OPTIMIZATION OF PHOSPHORIC ACID TREATMENT BIOCHAR USING RESPONSE SURFACE METHOD

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ABSTRACT: Biochar is derived from the crop residue as a multifunctional materials for agricultural applications and as a soil enhancer to improve soil fertility. The physical and chemical properties of biochar are improved via phosphoric acid treatment. The aim of this study is to optimize the acid treatment of biochar for two factor; 1) concentration of phosphoric acid and 2) heating temperature via Response Surface Methodology (RSM) by using Design Expert 10 software. A set of 11 experiments were carried out based on Central Composite Design (CCD) with three repetitions at center point. Hence, the responses were set in two factors; 1) pH and 2) negative surface charge. The biochar produced from slow pyrolysis process of rubber wood sawdust (RWSD) in a horizontal tube furnace heated at 5^0C/minute from room temperature to maximum temperature of 400^0C with holding time of 1 hour. Characterization of treated biochar was performed using Scanning Electron Microscopy (SEM) and SEM with EDX. Analysis of variance of the pH and negative surface charge indicated that the selected quartic model was significant with p-value of <0.05. Predicted parameters to obtain the maximum negative surface charge were 1 Mol of acid concentration and 85^0C of heating temperature with desirability of 98%.

KEYWORDS: *Optimization; Biochar; Rubber Wood Sawdust (RWSD); Acid Treatment; Negative Surface Charge*

1.0 INTRODUCTION

Biochar is a carbon rich product obtained in which biomass (wood, manure or leaves) is heated in a closed container with little or no existing air and it is distinguished from charcoal used as a soil amendment [1]. In recent year, biochar attracted researchers' interest due to its low cost and simplicity to be processed from agriculture waste [2]. Biochar is highly porous material and it can improve soil physical properties such as total porosity, pore distribution and density when it is applied to the soil [3-4]. The biochar also tend to increase the soil moisture content due to the formation of surface oxide, which is known as negative surface charge and in which it is able to increase nutrient levels and improve the cation exchange capacity (CEC) in soil [5]. A CEC value can hold and exchange nutrient such as ammonium, calcium and potassium efficiently in the soil [6]. A biochar modified with high density negative surface charge has better cation exchange capacity (CEC) to retain cation nutrients, such as ammonium (NH4+), in agricultural soil whereby the overall soil nutrient can be significantly improved [7].

Rubber Wood Sawdust (RWSD) biochar had been developed previously at 300^0C -700^0C through a slow pyrolysis process. Normally, alkalinity of the biochar will rise at higher temperature pyrolysis process which result in lower negative surface charge. The alkalinity can be reduced through the chemical activation technique which could generate significant effect on biochar properties. Phosphoric acid (H_3PO_4) can activate the carbon production, lead to an enhancement of porosity (micropore and mesopore) in a carbon structure [8-9]. Application of phosphoric acid as the chemical activator indicated that the density of the surface of functional group and surface roughness properties of the treated biochar may significantly improve [10]. Biochar with higher surface functional group and surface negative charge may reduce ammonia volatilization as shown in the study of acidified biochar which used peanut hulls (PH) and pine chips (PC) as its source, significantly lessen the ammonia loss by 58 to 63% [11].

Response surface methodology (RSM) is a mathematical and statistical technique that is used for experimental design and optimizes the chemical reaction and industrial processes. The objective of this paper is to investigate a combined effect of process parameters of temperature during heating and concentration of phosphoric acid that be used for treatment with biochar using Central Composite Design (CCD) model experiment design in Response Surface Methodology (RSM) by Design Expert Version 10.0.2.

2.0 METHODOLOGY

2.1 Biochar preparation

Rubber Wood Sawdust (RWSD) collected from sawmill in Melaka, Malaysia were sieved at about 100-200µm and then dried in room temperature for a day inside the incubator. Slow pyrolysis process were done using horizontal tube furnace (1.0cm diameter and 50.0cm length) at constant heating rate 5^0C/min before it were hold for 1 hour at 400^0C.

