Faculty of Resource Science and Technology

RESPONSE SURFACE METHODOLOGY STUDY ON THE REMOVAL OF HUMIC SUBSTANCES FROM TROPICAL BLACK WATER USING SAGO HAMPAS

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Response Surface Methodology Study on the Removal of Humic Substances from Tropical Black Water Using Sago Hampas

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DECLARATION

I declare that this thesis entitled ‘Response Surface Methodology Study on the Removal of Humic Substances from Tropical Black Water Using Sago Hampas’ is my own research paper except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature for any other degree.

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List of Abbreviations

ANOVA	Analysis of Variance
BBD	Box-Behnken Design
CCD	Central Composite Design
Cu	Copper
^{o}C	Degree celcius
DF	Degree of freedom
E_{465}	Absorbance at 465nm
Exp. No	Experiment number
$F_{calc.}$	F-value calculated
$F_{crit.}$	F-value critical
IHSS	International Humic Substances Society
Mg/ml	Milligrams per milliliter
M	Molar
Mg/L	Milligram per litre
Min	Minute
NaOH	Sodium hydroxide
Nm	Nanometer
µm	Micrometer
Pb	Lead
R^2	Regression coefficient
RMSE	Root mean square error
RSM	Response surface methodology
Rpm	Revolutions per minute
SS	Sum of square

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ABSTRACT

The study focuses on evaluation of the optimum conditions for the removal of humic substances from tropical black water using sago hampas. Response Surface Methodology (RSM) was conducted based on three-level-four-factor Box-Behnken Design in order to examine the optimum conditions for maximal adsorption of humic substances. The parameters studied were contact time (20-60 minutes), mesh size (500-900 µm), amount of dosage (100-300 mg/ml) and pH (3-7). The proportion of the total variation of the designated linear, interaction and quadratic model were 99.39 %, 99.34 % and 99.42 % respectively. The quadratic regression models were tested as the best-fit model which shows significant relationship between both the responses and the parameters. The optimum conditions based on the RSM were 40 minutes contact time with 700 µm sago hampas at 300 mg/ml and pH 3.

Key words: Humic substances, response surface methodology, Box-Behnken design, adsorption, optimum condition

ABSTRAK

Kajian ini bertujuan untuk menyelidik keadaan optima untuk menyingkirkan kandungan humik dari air hitam tropika dengan menggunakan hampas sagu. Kaedah tindakbalas permukaan (RSM) telah digunakan berdasarkan rekaan tiga tahap-empat faktor dengan model Box-Behnken bagi mengkaji faktor yang mempengaruhi interaksi parameter pada setiap peringkat untuk penjerapan optimum. Parameter yang digunakan ialah masa interaksi (20-60 minit), saiz jarring (500-900 µm), jumlah dos (100-300 mg/ml) dan pH (3-7). Perkadaran jumlah variasi model linear, interaksi dan kuadratik yang direka adalah 99.39 %, 99.34 % dan 99.42 % masing-masing. Model regresi kuadratik telah diuji sebagai model terbaik yang menunjukkan hubungan yang signifikan antara kedua-dua tindakbalas dan parameter. Keadaan optima yang diperoleh berdasarkan kaedah RSM ialah 40 minit masa interaksi dengan 700 µm hampas sagu pada 300 mg/ml dan pH 3.

Kata kunci: Kandungan humik, kaedah tindakbalas permukaan, rekaan Box-Behnken, penjerapan, keadaan optimum

1.0 Introduction

In Sarawak, there is a considerable size of peat swamp; this area is inhabited where people often encounters difficulties in getting access to clean water supply. This is because the rivers flowing through this area are tainted by peat swamp runoff rich in humic substances. According to Aiken *et al.* (1985), humic substances consist of humic acids, fulvic acids and humin. They are fundamentally formed by humification process involving decaying and transformation of plant and animals remains (Hayes *et al.,* 1989).

According to Uyguner and Bekbolet (2005), the presence of humic substances in water influences the water quality by producing undesirable color and contributing to increase in metal concentrations due to complexing reaction between humic substances and metals. Hence, it is important to minimize the concentration of humic substances in the wastewater treatment plant and the drinking water processing system (Castro *et al.,* 2000).

However, humic substances are difficult to isolate due to the differences in molecular size and their solubility in water (Yasin *et al.,* 2010). The process can be time-consuming and often required multiple purification steps. Some physicochemical methods have been designed to remove humic substances for example ion exchange, coagulation and flocculation and chemical precipitation nevertheless these methods are restricted by the high operational cost and often unsustainable (Feng *et al.,* 2011).

