Production of Sugarcane Bagasse Based Activated Carbon for Cd^{2+} Removal using Factorial Design

Musa Mutah, Kikuchi Akira, Abdul Majid Zaiton, Jaafar Jafariah, Salim Mohd Razman, Ismail Nor Eman

***Abstract* — An evaluation of the effect of preparation conditions on the production of activated carbon from sugarcane bagasse for Cd^{2+} removal was carried out using a 2-level full factorial design. Sugarcane bagasse based activated carbon was prepared in a single step steam pyrolysis using a horizontal tube furnace. The investigated parameters were temperature (700 - 800^{o}C), time (60 - 120 minutes) and steam flow rate (10 - 50 mL/min), within 11 experimental runs. Two responses were considered, the activated carbon yield and the removal % of Cd^{2+} from aqueous solution. The predicted results from the full factorial model were compared with the experimental values, with regression coefficients of R^2 = 0.986 for yield and R^2 = 0.989 for removal. Optimization was applied using desirability function with the selected optimum desirability of 0.592 for the set goals.**

***Keywords* — full factorial, activated carbon, cadmium, adsorption**

I. INTRODUCTION

In recent times wastewater containing toxic heavy metals is drawing the attention of health experts, due to the health impact on human being. The fact that even in trace quantity heavy metals have the ability to bio-accumulate in the body tissues to harmful levels is an issue of concern [1]. This has generated a lot of interest among researchers, considering the risk potential to a vast population of flora and fauna species, including humans through the food chain, thus the need to mitigate it. Heavy metals are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities [2], amongst them are essential elements like iron as well as toxic ones like cadmium, mercury, lead, copper, zinc, iron and arsenic [3]. There are various techniques being applied in the removal of heavy metals in water and wastewater, including microbial degradation, chemical oxidation, ion exchange, membrane filtration, chemical reduction electrodepositing, reverse osmosis and adsorption. Adsorption by activated carbon has high chemical and mechanical stability and high degree of surface reactivity, making it a method of choice in heavy metals removal. Extensive studies have shown that activated carbon has numerous applications viz; odor removal, removal of H_2S or CS_2, exhaust air cleaning, industrial wastewater, drinking water conditioning [4]. Activated carbon is a widely used adsorbent because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity [5]. It is possible to obtain high surface areas by physical or chemical activation, in some cases a combination may enhance the surface properties of the adsorbent, and increasing its adsorption capacity. This gives agricultural wastes and other precursors the possibility of effectively competing with the commercial activated carbon [6]. There are many ongoing studies on the development of low-cost adsorbents, many of which explore using waste materials for that purpose, and also several other works have reported a lot of work done on their application for the removal of various pollutants from aqueous and gaseous phases [6]. It is clear that both conventional and nonconventional wastes have been used to prepare activated carbon that can be applied within a wide range of treatment processes. Common among materials (precursors) from agricultural wastes that have used for activated carbon production are cherry stone, oil palm empty fruit bunch , corn cob, walnut shell, date pit, olive cake, orange peel, rice husk, sugarcane bagasse, cassava peel [4], [6]. In previous times most such agricultural waste end up being deposited in landfills, but the high cost associated with the use of commercial activated carbon, which is mostly coal based has led to search of alternative materials. This brought the rise in studies into the production of activated carbon from such wastes, creating wealth from waste and simultaneously using it to tackle environmental problems in waste and wastewater treatment. The potency of improving the quality and performance of activated carbon produced from agricultural wastes are highly increased by optimizing both the production and/or removal processes. In trying to study the effects of more than one factor on response in an experiment, the method of full factorial experiments is applied. In a full factorial experiment both of the coded levels (-1 and +1) are compared with each other and the effect of each of the factor levels on the response is then investigated according to the levels of other factors. If the number of levels and factors increases the experimental runs also highly increased. Applying factor planning it is possible to investigate the

Manuscript received March 01, 2012.

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effect of multiple variables simultaneously within a few number of runs [7].

The objective of this study was to find the best production conditions for making activated carbon from sugarcane bagasse using steam activation, with Cd^{2+} as target parameter. Cd^{2+} was selected as analyte because of its existence above the allowable limit of 0.01 mg/L in some Malaysian rivers [8], as well as for its toxicological effects [3], [9], [10], [11], [12] discussed among other heavy metals.

II. MATERIALS AND METHOD

A. Raw material and its preparation

Sugarcane bagasse was collected in plastic bags from stalls 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, until sample weight was constant. Samples were then stored in sealed bags for processing.

