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Activated Carbon Production from Agricultural Biomass Using Response Surface Method (RSM) for Cd (II) Removal

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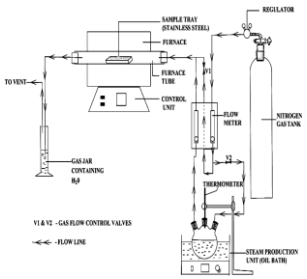
Graphical abstract



Abstract

The production of activated carbon (AC) from sugarcane bagasse (SCB) was carried out using central composite design of response surface method to run a limited number of experiments with the possibility of revealing the interaction of three selected factors of temperature, time and nitrogen/steam flowrate at different levels. Two second order quadratic regression model equations were developed using statistical analysis with Design Expert® software. The models were used for the prediction of removal of Cd^{2+} and carbon yield. Correlation coefficients (R^2) were 0.957 for removal and 0.985 for yield, showing the sufficiency of the model in predicting response within 13 experimental runs. Characterization of the product with optimal performance which was produced at 900ºC, with nitrogen/steam flow of 100 mL/min and activation time of 30 minutes, was carried out. The performance showed this AC sample was able to remove 62.42% Cd^{2+} from an aqueous solution with concentration 2 mg/L within 2 hours at optimized conditions. Experimental results indicated that AC from SCB had good prospect for Cd^{2+} removal.

Keywords: Activated carbon; adsorption; central composite design; response surface method; sugarcane bagasse

1.0 INTRODUCTION

The pollution of environmental water can be attributed to anthropogenic and non-anthropogenic sources [1], over the years the effect of anthropogenic pollution i.e pollution caused as a result of human activities which includes: drilling, mining, river channelization, dumping of domestic and industrial waste has become an issue of great concern to environmentalists. Common among pollutants generated as a result of such activities are heavy metals, volatile organic compounds, cyanide, phenols, toxic organics, suspended solids, nitrogen, phosphorus and turbidity. The presence of this pollutants in the environment poses great health risks. Over the years various treatment technologies have been developed for the removal, such pollutants; *viz* chemical precipitation, ion-exchange, membrane separation, electrocoagulation, solvent extraction, reduction, reverse osmosis and adsorption [2,3].

The detrimental effect of heavy metals on a variety of living species and the environment has been an issue of concern to both government and environmentalists. Ingestion of these metals even in trace amounts poses serious health risks because of its bioaccumulative nature [4].

Cadmium is one of the toxic elements found in effluent from electroplating, mining, painting, battery and electronic industries and landfill leachates, it is harmful to both humans and the environment [5-9]. It is associated with reproduction problems as it affects sperm production in men and birth weight in infants [6]. It is carcinogenic and a causal factor in other cardiovascular illnesses [10, 11]. Thus, because of its inherent toxicity and existence above the allowable limit of 0.01 mg/L in some Malaysian rivers [12], Cd^{2+} was selected analyte for this study.

Activated carbon (AC) adsorption has high chemical and mechanical stability and high degree of surface reactivity. Extensive studies have shown that AC has numerous applications viz; odour removal, removal of H_2S or CS_2, exhaust air cleaning, industrial wastewater and drinking water conditioning [13-17]. AC is generally considered to have beneficial environmental effects, thus its recommendation by USEPA to treat waste water effluent from the food industry [18]. Despite the prolific use of this adsorbent for water and wastewater treatment, carbon adsorption is an expensive treatment process and this has prompted a growing search for a good substitute of AC [19-22]. In continuing search for efficient adsorbents from new and cheap readily available raw material, agricultural wastes and other alternative precursors are

being processed into AC to be used in the removal of various pollutants from water and wastewater.

The objective of this study was to investigate the favorable conditions under which sugarcane bagasse activated carbon could be produced for the removal of a target heavy metal (Cd^{2+}) considering the production time, temperature and steam flow rate at activation. In order to achieve this, the use of response surface method (RSM) design technique was applied to select the best performing sample within a limited number of experimental runs.