Adsorption using agricultural wastes is an alternative technology. This option is more economical, environmental friendly and better in efficiency as the materials can be found in abundance. Numerous studies had revealed the promising adsorption performance of various agricultural wastes such as sago hampas (Quek *et al.,* 1998), orange peel (Feng *et al.,* 2011), sawdust (Lim *et al.,* 2008), mango peel (Iqbal *et al.,* 2009), rice husk (Ajmal *et al.,* 2003) and banana peel (Ashraf *et al.,* 2011). The adsorption performance is often governed by various parameters such as pH, temperature, initial concentration, contact time and etc. Very often, the optimum condition is determined using the one-factor-at-a-time approach. The contributing factors are optimized by changing one factor at a time whilst keeping other variables constant. This approach is easy to implement and helps to identify the significant parameters affecting the response of a system investigated. Nevertheless, the method is time restrictive especially when many variables are involved in addition, the combined effects are ignored.

It is crucial to consider the combined effects of various parameters for the optimal adsorption conditions. Cordova *et al.* (2011) stated that the interactions among operational conditions are used for generating a statistical model that represents the response surface of biosorption processes. The information acquired is essential for understanding the optimal design of an adsorption system and the necessary modification measures.

Objective

In this study, we employ the response surface methodology to examine the effects of four factors i.e., pH, contact time, mesh size and amount of dosage for removing humic substances from the tropical black water using sago hampas.

2.0 Literature Review

2.1 Sago Hampas

Sarawak is known to produce tonnes of sago hampas daily due to the starch extraction process at sago processing factories (Awang Adeni *et al.,* 2010). Sago hampas are the by products resulting from the action of crushing and sieving of sago. On dry basis, 60 to 70% of sago hampas is starch; Table 1 shows the composition of sago hampas.

Vickineswary *et al.* (1994) suggests that sago hampas mainly consists of cellulose and lignin in the lignocelluloses structure and known to have biosorption properties. It was also known as an excellent adsorbent for lead (Pb) due to its high sorption capacity. A study by Quek *et al.* (1998) revealed that the optimum pH range for the adsorption of lead (Pb) and copper (Cu) were between 4 and 5.5. The adsorption of Pb was higher (46.60 mg/ml) compared to that of Cu (12.4 mg/ml). Preparation of sago hampas as activated carbon was considered as one of the effective way for the removal of metal ions in waste water.

Table 1: The composition of sago hampas on dry basis (Abd. Aziz, 2002).

Component	**Percentage**
Starch	65.70
Crude fiber	14.80
Crude protein	1.00
Ash	4.10
Moisture	59.10

Sago hampas has also been used for various applications for example, as feedstock for farm animals i.e., cow, pig and horses. Apart from that, sago hampas is a useful growth media for oyster mushroom and further modification for utilization in food industries (Abd. Aziz, 2002).

2.2 Response Surface Methodology (RSM)

Response surface methodology is a collective mathematical and statistical method used to examine the relationship between the response and the factors affecting the response (Carley *et al.*, 2004). This method has been widely used to optimize reacting parameters due to its benefit in minimizing the number of analysis to analyze interaction between parameter (Montgomery, 2005), reducing chemical consumption and less analytical works (Fereira *et al.*, 2007). Moreover, the RSM has been proven as an important statistical tool for examination of numerous treatment processes. The method examines the optimum conditions through experimental methods where the experiments can be designed according to many options. The simplest is the full factorial design.

A full factorial experiment is an experiment whose design consists of two or more factors, each with discrete possible levels and is often known as the screening design (Lenth, 2009). Furthermore, a full factorial design experiment often conducted to estimate the factor effects as well as to demonstrate the responses in relation to the factors. The number of experiment is calculated as 2^k where k is the number of factor each with two levels. An experiment with 2 factors involves 4 experiments that take on all possible combinations. However, this design can become very complicated when a large number of factors are involved e.g., 10; the total number of experiments will be $2^{10} = 1024$. Other designs that require fewer experiments such as fractional design, Central Composite Design (CCD), Box Behnken Design (BBD) and etcs can be used.

2.2.1 Central Composite Design

The Central Composite Design (CCD) is the design which included both the full or fractional factorial design that is often used to estimate the second order response surface (Otto, 2007). According to Park *et al.* (2008), the resulting regression coefficient of the second order polynomial equation is very useful for the linear, interaction and quadratic terms. There are three points present in a CCD namely: axial point ($2. n$), cube point (2^n from full factorial design) and center point (α, center point created by nominal design). CCD is very important in providing information on the experimental variable effects and the overall experimental error in a minimum numbers of runs. However, the adjustments of level are sometimes difficult to achieve due to the present of star points, α outside design (Morgan, 1997). The design for CCD with three factors and α star point were illustrated in Figure 1.