2.2 Experimental design and preparation of acid treatment on biochar

Figure 1 illustrated the method employed for acid treatment of the biochar. 10g of prepared biochar were blended with 400mL of phosphoric acid (H_3PO_4) at various concentrations. Each sample was heated and stirred using magnetic hot plate stirrer for an hour. It was left cooled to room temperature before being vacuum-filtered. The filtered solid samples were dried in the oven for 24 hours.

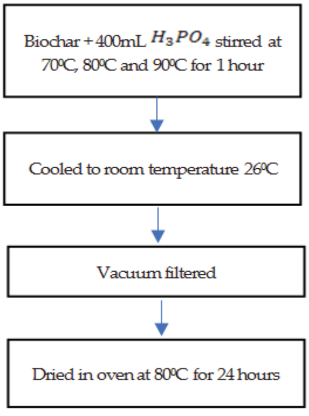


Figure 1: Flow chart of acid treated process on biochar

The acid treatment of biochar was designed based on Composite Design (CCD) via Response Surface Methodology (RSM) by using Design Expert version 10.0.2. It was to identify the optimum value of two (2) process factors: (1) concentration of acid (Molarity) and (2) heating temperature (^{0}C) for pH and negative surface charge as response (Table 1). The experimental design was set for 3 center points. Each of the independent variables was varied over three acid treatment minimum -1, maximum +1 and center point 9 based on preliminary study. The total number of experiment obtain for this two factors were 11 as shown in Table 2 in the coded term.

Table 1: Independent variables of the CCD Design

Experiments	Concentration (M)	Temperature (^{0}C)
1	0	+1.4
2	0	0
3	+1	+1
4	0	-1.4
5	+1	-1
6	-1	+1
7	0	0
8	+1.4	0
9	0	0
10	-1	-1
11	-1.4	0

Table 2: 2^2 Factorial Design Matrix

Levels of value	Concentration (X_1 ; $Molarity$)	Temperature (X_2 ; ^0C)
-1	0.5	70
0	1.0	80
+1	1.5	90

2.3 Determination of pH

1.5g of treated biochar added to 30ml of deionized water with weight to volume ratio of 1:20. The mixture was shaken by using WiseCube shaker for 5 minutes and the pH was measured by using Hanna pH meter. Each measurement was an average of three repeated readings.

2.4 Determination of negative surface charge

Negative surface charge of carbon was determined by using Bohem titration technique [12]. 0.25g of treated biochar was mixed 25mL 0.1M NaOH solution and stirred in a closed vessels inside the laboratory shaker WiseCube for 24hours. The solution was filtered and 10mL of aliquot was added to the 15 mL 0.1M HCl. 2-3 drops of bromothymol blue is added as an indicator and then back titrated with 0.1M NaOH. All the titrated sample was recorded to determine the negative surface charge of the samples. The total negative surface charge is calculated using Equation (1) and expressed in mmol/g [13-14].

$$C_s = \frac{U_b R_b N}{M_c} \tag{1}$$

C_s = Total negative surface charge per weight of adsorbent (mmol/g);
U_b = Difference in NaOH uptake between titrated sample and titrated blank (ml);
R_b = Ratio of base volume in original slurry to filtrate volume used in titration;
N = Normality of HCl (N);
M_c = Weight of Carbon (g).

2.5 Characterization using Scanning Electron Microscope (SEM) with energy dispersive X-ray spectroscopy (EDX)

The surface microstructural analysis of the optimize sample of acid treatment biochar and biochar before treatment was determined using SEM magnified 1000 X with the voltage set to 3.0kV. Carbon and oxygen content on the surface of the biochar sample were examined by using SEM-EDX spectroscopy with the voltage 1.0kV. Both samples were platinum coated using auto fine sputter coating technique set to 30A.