2.0 MATERIALS AND METHODS

2.1 Preparation of Raw Material

Sugarcane bagasse was collected from juice processing stores at Taman Universiti, Skudai in Johor. The samples were initially washed under running tap water and sun dried. The dried samples were then cut to size approximately 1 cm and washed several times with ultra pure water (UPW). This was followed by oven drying at 105°C for 24 hours. Samples were then stored in sealed bags for processing.

2.2 AC Production

The dried sugarcane bagasse samples were used for the production of AC in a single step steam pyrolysis. The number and levels for production were predetermined using Design Expert® 7.1.6 software from Stat Ease Inc. A total of 13 runs was made with the center point replicated 3 times. The factors considered for this design were temperature, time and flow rate. The temperature was selected for a high level of 950°C and a low of 850°C, time had a high of 45 minutes and low of 15 minutes, while the Nitrogen/steam flow rate was at a high of 200 mL/min and a low of 100 mL/min. This is as shown in Table 1.

Table 1 Actual and coded levels of experimental conditions

A. Temperature (°C)	B. Time (mins)	C. N_2/Steam flow (mL/min)
850 (-1)	15 (-1)	100 (-1)
900 (0)	30 (0)	150 (0)
950 (+1)	45 (+1)	200 (+1)

The samples were weighed in quantities of 10 g, evenly spread inside a stainless steel sample holder and placed in a quart tube with 4.6 cm outer diameter and 100 cm length for pyrolysis in a Carbolite brand tube furnace GHA 1200 as presented schematically in Figure 1. Samples were initially carbonized under N_2 flow at 500 mL/min for 30 minutes at temperature of 750°C. Upon attaining the required carbonization time, steam is introduced into the system for activation at required conditions. N_2 was used to flow steam during activation. At the end of activation time steam flow and temperature were stopped while the sample was allowed to cool under N_2 flow. Upon cooling samples were removed and weighed to obtain the yield. The samples were then crushed and sieve through a 150 µm sieve, after which they were packed and stored in a dessicator for adsorption studies. This stage basically marks the completion of the AC production process. As the experimental procedure required production to be done at varying settings, this procedure was repeated for all 13 runs.

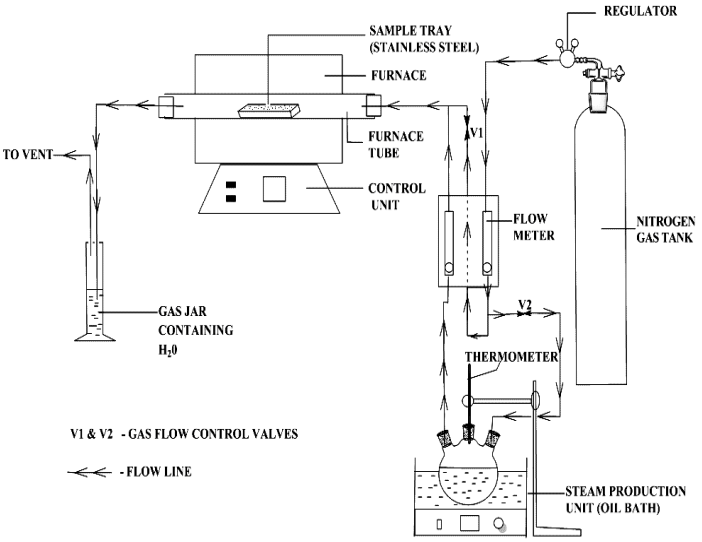


Figure 1 Production system set up with steam generation

The yield was obtained as follows:

$$\text{Yield} = W_1/W_2 * 100 \quad (1)$$

where W_1 is the weight of produced AC (g) and W_2 is the initial weight of SCB (g).