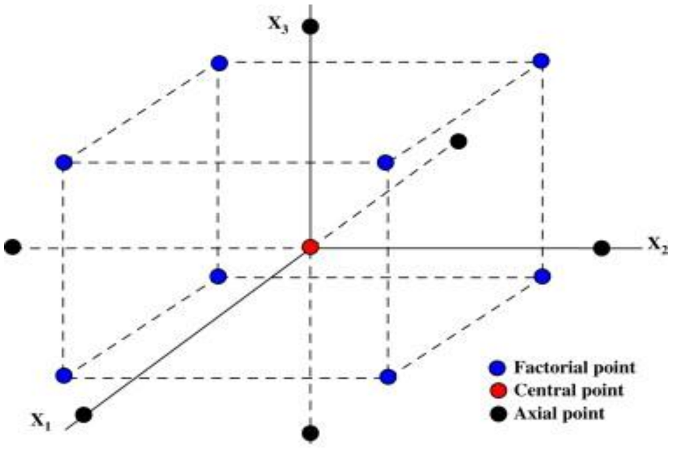

Figure 1: The central composite design for three factors (Cho &Zho, 2007)

2.2.2 Box- Behnken Design

Box-Behnken design (BBD) is known as the one-step response surface design which requires only three levels to run an experiment (Edward & Mee, 2011). As suggested by Ferreira *et al.* (2007), it was a good design because it enables estimation of parameters for the quadratic model, detection of lack-of-fit of the model as well as building of a sequential design. However, the BBD might only include the responses in correlation with only a single factor.

BBD is beneficial as the design is not presented in order where all the factors are at their highest or lowest levels and this type of order inhibits errors in the resulting responses. BBD method is also considered a good choice in RSM study compared to CCD method (Fu, 2009). In a study by Sudamalla *et al.* (2012), BBD was used to optimize the operating parameters for adsorption of crystal violet by activated carbon prepared from mango kernel. The study showed that BBD was able to evaluate the interactions between the factors efficiently. Table 2 shows the number of experiment for different factors with three replications.

Table 2: The number of experiments for different factors with three replications in the center of each design (Otto, 2007)

Number of factors	**Number of experiments**
3	15
4	27
5	46
6	54
7	62

2.3 Adsorption and the mechanism

Adsorption is a promising ways as the technology promotes high-efficiency. The adsorption ability mainly relates to the type of adsorbent used due to their physical and chemical characteristics (Annadurai *et al.,* 2002). Adsorption generally occurs in two ways: physical adsorption and chemical adsorption (Allen & Koumanova, 2005). Physical adsorption (physisorption) takes place due to the interaction between weak interparticle bonds and both the adsorbent and adsorbate. On the other hand, the chemical adsorption (chemisorptions) occurs when strong interparticle bonds are involved in the reactions of adsorbate and adsorbent.

Ravikumar *et al.* (2005) suggested that the statistical experimental design can be used to improve the percentage yield and minimized the time and operational cost. According to Mohan and Charles (2007), agriculture by-products and industrial wastes have excellent adsorption capacities. They have been commonly employed for removal of heavy metals in wastewater. The efficiency of the agricultural wastes as adsorbents is very much influenced by the preparation conditions (Nwabanne *et al.,* 2011). They affect the pore size distribution and physico-chemical characteristics such as ash content, surface area, volatile matter, bulk density and iodine number hence the adsorption capabilities (Shopova *et al.,* 1997). The adsorption performance can be further affected by the operating conditions such as contact time, initial concentration, adsorbent dosage, pH and agitation speed.

The adsorption capacity was reported to increase with the adsorbent dosage. However, a further increase in the dosage could result in declined performance due to the lack of adsorbate for adsorption (Ozer *et al.,* 1998). A study by Huang *et al.* (2009) suggested that an increase in contact time would improve the adsorption capability. An optimum initial concentration on the other hand determines the effective collision between the adsorbate and adsorbent (Alam *et al*., 2007). Further increase in the initial adsorbate concentration will result in decrease of the removal percentage. This is due to the increase in the quantities of ions competing for binding sites and also due to reduction of active sites on the adsorbent at higher concentration.

Temperature is another important factor. When the temperature increases, the diffusion rate of adsorbate molecules into adsorbents will be increased. Nevertheless in some cases, although the rate of diffusion increases, the adsorptive capacity could decrease with the increase in temperature (Yasin *et al.,* 2010). This happened due to the massive destruction on the surface of the adsorbent caused by the high temperature. The pH indicates the affinity of the weak organic basic and acid for activated carbon (Fox *et al.,* 1973). Adsorption capacity is higher when the pH is in the range whereby the molecules are in its neutral form. When the molecules are ionized, the affinity for water is higher and therefore the adsorption capacity decreases.