3.0 RESULTS AND DISCUSSION

3.1 Analysis of variance of pH

Analysis of variance (ANOVA) was used for graphical analyses of data to classify the relationship between the independent variables and its response. The statistical significance was checked by the F test while the quality of the fit process polynomial model was expressed by the value of the correlation coefficient (R^2). Table 3 showed the ANOVA for pH response in acid-treatment biochar.

The F-value of this pH model is 38.10 which indicate the quartic model is significant. This "Model F-value" occurs due to the noise with chance of only 2.58%. When the value of "P>F" is less than 0.05, it shows that the model terms are significant. In this experiment, A, A^2, B^2, A^2B , AB^2 and A^2B^2 are the significant model terms while others are not significant and can be eliminated from the models term. The model terms are not significant when the values are greater than 0.1. The "Adequate Precision" values are 0.9674 which shows the signal to noise ratio. Adequate accuracy greater than 4 is desirable, as it measures the signal to noise ratio of 20.989. R-squared value of the model indicates that there are 0.9935 and since, R-squared value closed to 1 illustrated good agreement between the calculated and observed result [15]. The regression equation for pH is shown in Equation (2).

From the pertubation graph in Figure 2, it indicates that pH increase follows with the increasing concentration and temperature during heating while response graph based on 3D plot graph at Figure 3 illustrated that the higher acid concentration will reduced the pH value which indicate the sample more acidic. These was due to the additional of the H^+ ion from acid solution to the treated biochar. Based on [16], the higher the concentration of H_3O^+ (or O^+) in a solution, the more acidic the solution is while no significant effect caused by the heating temperature.

Table 3: ANOVA analysis for analysis of variance for the quartic model for pH

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	R^2	Adjusted R^2
Model	0.28	8	0.036	38.10	0.0258	0.9935	0.9674
X_1	0.02	1	0.020	221.43	0.0436		
X_2	5E-05	1	5.00E-05	0.054	0.8385		
X_1X_2	9E-04	1	9.00E-04	0.96	0.0202		
X_1^2	0.045	1	0.045	48.06	0.0236		
X_2^2	0.038	1	0.038	40.89	0.0499		
$X_1^2X_2$	0.0117	1	0.017	18.57	0.0063		
$X_1X_2^2$	0.15	1	0.15	156.28	0.0202		
$X_1^2X_2^2$	0.045	1	0.045	48.04			
Pure Error	1.867E-03	2					
Cor Total	0.29	10					

$$pH = \begin{array}{l} 1.31 + 0.0713X_1 + 3.5711E-03X_2 - 0.015X_1X_2 + 0.099X_1^2 + 0.0911X_2^2 \\ -0.094X_1^2X_2 - 0.227X_1X_2^2 - 0.15X_1^2X_2^2 \end{array} \quad (2)$$

