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RESEARCH ARTICLE

PHYSICOCHEMICAL ACTIVATION OF OIL PALM SHELLS USING RESPONSE SURFACE METHODOLOGY: OPTIMIZATION OF ACTIVATED CARBONS PREPARATION

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ABSTRACT

The preparation of activated carbons derived from oil palm shells, chemically activated by potassium hydroxide and physically activated by steam was investigated in this paper. The Methodology of Experimental Design (MED) was used to optimize the preparation conditions. The effects of two preparation variables: the activation temperature ranging from 601 to 799°C and the impregnation ratio ranging from 0.6 to 3.4 were studied on the activated carbon yield (R/AC-KOH), the iodine adsorption capacities (I_2/AC-KOH) and methylene blue adsorption capacities (MB/AC-KOH) results. The experimental results from the analysis of variance (ANOVA) permits to identified the significant factors on each experimental design response. The optimum conditions for activated carbons physicocshemically activated by KOH and steam (AC-KOH) were activation temperature of 630°C, and impregnation ratio of 1/1 which lead to the activated carbon yield of 38.71%, I_2/AC-KOH of 803.72 mg/g and MB/AC-KOH of 457.36 mg/g. The morphologies of the raw material and activated carbon obtained under optimum conditions were visualized using Scanning Electron Microscopy.

INTRODUCTION

The progressive increase of wastes is becoming a major environmental problem due to the growing use of industrials technologies. It is proof that, the wastes discharged are very difficult to be managed, since some of them are resistant to biodegradation. Many industries processing extract their main products and discharge large amount of wastes which cause serious ecological problems. Therefore, wastes pollution is remaining a major environmental problem. The ways of managing this kind of pollution, is for example to find or prepare new adsorbents, from various lignocellulosic materials or agricultural wastes such as coconut shell (Laine *et al*., 1989 ; Daud *et al.,* 2004; Ru-Ling Tseng *et al.,* 2007; Rosas *et al*., 2007; Azevedo *et al.*, 2007; Afrane *et al.,* 2008; Tan *et al.,* 2008(a); Tan *et al.,* 2008(b); Ioannidou *et al.,* 2010), dates or peach stones (Haimour *et al.,* 2006; Veksha *et al.,* 2009; Débora *et al.*, 2010)**,** corn cob (Narges Bagheri *et al.,* 2009, Yong Sun *et al.*, 2010)**,** rice straw (Kumagai *et al.,* 2007 ; Kalderis *et al.,* 2008), oil palm stones and shells (Lua *et al*., 2006; Guo *et al.,* 2007; Tan *et al.,* 2007; Allwar *et al.,* 2008). In fact, the manufacture of activated carbons is mainly to combat environmental pollution (Ahmad *et al.,* 2007; Donni Adinata *et al.,* 2007(a); Qipeng *et al.,* 2008; Tan *et al.,* 2008; Alcaniz-Monge *et al.,* 2009; Foo *et al.,* 2009; Qipeng *et al.,* 2009; Zahangir Alam *et al.,* 2009; Piotr Nowicki *et al.,* 2010; Sumathi *et al.,* 2010(a) Sumathi *et al.,* 2010(b)). Thus lignocellulosic materials are gaining more and more interest in manufacture of adsorbents. As interesting set of characteristics, including, a greater diversity, inexpensive cost, largely available, currently no economic value and physicochemical properties such as high density. This material also exhibits remarkable amount of carbon and low ash contents. In the present study, we prepared activated carbons from oil palm shells by physicochemical activation. Oil palm shells containing high carbonaceous materials are generated in large quantity as a major by-product of the oil palm milling industry. Oil palm shells are usually burned as a low-value energy resource or discarded in the field, both of which are unfavorable to the environment. It was reported earlier that, oil palm shells consisted of high amount of lignocellulosic materials with high carbonaceous materials are used as the precursor in the production of activated carbons. Thus, they should be possible to be pyrolysed to form a porous material that is suitable to be used as adsorbents (Tan *et al.,* 2004; Tan *et al.,* 2008; Tan *et al.,* 2009; Bakhtiar *et al.,* 2010; Arami-Niya *et al.,* 2011). In the literature, there are two methods to produce activated carbons, namely physical activation and chemical activation. Previous works on these methods of preparation had been reported. Their advantages are simplicity, a short production time, lower temperature of activation and good development of the porous structure, thus a higher yield (Donni Adinata *et al.,* 2007(b); Ahmadpour *et al.,* 1996).