B. Production of activated carbon

The production process began with weighing 10 g of sugarcane bagasse samples earlier prepared and placing it in a sample holder. Physical activation was performed by carbonization using nitrogen gas followed by activation with steam at different temperatures, time duration and gas flow rates in order to produce the required activated carbon. Selection of production temperature was based on thermogravimetric analysis (TGA) of raw bagasse sample to determine stages of moisture and organic content loss, as well as reference to other work in this area [13]. The selected levels of the variables are shown in Table 1. A 2-level full factorial design (FFD) with three central points was selected for the optimization process, bringing the toatal number of runs for this experiment to 11. The sugarcane bagasse was carbonized and activated in a high temperature horizontal tube furnace (GHA 1200 Carbolite furnace, UK), with a length of 100cm, internal diameter of 4.6 cm and external diameter of 5 cm for the quartz tube. The tube was inserted inside the horizontal furnace and its two ends were sealed by the inlet and outlet enclosures made of silicon stoppers fitted with glass pipe connectors. The inlet enclosure was used for nitrogen gas supply with a switch valve that allows transfer to steam during activation. Two flow meters, one for nitrogen gas and the other for steam were fixed and connected to the system. Steam was generated in a three-neck flask placed in an oil bath containing silicon oil to generate steam at a temperature of 110°C. Nitrogen gas was flowed through the system at 300 mL/min for carbonization and regulated within the design space for activation as shown in Table 1, ranging between 10 and 50 mL/min and set at required temperatures (700 – 800°C) and continued for 60 – 120 minutes with the heat rate of the horizontal furnace set at 23°C/min. During the activation period nitrogen gas was used to flow steam. On completion of the activation run time, system temperature was set to 40°C and allowed to cool in an inert atmosphere under slow nitrogen flow. The activated carbons produced were taken out from the quartz tube, ground and sieved to size passing through 150 µm sieve. The samples were washed with UPW and 0.1 M HCl was used to adjust the slurry pH to ~7. The samples were then dried for 24 hours at 105°C and stored for further use.

C. Modeling by full factorial design

In the development of an activated carbon production process, three factors influencing the process viz; temperature, time and nitrogen/steam flow rate were studied. Experiments in which one factor at a time (1-FAT) is considered could be quite tedious and time consuming [14]. Thus, a factorial design can reduce this inconvenience by optimizing several parameters collectively [15].

The experiment is divide into three phases; the design, the analysis and the optimization. The effect of each factor on response is measured as the same time considering the interaction at different levels of other factors, thus revealing an in depth information via use of Design Expert® 7.1.6 software from Stat Ease Inc.

Factorial design is a technique where precision is taken in estimating interactions of different factors and the overall effect of major factors. In full factorial design a combination of every setting of every factor is also matched with every setting of every other factor, thus making it good in assessing treatment variations. The basic experimental design is to input all factors at two-levels, called 'high' and 'low' in actual terms or represented by the coded levels of '+1' and '−1'. For any experiment with k number of factors each at two-levels, a full factorial design will have 2^k runs. This study used a three factors full factorial design with 11 runs to model the sugarcane bagasse activated carbon production process. Two responses were targeted yield and removal both expressed in percentages. The yield was determined as follows;

$$\text{Yield (\%)} = \frac{\text{Weight of produced activated carbon}}{\text{Initial weight of sugarcane bagasse}} \times 100 \quad (1)$$

D. Adsorption test

The adsorption of Cd^{2+} by the sugarcane bagasse activated carbon that was produced in 11 different runs was carried out for various contact times from 1 to 120 minutes, which range was selected based on trial tests. 0.05 g of 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 of the adsorbent in the mixture. The mixture was then placed on a mechanical shaker at an agitation speed for 120 rpm for the desired time. After the shaking time elapsed, samples were taken from the flasks and filtered through 0.45 µm syringe filter before being taken for analysis of residual Cd^{2+} content.

Table I: Experimental factors and their levels (actual and coded) for full factorial design (FFD) runs

Temperature (°C)	Time (mins)	N_2/Steam flow (mL/min)

700 (-1)	60 (-1)	10 (-1)
750 (0)	90 (0)	30 (0)
800 (+1)	120 (+1)	50 (+1)

The percentage removal (R%) is defined as the ratio of difference in metal concentration before and after adsorption ($C_i - C_e$) to the initial concentration of Cd^{2+} in the aqueous solution (C_i) [16], which was calculated using equation (2).