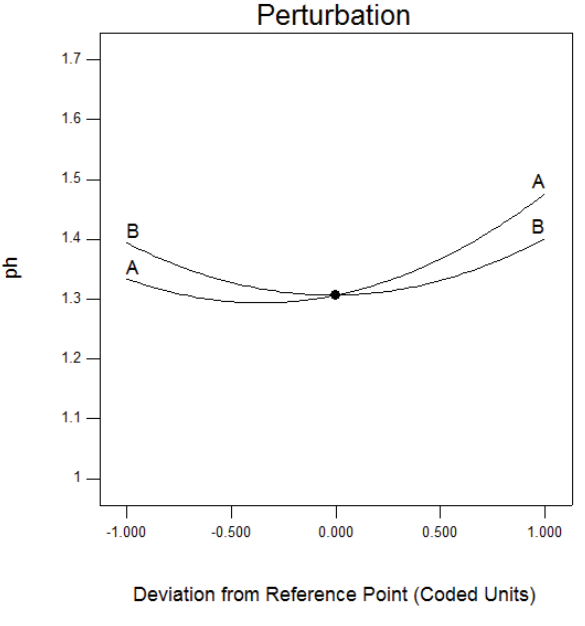


Figure 2: Pertubation plot on pH for acid-treatment biochar

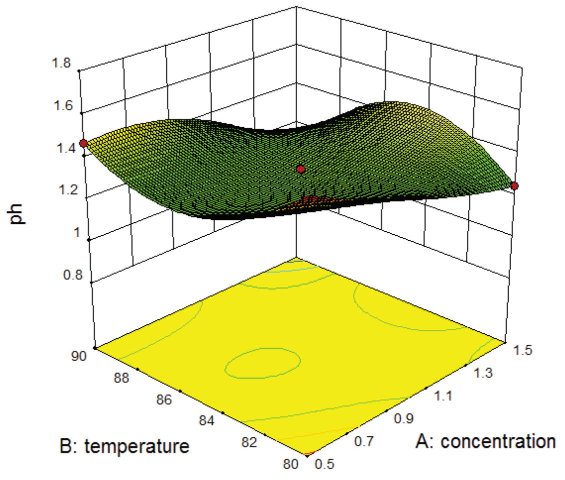


Figure 3: 3D plot of treated biochar pH value against process temperature and acid concentrations applied

3.2 Analysis of variance (ANOVA) of negative surface charge

Table 4 showed the ANOVA analysis of the negative surface charge which indicates that value of "P>F" less than 0.05 which the quartic model terms are significant because 95% confidence level is considered. In this case, the input and interaction A, AB, A^2, B^2, A^2B, AB^2, A^2B^2 are significant while the input factor B shows not significant. There are only 0.86% of error chance occur due to noise. The R-squared and "Predicted R-squared" values of the model with the reasonable agreement are 0.9978 and 0.9892. Adequate Precision greater than 4 is desirable, as it measures the signal to noise ratio of 39.565. The perturbation graph are shown in Figure 4 proved that Factor A's graph is higher than factor B, which is more significant.

Table 4: ANOVA analysis for analysis of variance for the quartic model for negative surface charge

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	R^2	Adjusted R^2
Model	7.79	8	0.97	115.94	0.0086	0.9978	0.9892
X_1	0.20	1	0.20	23.63	0.0398		
X_2	2.000E-004	1	2.00E-004	0.024	0.8915		
X_1X_2	0.52	1	0.52	61.71	0.0158		
X_1^2	0.65	1	0.65	77.18	0.0127		
X_2^2	0.40	1	0.40	48.06	0.0202		
$X_1^2X_2$	0.74	1	0.74	88.32	0.0111		
$X_1X_2^2$	2.76	1	2.76	328.18	0.0030		
$X_1^2X_2^2$	1.89		1.89	224.41	0.0044		
Pure Error	0.017	2	8.400E-003				
Cor Total	7.81	10					

Negative surface charge, Y =

$$4.85 - 0.23X_1 - 7.143E - 03X_2 + 0.36X_1X_2 - 0.38X_1^2 - 0.30X_2^2 + 0.61X_1^2X_2 + 1.18X_1X_2^2 + 0.98X_1^2X_2^2 \quad (3)$$

The regression equation for different variables is shown in Equation (3). This mathematical interaction represents the quantitative effects of the independent variables and their interaction effects to the response of quartic model. Positive values reflect effects that lead to optimization whereas negative values are the factors which provides opposite effect on the response. From the equation, Y values show the responses , $X_1$and X_2 show the factor concentration and temperature, respectively. Figure 5 shows the 3D plot graph of negative surface charge response. It shows that the acid concentrations increased the negative surface charge measurement also rose. It also depicts that the results on the negative charge from biochar's abundant acid surface functional groups that are expected to be predominantly negatively charged depend on pH conditions [17]. Both plots are revealed that no significance effect from the temperature on both responses.