2.3 Adsorption Test

In order to determine the potential performance of the produced AC samples, adsorption tests were run for each of the 13 samples with the run time having been predetermined through trial test. A quantity of 0.05 g of AC samples was added into a 100 mL conical flask containing 50 mL of 2 mg/L Cd^{2+} solution, prepared from 1000 mg/L stock solution obtained from VWR International Ltd, England. This was equivalent to 1 g/L (w/v) of the adsorbent/adsorbate mixture. The mixtures were then placed on a mechanical shaker at an agitation speed of 120 rpm for the desired varying times. Upon completion of the shaking time, samples were taken from the flasks and filtered through 0.45 µm syringe filter.

The percentage removal (R%) is defined as the ratio of difference in metal concentration before and after adsorption ($Ci - Ce$) to the initial concentration of Cd^{2+} in the aqueous solution (Ci) was calculated using equation below [23].

$$R\% = (C_i - C_e)/ C_i * 100 \quad (2)$$

2.4 Characterization

The sample which exhibited the best removal of Cd^{2+} from aqueous solution (produced at 900°C, with nitrogen/steam flow of 100 mL/min and activation time of 30 minutes) was characterized to obtain the BET surface area and FTIR spectra. Furthermore, thermgravimetric analysis that was run on the precursor (SCB).

3.0 RESULTS AND DISCUSSION

3.1 Development of Regression Model

The complete design matrix showing the obtained experimental results as well as the predicted responses is shown in Table 2. Central composite design (CCD) was used to develop correlation between the activated carbon preparation variables to the Cd^{2+}

removal and AC yield. The removal was found to range between 39.32 and 62.42%, where as the AC yield ranged between 11.9 and 17.9%. A triplicate of the center point was used to determine experimental error. The signal to noise ratio indicates experimental error which in this design is given by the 'adequate precision' A ratio greater than 4 is desirable, for this experiment the removal had a ratio of 15.177, while the yield had 22.483 both indicating adequate signal. For both removal and yield quadratic models were used as suggested by the software, after applying backward elimination regression to exclude insignificant terms the removal and yield are represented in terms of their coded factors as equations (3) and (4).

$$\text{Removal} = 48.61 + 0.53A - 5.55B - 1.78C - 5.81AC - 7.9A^2 + 12.71C^2 \quad (3)$$

$$\text{Yield} = 14.40 - 0.15A + 2.30B - 0.80C - 1.45AB + 2.45AC - 0.95BC + 1.39A^2 + 0.54C^2 \quad (4)$$

The effect of individual variables and interactional effects were estimated using equations (3) and (4). These results indicate that there is a good correlation both for removal and yield with this model from R^2 values presented in Figures 2a and 2b for Cd^{2+} removal and AC yield respectively. The response surface analysis of variance (ANOVA) gives a further insight into the adequacy of the models to be used in navigating the design space. The ANOVA for removal gives a model F-value of 21.99, while that of yield was 32.53 implying that both models were significant. Prob > *F* less than 0.05 shows model term as significant and an insignificant lack of fit is required. In this study the Prob > *F* values were 0.0008 for removal and 0.0022 for carbon yield. The details of the analysis are as presented in Tables 3a and 3b. These conditions were favorably met in this study. The use of experimental design to study process factors has been applied by several authors in the development of adsorption process in various applications [24, 25].The graphical representation of the model facilitates an examination of the effects of the preparatory conditions on response.

Table 2 Experimental design matrix showing predicted and actual responses

Temperature	Time	C:Nitrogen/steam flow	Cd removal by AC		Yield of AC from SCB	
			(Experimental)	(Predicted)	(Experimental)	(Predicted)
(°C)	(Mins)	(mL/min)	(%)	(%)	(%)	(%)
950	45	100	57.30	55.98	16.3	16.33
950	15	200	52.50	51.90	17.9	17.93
850	45	200	50.02	51.38	16.0	16.03
850	15	100	53.76	54.40	15.0	15.03
850	30	150	42.18	40.18	16.0	15.94
950	30	150	39.32	41.23	15.7	15.64
900	15	150	56.00	54.16	11.9	12.10
900	45	150	44.91	43.07	16.5	16.70
900	30	100	62.42	63.09	15.8	15.74
900	30	200	60.30	59.54	14.2	14.14
900	30	150	48.08	48.61	14.6	14.40
900	30	150	47.10	48.61	14.8	14.40
900	30	150	46.88	48.61	14.1	14.40

