of activation time and has been removed from the equation.

TABLE 5. PERCENTAGE OF COLOUR REMOVAL

Impregnation ratio	OD reading (Optical Density)	Colour removal (%)
0.50	0.052	90.2
0.75	0.030	93.6
1.00	0.002	99.2
1.25	0.000	100
1.50	0.078	99.8

TABLE 6. ADSORPTION CAPACITY OF MG

Impregnation ratio	Initial concentration (g/l)	Final concentration (g/l)	Adsorption capacity
0.50	150	14.7	90.2
0.75	150	9.6	93.6
1.00	150	1.2	99.2
1.25	150	0	100
1.50	150	0.3	99.8

From Table 4, the maximum percentage removal is 100% during the impregnation ratio 1.25. However, there is not much difference in the percentage of colour removal from impregnation ratio of 1.0 to 1.50 where the percentages are above 99%. Therefore, the best product selected is PKSAC impregnated with K_2CO_3 by ratio of 1.0 as it has a chemical volume and the cost determining factor is taken into account. The coefficient of determination, R^2 obtained from the regression analysis is 94.1%. The adjusted R^2 obtained is 92.4%. The polynomial regression model relating the adsorption capacity with independent variables of x1, x2 is

Adsorption capacity = 79.5 + 0.535 x1 - 0.00333 x1*x1

Where; x_1 is variable of K_2CO_3 weight, x_2 is the variable of AC weight.

C. Statistical Analysis

After the most potential product of activated carbon was selected optimization of maximum condition was analysed. Five parameters, contact time, initial concentration, adsorbent dosage, pH and agitation speed were observed to study the optimum condition for adsorption capacity. The optimum combination of major variables was determined by using Minitab Release 14 software and Statisca 6 by doing modelling. The results obtained for the experimental and theoretical adsorption capacity is indicated in Table 6. The polynomial regression model relating the adsorption capacity with independent variables x_1, x_2, x_3, x_4, and x_5 is

Adsorption capacity (mg/g) = 72.6 + 0.328 x1 + 0.704 x2 - 68.1 x3 + 6.31 x4 - 0.194x5 - 0.000752 x1*x1 - 0.000182 x2*x2 + 9.62 x3*x3 - 0.353 x4*x4 - 0.000275 x5*x5 - 0.000778 x1*x2 + 0.0321 x1*x3 - 0.0323 x1*x4 + 0.000563 x1*x5 - 0.0939 x2*x3 - 0.0104 x2*x4 + 0.000844 x2*x5 + 0.553 x3*x4 + 0.0121 x4*x5

Where; x_1 = contact time (min); x_2 = initial concentration (mg/L); x_3 = adsorbent dosage (g); x_4 = pH; x_5 = agitation speed (rpm)

The coefficient of determination, R^2 obtained from the regression analysis is 99.6%. The adjusted R^2 obtained is 98.9%. The *t*-distribution and the corresponding *p*-value along with the second order polynomial coefficients were evaluated using Minitab software. The *p*-values serve as a tool for checking the significance of each of the coefficients. The pattern interactions between the variables are indicated by these coefficients. The variables with low probability level contribute to the model, whereas the others can be neglected and eliminated from the model. The larger the magnitude of the test value and the smaller the *p*-value indicates the high significance of the corresponding coefficient.

The *p*-values for the linear, quadratic and interactive terms are as follows: 0.012, 0.000, 0.000, 0.000, 0.010, 0.009, 0.000, 0.005, for constant, x_3, x_4, x_3*x_3, x_4*x_4, x_1*x_4, x_2*x_3, and x_2*x_5 respectively. The *p*-values with the coefficient of 0.000 are the most significant. In this case, the most significant interaction effect is the adsorbent dosage.

TABLE 7. OPTIMIZATION CONDITION OF ADSORPTION CAPACITY OF MALACHITE GREEN

time (min)	Con(mg/L)	Dosage (g/L)	pH	(rpm)	Adsorption Capacity	
					observed	experimental
120	150	3	3	150	45.9360	43.917
90	100	4	5	100	23.9730	24.580
150	100	4	9	100	24.5890	25.775
150	100	2	5	100	53.0400	54.535
120	150	3	7	150	46.4380	47.189
90	100	4	9	200	23.5620	24.699
120	150	3	7	50	46.5750	44.203
150	100	4	5	200	24.0410	25.440
150	100	2	9	200	44.6580	45.856
150	200	4	9	200	48.0140	49.130
90	100	2	5	200	44.1100	44.719
90	100	2	9	100	50.5300	51.760
90	200	4	9	100	47.0890	47.410
180	150	3	7	150	46.8040	43.610
90	200	4	5	200	48.0140	48.545
120	150	3	7	150	46.7120	47.189
120	150	3	7	150	46.8950	47.189
120	150	3	11	150	41.8850	39.165
120	250	3	7	150	79.8170	78.183
150	200	4	5	100	48.5270	49.105
150	200	2	5	200	95.4110	95.990
90	200	2	9	200	94.8630	95.185
120	150	3	7	150	46.7120	47.189
90	200	2	5	100	94.5890	95.210
120	150	3	7	150	46.6670	47.189
60	150	3	7	150	46.8950	45.353
120	150	3	7	150	46.5750	47.189
150	200	2	9	100	78.0900	79.301
120	150	1	7	150	121.4160	119.153
120	150	3	7	250	47.0320	44.675
120	50	3	7	150	15.6620	12.555
120	150	5	7	150	54.6400	52.185

LII. ONCLUSION

It can be concluded that the results of is study showed that activated carbon prepared from palm kernel shell is a potential useful adsorbent for the adsorption of malachite green. In this experimental design, five variables (contact time, initial concentration, adsorbent dosage, pH, and agitation speed) were used for obtain the optimum condition for adsorption capacity that was rum using Minitab Release software and Statistica. The R^2 and experimental values can be obtained by using this software to obtain regression curve, surface plot, and contour plot. Form this study, the best candidate for adsorption of MG gives 121.416 mg/g adsorption rate.

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