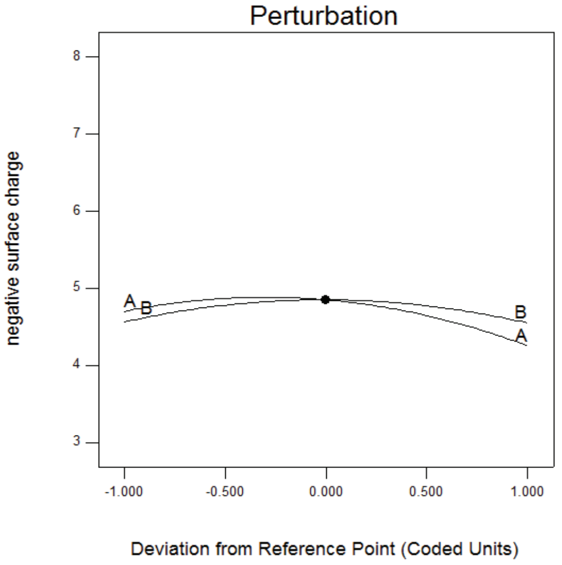


Figure 4: Pertubation plot on negative surface charge for acid treatment biochar

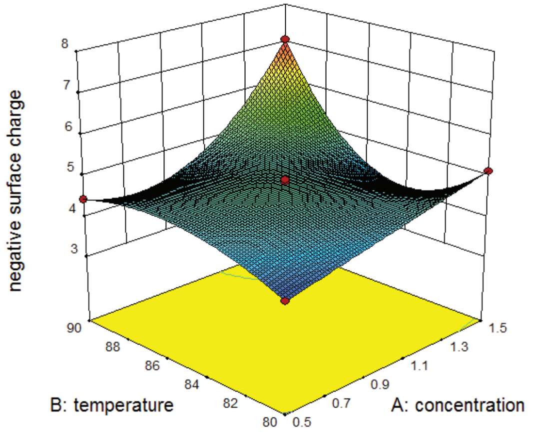


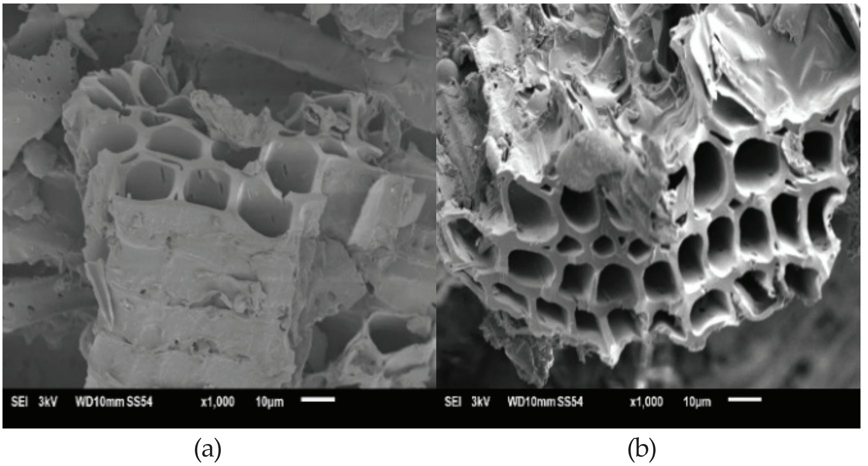
Figure 5: 3D plot of treated biochar negative surface charge value against process temperature and acid concentrations applied

3.3 Optimization process

The optimization process was carried out to determine the optimum value of concentration of acid and temperature during heating for treatment bioch ar. According to the software used, pH was set in the range while negative surface charge was chosen to be maximized. This is the reason to get the best optimum parameter for the biochar that have higher surface charge that help to reduce ammonium content while applying in the soils. The program combines the individual desirability into a single number and optimizes this function based on the response goal.