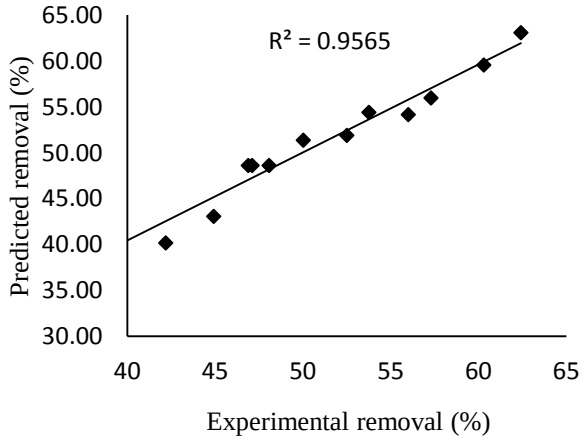


Figure 2a Removal of Cd (II) predicted versus experimental

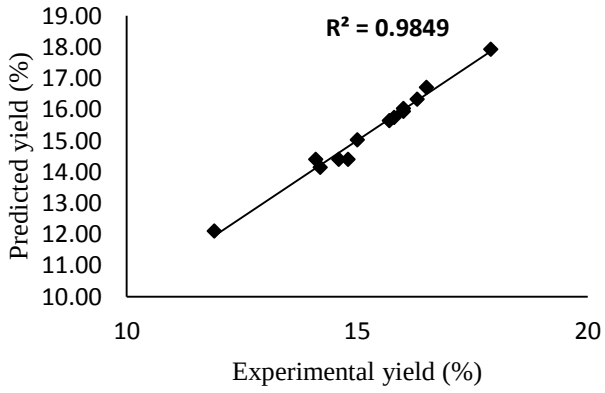


Figure 2b Carbon yield predicted versus experimental

Table 3a Analysis of variance (ANOVA) for cadmium removal response surface model

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	Remark
Model	558.6583	6	93.10972	21.99682	0.0008	significant
A-Temperature	1.664267	1	1.664267	0.393177	0.5537	-
B-Time	61.49405	1	61.49405	14.52774	0.0088	significant
C-Nitrogen/steam flow	18.93927	1	18.93927	4.47433	0.0788	-
AC	45.00813	1	45.00813	10.633	0.0172	significant
A^2	172.4758	1	172.4758	40.74676	0.0007	significant
C^2	446	1	446	105.3658	< 0.0001	significant
Lack of Fit	24.58097	4	6.145242	15.05695	0.0632	not significant

Table 3b Analysis of variance (ANOVA) for activated carbon yield response surface model

Source	Sum of Squares	df	Mean Square	F Value	Prob > F	Remark
Model	25.2413	8	3.155162	32.53323	0.0022	significant
A-Temperature	0.045	1	0.045	0.464	0.5332	-
B-Time	10.58	1	10.58	109.0916	0.0005	significant
C-Nitrogen/steam flow	1.28	1	1.28	13.19822	0.0221	significant
AB	2.803333	1	2.803333	28.90548	0.0058	significant
AC	8.003333	1	8.003333	82.52326	0.0008	significant
BC	1.203333	1	1.203333	12.4077	0.0244	significant
A^2	5.320402	1	5.320402	54.85926	0.0018	significant
C^2	0.799212	1	0.799212	8.240762	0.0454	significant
Lack of Fit	0.127931	2	0.063966	0.492042	0.6702	not significant

3.2 Effect of Production Conditions on Yield and Removal

It was seen from the results that higher temperature had a negative effect on the yield and increased flowrate had positive effect. This could be attributed to the possibility of better pore development at higher flow rates [12]. At the initial stage the effect of increase in the steam flowrate had some reduction effects, this became lower with higher temperatures.