3.0 Materials and Methods

3.1 Preparation of sago hampas

Sago hampas was used for the adsorption study. Karthika et al. (2010) suggested that, the potential of sago hampas utilized as adsorbent were due to the present of functional groups such as carboxyl (-C-O-C), phenolic (-OH) and carbonyl (-C-O) on the surface carbon of the sago waste. The presence of functional groups enables the adsorption of the humic substances onto the surface of sago waste. Sago hampas is the fibrous pith residue left after starch extraction from sago palm (Figure 2). The raw material was washed thoroughly with tap water to remove dirt and unwanted substances. They were dried in an oven at 105 ^{o}C for 24 hours, ground and sieved according to three sizes: 500 µm, 700 µm and 900 µm.

Figure 2: The sago hampas used for adsorption of humic substances

3.2 Experimental design

The experimental design employed was a three-level-four-factor Box-Behnken Design with 27 experiments including 3 replications in order to obtain accurate estimation of the experimental error (Myer & Montgomery, 2002). The factors considered are contact time, mesh size, amount of dosage of adsorbent and pH. Table 3 summarizes the uncoded and coded level for the factors. It is common to place the variables on a common scale with the highest coded value assigns as +1 and the lowest to -1. The reason is to make sure each variable is considered on a comparable scale.

Table 3: Uncoded and coded levels of the independent variables

Factors	**Coded level**		
	-1	**0**	**1**
Contact time (min)	20	40	60
Mesh size (µm)	500	700	900
Amount of dosage (mg/100mL)	100	200	300
pH	3	5	7

The optimization experimental design according to the Box-Behnken Design is shown in Table 4. Experiments are conducted in designated conditions; for example in experiment 1, a 200 mg of sample at 500 µm (with pH adjusted to 5) was agitated in 100 mL of tropical peat water for 20 minutes.

Table 4: Box-Behnken Design for three-level-four-factor experiments.

Exp. No	Contact time **X_1**	Mesh Size **X_2**	Dosage **X_3**	pH **X_4**
1	-1	-1	0	0
2	-1	1	0	0
3	1	-1	0	0
4	1	1	0	0
5	0	0	-1	-1
6	0	0	-1	1
7	0	0	1	-1
8	0	0	1	1
9	-1	0	0	-1
10	-1	0	0	1
11	1	0	0	-1
12	1	0	0	1
13	0	-1	-1	0
14	0	-1	1	0
15	0	1	-1	0
16	0	1	1	0
17	-1	0	-1	0
18	-1	0	1	0
19	1	0	-1	0
20	1	0	1	0
21	0	-1	0	-1
22	0	-1	0	1
23	0	1	0	-1
24	0	1	0	1
25	0	0	0	0
26	0	0	0	0
27	0	0	0	0

The data from the experiment was fitted to linear, interaction and quadratic design using Microsoft Excel.

3.3 Water sample

Water from the Asa Jaya Treatment Plant was used for RSM. The plant uses the Asa Jaya River as its source. The river is highly colored and is surrounded with peat swamp suggesting its rich humic content. The sample was filtered through 0.45 µm membrane filter and agitated with sago hampas at different dosage, mesh size, time and pH as suggested in Table 4. Note that the speed of agitation was fixed at 100 rpm and the pH was altered by adding 0.25 M sodium hydroxide (NaOH).

3. 4 Adsorption of humic substances

The response measured is the absorbance at 465 nm a UV-Vis spectroscopy. This spectrophotometric measurement method has been well established for quantification of humic substances. The absorbance at 465 nm is a linear function of humic substances content (Dick & Burba, 1999). Figure 3 shows the relationship between the concentration of standard humic acid (Sigma Aldrich) and the absorbance at 465 nm.