The optimum values presented by the graph model are in agreement with the numerical optimization generated by Design Expert Software. The optimization criterion of the acid-treated biochar are 1 mol concentration of phosphoric acid and 85^0C of heating temperature (Experiment 1). The desirability of these criterions is close to unity with the value of 0.98 as shown in Table 5. Lab experiment was conducted and it was confirmed that the validation of the optimization which was shown in the result is 4.75 mmolH+ of the negative surface charge. This selected treated biochar is compared with the control biochar that does not been treated with acid using SEM and SEM-EDX to prove the software selected.

Figures 6 and 7 show the SEM images and EDX results of treated biochar (BC-T) with the controlled biochar (BC-C). It also showed that there were more pores appeared in the acid treated biochar against controlled biochar. Furthermore, the EXD results indicated that the high Carbon (C) may have in the treated biochar and Phosphorous (P) element appeared to be localized at some pore acid treated biochar. This also implied that localized reactions occurred during H_3PO_4 treatment. Possibly, this may associate with the formation of organic phosphate on the treated biochars that could act as the nutrient source.



(a) (b)

Figure 6 : SEM images with (a) BC-C (control biochar) with (b) BC-T(treated biochar)

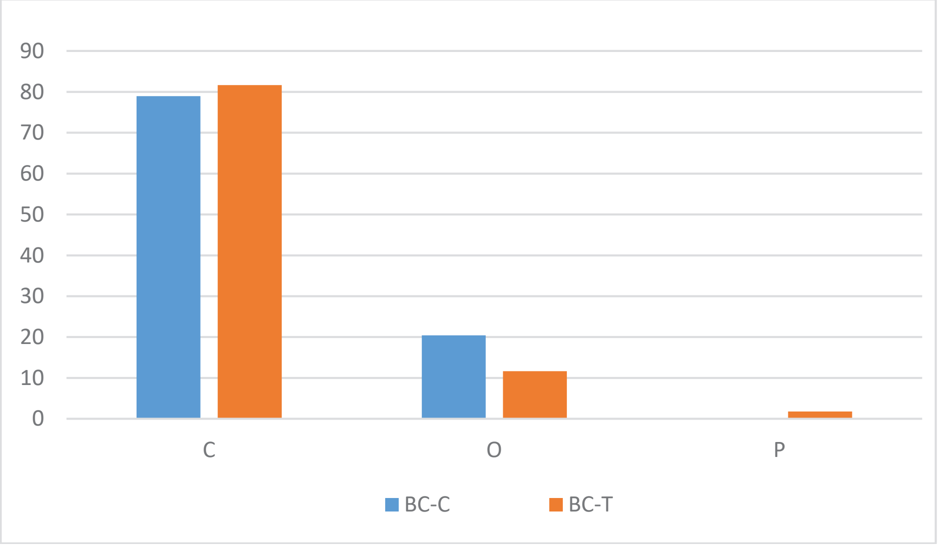


Figure 7 : Graph of the EDX results with BC-C (control biochar) and BC-T (treated biochar)

Table 5: Optimization results for acid-treated biochar using Design Expert Software

NO	Concentration (Molarity)	Temperature (^{0}C)	pH	Negative surface charge (mmolH+)	Desirability
DOE (experiment 1)	1.0	85	1.34	4.87	0.98
Lab Experiment	1.0	85	1.3	4.75	

4.0 CONCLUSION

The interaction between independent variables; (concentration and heating temperature) with response (pH and negative surface charge) was investigated using RSM with CCD. Statistical analysis for model's responses (pH and negative surface charge) was significant at P value less than 0.05. The experimental results also showed that at 1 Mol phosphoric acid and 85^{0}C of heating temperature gave the maximum negative surface charge of 4.87mmolH+ and 1.34 pH in range value for the acid treated biochar. From the SEM and EDX tests, it proved that selected sample (Experiment 1) gives better results compare to untreated biochar.

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