Better performances were recorded with samples produced at the high of temperature. This could be explained by the tendency for removal of volatiles and clearing of tar and other residuals in the pores [26]. There may be need to investigate the long duration to attain maximum removal at 2 hours, there are studies that are in agreement with this finding [27], however others show shorter attainment time [12, 19]. According to the *F* values N_2/steam flow rate affected the production most, followed by temperature and then time with Prob>*F* of <0.0001, 0.0007 and 0.0088 respectively (Table 3a). For the yield it was found that time had the most significant effect, followed by the interaction between time and N_2/steam flow as indicated by the Prob > *F* values shown in Table 3b.

As earlier emphasized the graphical representation of models in three dimensions (3D) gives more insight on the effect of production condition on AC yield as presented in Figure 3. The plot showing the effect of time and temperature on yield (a) show higher yield at low temperature which could be explained by a likely incomplete decomposition of the bagasse, while increased N_2 flow is associated with a lower yield (b) and (c).

3.3 Characterization

Brunauer Emmett and Teller (BET) surface area of the best performing sample was assessed using N_2 adsorption a Micrometrics Pulse ChemiSorb 270S after degassing the sample with N_2 flow at 77K. BET equation was used to obtain a surface area of 287.23 m^2/g.

The FTIR spectroscopy yields valuable information on chemical structure of sugarcane bagasse especially its lignocellulosic properties. The strong broad band at ~3342 cm^{-1} is indicative of O-H stretching vibrations associated with hydroxyl groups involved in hydrogen bonds. The band at ~2900 cm^{-1} corresponds to C-H vibrations of the methyl and methylene groups, however this is more appropriately referred to as a methyne C-H stretch. Furthermore, FTIR spectra obtained (Figure 4) showed that the AC produced had vibrations in the region around 1600 cm^{-1} indicating C=C stretch and C-O between 1000~1200 cm^{-1} which could indicate alcohols, ethers, carboxylic acid and esters [28].

SCB of weight 10 mg was used to run TGA. Non-isothermal condition was applied under nitrogen flow, starting from room temperature to 1000°C with a heating rate of 10°C/min. TGA curves of the decomposition of raw sugarcane bagasse indicated four regions of weight loss: attributed to loss of moisture (1), then effects of charring, probably explained as hemicellulose (2) and

cellulose (3) decomposition and then the breaking down of lignin content (4) [29] as seen in Figure 5.