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

III. RESULTS AND DISCUSSION

A. Experimental design and regression modeling

The three parameters studied in the experiment were A – Temperature, B – Time and C – Flow rate considering their effect on the produced activated carbon when applied for the removal of Cd^{2+} from aqueous solution. The design matrix as well as predicted and experimental responses are given in Table 2. The results were analyzed using Design Expert® 7.1.6 software and along with the main effects the interactions of different factors were determined. The mathematical regression model for the 11 runs factorial design is given as:

$$R\,(\%) = 41.84 - 1.34A + 0.44B - 2.86C - 0.84AB - 3.74AC + 1.09BC \quad (3)$$

where R (%) is the percentage removal of Cd^{2+}

$$Y\,(\%) = 15.79 - 1.09A - 0.34C - 0.16AC \quad (4)$$

B. Analysis of variance (ANOVA)

This process gives further insight into adequacy of a model in navigating the design space. The change in level of a factor leads to a change in its response which is referred to as its effect. The main effects are from the primary factors of interest in an experiment, temperature, time and flow rate all contributed significantly to the performance of activated carbon produced. ANOVA includes Fisher's F-test of model significance, probability $p(F)$ and coefficient of determination R^2 [17]. Furthermore, the estimation of Student's t-value for the estimated coefficients and the associated probabilities $p(t)$ included. For removal, a model F-value of 39.32 implied the model was significant, Prob>F less than 0.05 indicates the model terms significance and in this case A, C, AC and BC were significant model terms with an insignificant Lack of Fit F-value of 0.047. For the yield model F-value was 139.59 also indicating good significance with A, C and AC being significant model terms, and an insignificant Lack of Fit F-value of 1.12 which gives a good overall model and prediction.

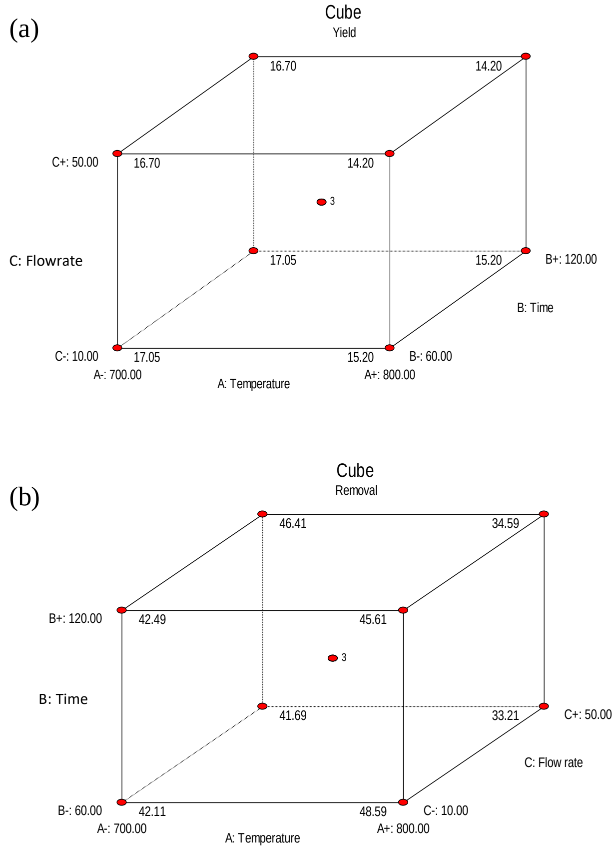

Fig. 1: Cubic full factorial design model for Temperature, Time and Flowrate (a) Yield (b) Removal.

Table II: Full factorial design matrix with predicted and actual responses

Factor 1	**Factor 2**	**Factor 3**	**Response 1**		**Response 2**	
Temperature	Time	C:Steam flow	Removal (Actual)	Removal (Predicted)	Yield (Actual)	Yield (Predicted)
°C	Mins	mL/min	%	%	%	%
700	60	10	42.2	42.1	17.2	17.05
800	60	10	48.5	48.6	15.1	15.2
700	120	10	42.4	42.5	16.9	17.05
800	120	10	45.7	45.6	15.3	15.2
700	60	50	41.6	41.7	16.8	16.7
800	60	50	33.3	33.2	14.3	14.2
700	120	50	46.5	46.4	16.6	16.7
800	120	50	34.5	34.6	14.1	14.2
750	90	30	39.1	40.0	15.7	15.7