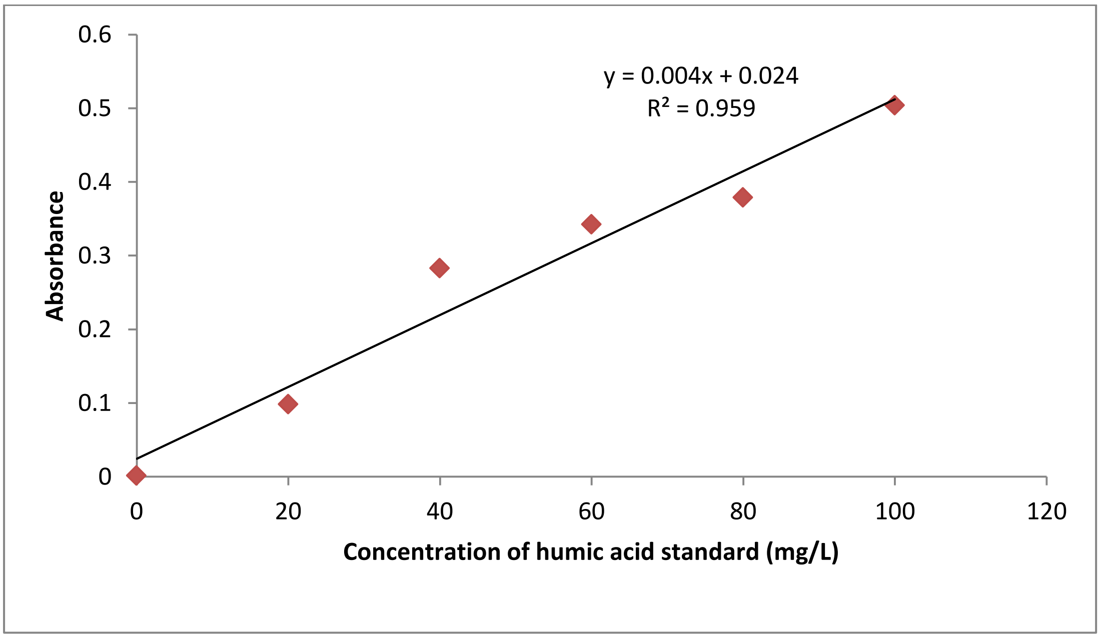

Figure 3: The relationship between the concentration of standard humic acid and the absorbance at E_{465}

The absorbance of raw water sample at 465 nm was recorded at 0.0771. If adsorption of humic substances occurs, a decline in the absorbance value will be indicated. This parameter provides information as to whether humic substances have been adsorbed and whether the adsorption performance of one experiment is better or worse than another. It is agreed that the removal performance could not be quantitatively reported with this approach as there is no suitable standard for measurement of humic substances nevertheless, this method is less time consuming compared to other methods such as the International Humic Substances Society (IHSS) method and the chromatographic method.

4.0 Results and Discussion

The results of RSM were summarized in Table 5. The data can be fixed into various models such as linear, interaction and quadratic as described in the following equations where $\hat{y}$ is the predicted response, b_0 is intercept while b_1, $b2$….are the regression coefficient for different factors and X is the independent factors. In this study, the data is fitted to linear, interaction and quadratic models.

$$\hat{y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 \qquad \textit{(Linear model)}$$

$$\hat{y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4 \qquad \textit{(Interaction model)}$$

$$\hat{y} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{11} X_1^2 + b_{22} X_2^2 + b_{33} X_3^2 + b_{44} X_4^2 + b_{12} X_1 X_2 + b_{13} X_1 X_3 + b_{14} X_1 X_4 + b_{23} X_2 X_3 + b_{24} X_2 X_4 + b_{34} X_3 X_4$$

$$\textit{(Quadratic model)}$$

Table 5: The result of experimental RSM

Exp. No	**Intercept**	Contact time **X_1**	Mesh Size **X_2**	Dosage **X_3**	pH **X_4**	**E_{465} value recorded**
1	1	-1	-1	0	0	0.0818
2	1	-1	1	0	0	0.0743
3	1	1	-1	0	0	0.0794
4	1	1	1	0	0	0.0811
5	1	0	0	-1	-1	0.0667
6	1	0	0	-1	1	0.0878
7	1	0	0	1	-1	0.0656
8	1	0	0	1	1	0.0864
9	1	-1	0	0	-1	0.0770
10	1	-1	0	0	1	0.0945
11	1	1	0	0	-1	0.0761
12	1	1	0	0	1	0.0823
13	1	0	-1	-1	0	0.0861
14	1	0	-1	1	0	0.0721
15	1	0	1	-1	0	0.0902
16	1	0	1	1	0	0.0725
17	1	-1	0	-1	0	0.0823
18	1	-1	0	1	0	0.0720
19	1	1	0	-1	0	0.0835
20	1	1	0	1	0	0.0725
21	1	0	-1	0	-1	0.0725
22	1	0	-1	0	1	0.0857
23	1	0	1	0	-1	0.0669
24	1	0	1	0	1	0.0817
25	1	0	0	0	0	0.0727
26	1	0	0	0	0	0.0733
27	1	0	0	0	0	0.0739