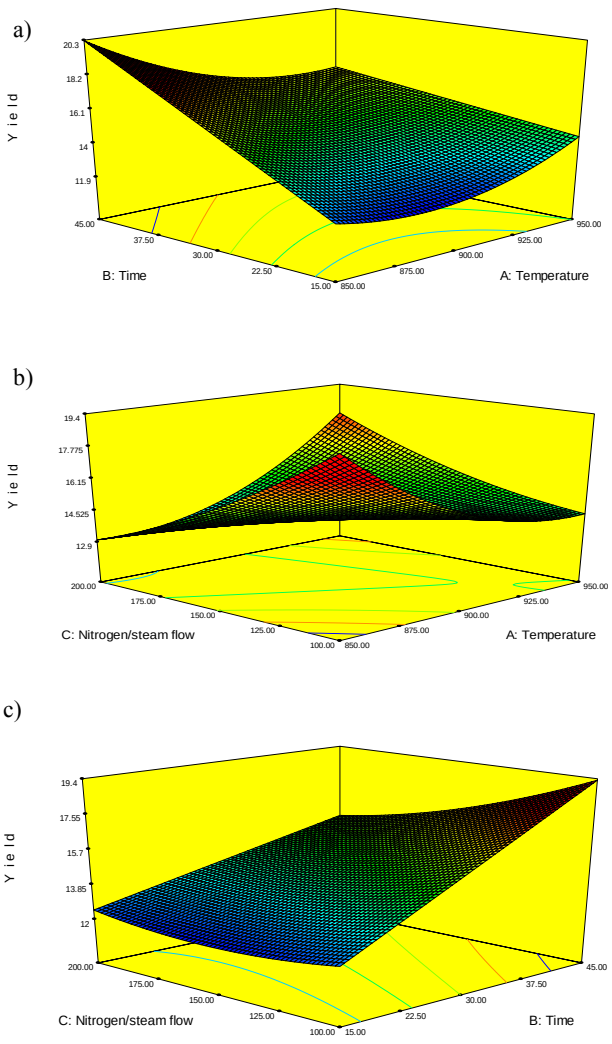


Figure 3 3D surface plots showing effects of production conditions on yield a) Temperature vs time effect, b) flow rate vs temperature effect c) flow rate vs time effect

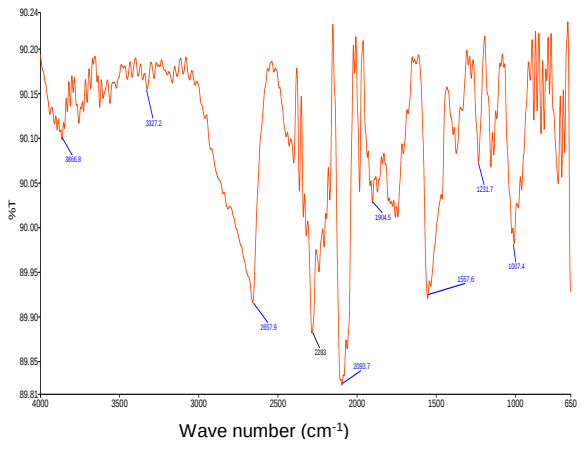


Figure 4 FTIR spectra of sugarcane bagasse activated carbon

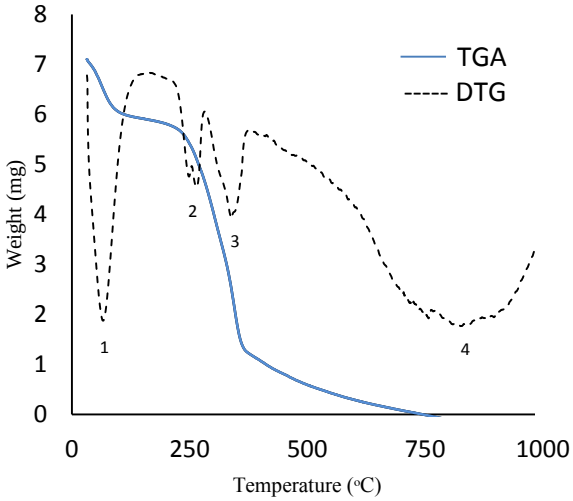


Figure 5 TGA thermogram of raw sugarcane bagasse

4.0 CONCLUSION

AC production from SCB was successfully carried out with the best performing sample produced at a temperature of 900°C, with nitrogen/steam flow of 100 mL/min and activation time of 30 minutes from 13 samples. A central composite design of response surface method was applied to clearly illustrate the effects and interaction of temperature, time and nitrogen/steam flowrate on the performance of AC produced in the removal of Cd^{2+}. It was found that N_2/steam flowrate had the most significant effect on production, followed by temperature and then time, with their interactions also making relevant contributions. A comparison between the predicted and experimental responses showed high correlation with coefficients (R^2) of 0.957 and 0.985 for removal and yield respectively, indicating the efficacy of the model. FTIR peaks revealed functional groups with active sites similar to commercial activated carbon and BET surface area was 287.23 m^2/g. It was also possible to achieve 62.42% removal of Cd^{2+} in this study. The application of a designed experiment using RSM was used to determine the most suitable production conditions within limited experimental runs.

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