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750	90	30	41.3	40.0	15.5	15.7
750	90	30	39.7	40.0	15.8	15.7

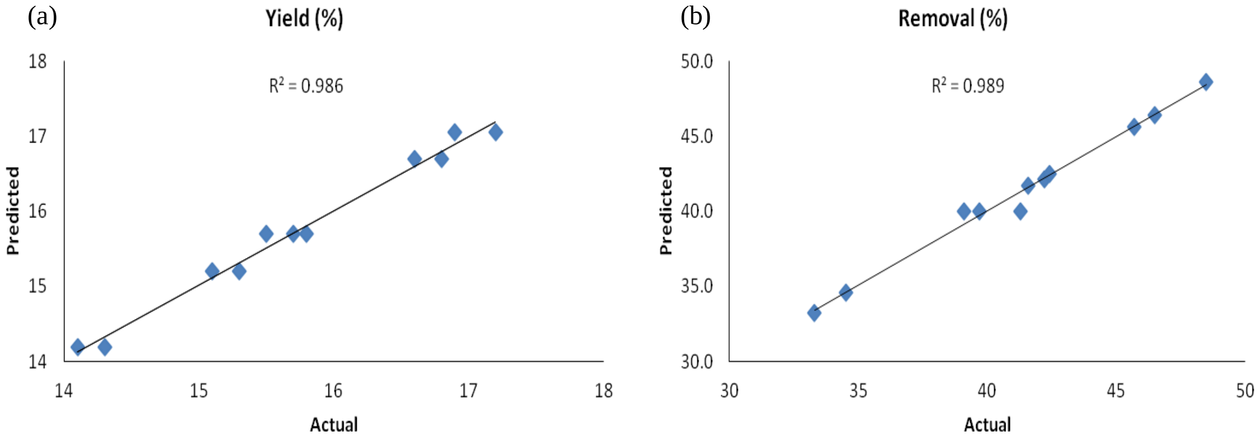

Fig. 1: Predicted vs experimental values for (a) activated carbon yield (b) Cd^{2+} removal

C. Optimization

The desirability (D) function was applied to optimize different combinations of production parameters of temperature, time and steam flow rate, targeting two responses activated carbon yield and removal of Cd^{2+}. This function condenses factor effects into one overall desirability through a specific set of goals. The goals considered to achieve maximum desirability were set by ranging temperature between 700 - 800°C, minimizing the run time and minimizing the flow rate. The goal was to maximize both responses of yield and removal. The desirability for any given set of responses range between 0 – 1 (0 indicating the least desired result and 1 the most desired). In this experiment desirability for the two responses was 0.592 indicating that the goals set were used to achieve a satisfactory result, making reasonable compromise towards getting desired response. Fig. 3 shows the graphical desirability for this experiment.

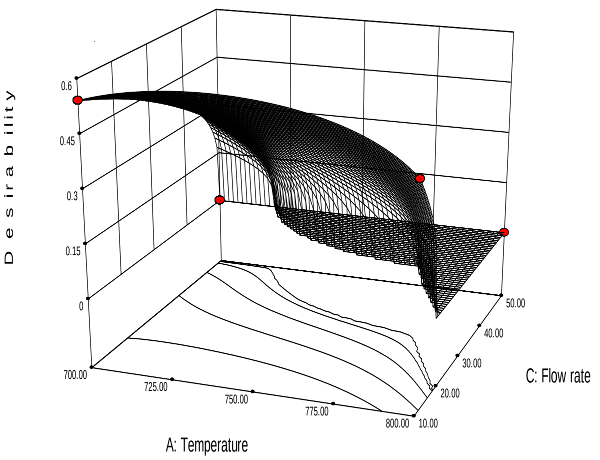

Fig. 3: Wire frame view of 3D desirability graph of combined responses; yield and removal.

IV. CONCLUSION

A full factorial design was applied to a production process for sugarcane bagasse based activated carbon production revealing the interaction of production parameters. Analysis of variance (ANOVA) was successfully used in modeling the experiment, while desirability (D) function was used to optimize the responses within a set range of goals. The use of Design Expert was well illustrated in a production process optimization within a limited number of experimental runs.

ACKNOWLEDGMENT

The authors will like to appreciate the Ministry of Higher Education (MOHE) Malaysia, Ministry of Science, Technology and Innovation (MOSTI) Malaysia and the Universiti Teknologi Malaysia for supporting this study with grants ERGS (4L015), GUP (01H58) and TECHNOFUND (4H008).

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