Particularly in the chemical activation process, the carbonization and the activation steps proceed simultaneously by carrying out thermal decomposition of the raw material impregnated with certain chemical agent such as phosphoric acid (Hayashi *et al.,* 2000; Haimour *et al.,* 2006; Rosas *et al.,* 2007; Solange *et al.,* 2010), potassium hydroxide (Ahmadpour *et al.,*1996; Yang *et al.,* 2004; Fierro *et al.,* 2006; Baocheng Jiang *et al.,* 2008; Abdel-Nasser A. El-Hendawy, 2009; Carrott *et al.,* 2010; Feng-Chin Wu *et al.,* 2010) or zinc chloride (Chen *et al.,* 2002; Qingrong Qian *et al.,* 2007; Zhaolian Zhu *et al.,* 2007; Sait Yorgun *et al.,* 2009; Suat Uçar *et al.,* 2009) in an inert atmosphere. These impregnate are used as dehydrating agents and oxidants that influence pyrolytic decomposition and inhibit formation of tar, thus enhancing the yield of carbon (Solange *et al.,* 2010). The quality of activated carbons obtained depends mainly of the precursor used and the preparation conditions. The factors like, the

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impregnation ratio, the activation time and temperature, the carbonization time and temperature, activators used, and particles sizes interact between them. In many studies, one factor is fixed at a certain level, varying another to determine the best condition. This procedure has disadvantages such as: the lack of research on the interactive effects on the factors studied, and the large number of experiments required, which consequently require more time with a higher cost and consumption of reagents (Bezerra *et al.*,2008). The comprehension of these interactions between factors is essential in determining the characteristics of prepared activated carbons (Derbyshire *et al.,* 1971; Matson *et al.*, 1971; Hassler Wiley, 1974; Suarez-Garcia *et al.,* 2002(a); Suarez-Garcia, 2002(b)). And it is also a useful tool to optimize the preparation conditions. The aim of this paper is to explore the effect of these factors cited up on the preparation conditions of the activated carbon by physicochemical activation in order to optimize them, by using the Methodology of Experimental Design. This method consists of diverse mathematical models and statistical techniques based on the adjustment of equations models to the experiment data to describe the behavior of the independent variables (Bezerra *et al.,* 2008). In recent years, some authors have applied this optimization method to the production of activated carbons (Baçaoui *et al.,* 2002; Hameed *et al.,* 2008; Hameed *et al.,* 2009; Sumathi *et al.,* 2009; Hui Deng *et al.,* 2010; Kunquan Li *et al.,* 2010; Vargas *et al.,* 2010). Rare were the studies using oil palm shells chemically activated with KOH, and physically activation with steam through The MED for optimization.

MATERIALS AND METHODS

Sample collection and preparation of activated carbon

The raw material for the preparation of activated carbon was the oil palm shells collected from an oil palm mill company Socaplam in the locality of Bongo-Cameroon. The oil palm shells was washed several times using tap water and finally with distilled water to reduce oil impurities and then dried in the oven at 110°C to remove excess water, until constant weight. The dried oil palm shells samples were grinded in a porcelain mortar and sieved to a particle size of 1.0 –2.0 mm and stored at room temperature for further used.

Experimental methods

The oil palm shells with particle size of 1.0 – 2.0 mm, was first carbonized in a furnace at 800°C for 1 hour with the nitrogen flow rate of 100mL/min and maintained until the cooling of the furnace. After carbonization process, an exact amount of the carbonized material obtained was weighed and added into beakers containing a saturated solution of potassium hydroxide at the ratio desired. Each mixture was mixed throughout 02 hours at 60°C, and then was dried at 120°C overnight for complete evaporation of water. The reactor was loaded with 10g of impregnated sample and then placed into the graphite furnace. The furnace was raised at the pre-determined activation temperatures desired from 601 to 799^{o}C. It was held at this temperature for a period of 02 hours under steam activation, at a constant flow rate of 0.1 mL/ min. After cooling to the ambient temperature, the samples were washed with 0.1N hydrochloric acid, then with distilled water for several times. The washing process was done until the absence of chloride ions in the washing water such as its pH ranged 6 –7 (Moreno-Castilla *et al.,* 2001), and then dried in the oven at 110^{o}C for 24 hours. The weight lost was obtained from the weight before and after pyrolysis to calculate the yield. The samples obtained were crushed into powder form and kept well for further tests.

Methodology of Experimental Design

The methodology of experimental Design is a statistical technique for modeling and analysis of problems in which a response of interest is influenced by several factors (Baçaoui *et al.,* 2001) The MED is utilized to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interactions between the parameters (Azargohar *et al.,* 2005). The two parameters investigated in the present study were coded as the activation temperature(X_1) and the impregnation ratio (X_2). The experimental design matrix of 12 experiments and results are given in the table 1 below. Each row represents an experimental run, and each column represents the variables tested. The three responses analyzed were the activated carbons yield, (Y_1), the iodine and methylene blue adsorption capacities of activated carbons impregnated with KOH noted respectively by: R/AC-KOH (Y_1), I_2/AC-KOH (Y_2) and MB/AC-KOH (Y_3). Each response was used to develop a model which correlates the responses to the two variables using a polynomial equation given by the following equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_1X_1X_1 + b_2X_2X_2 + b_{12}X_1X_2 \quad \text{…….. (1)}$$

Where Y is the predicted response, b_0 a constant coefficient, b_i a linear coefficient; b_{ii}, a quadratic coefficient; b_{ij} an interaction coefficient, X_1 and X_2, the coded values of the activated carbons preparation variables. The experimental data were analyzed using a statistical software design expert named NEMROD, for regression analysis to fit the equations developed and also to evaluate the statistical significance of the equations obtained.

Activated carbons yield: R/AC-KOH (Y1)

The activated carbons yield was calculated using the following formula:

$$\text{Yield (\%)} = \frac{\quad}{\quad} \times 100 \quad \text{…….. (2)}$$

Where m and m_0 are the dry weight of final activated carbon (g) and dry weight of precursor (g), respectively.

Iodine adsorption capacity of the activated carbons: I_2/AC-KOH (Y2)

Iodine was considered as probe molecule for assessing the adsorption capacity of adsorbent for solutes of molecular sizes <10 Å. The iodine number is defined as the milligrams of iodine adsorbed by 1g of carbon. The iodine adsorption was determined using the sodium thiosulfate volumetric method (ASTM D4607-94, 2006). The iodine number was estimated by mixing the activated carbon with 0.02 N iodine solution shaken occasionally and then by titration of the solution against $Na_2S_2O_3$.

Methylene blue adsorption capacity of the activated carbons: MB/AC-KOH (Y3)

Methylene blue was considered as probe molecule for assessing the adsorption capacity of adsorbent for solutes of molecular sizes >15A°. The methylene blue number is the milligrams of methylene blue adsorbed by 1g of carbon (Hassler, 1974). The concentration of methylene blue was measured by using a beam UV–visible spectrophotometer Anthelie data at the maximum absorbance wavelength of 660 nm.

The iodine and methylene blue numbers Cads (mg/g) were calculated using the following formula:

$$\text{Cads} = \frac{(\quad)}{\quad} \quad \text{…….. (3)}$$

Where C_0 and Ce (mg/L) are the liquid-phase concentrations of iodine at initial and at equilibrium, respectively. V is the volume of the solution (L) and m is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

Responses analysis and interpretation

The experiments at the center point of the complete design matrix (experiments n°9 to 12) were used to determine the experimental error and to verify the reproducibility of experimental data. The activated carbon yield obtained ranged from 3.64 to 31.40%, the adsorption

Table 1. Experimental Design Matrix and the Corresponding Experimental Responses

N° Exp	X1	X2	Y1 (%)	Y2 (mg/g)	Y3(mg/g)
1	-1.0000	-1.0000	31.40	634.0	418.00
2	1.0000	-1.0000	8.40	476.0	325.00
3	-1.0000	1.0000	23.51	444.0	233.00
4	1.0000	1.0000	9.70	475.5	259.00
5	-1.4142	0.0000	25.90	466.0	215.00
6	1.4142	0.0000	17.40	412.5	237.00
7	0.0000	-1.4142	22.00	729.0	400.00
8	0.0000	1.4142	3.64	540.0	331.00
9	0.0000	0.0000	11.34	450.0	279.00
10	0.0000	0.0000	11.59	444.0	288.00
11	0.0000	0.0000	10.09	444.0	300.00
12	0.0000	0.0000	11.00	444.0	295.00

X_1 = coded value of the activation temperature
X_2 = coded value of the impregnation ratio
Y_1 = activated carbons yield, R/AC-KOH
Y_2 = iodine adsorption capacities, I_2/AC-KOH
Y_3 = methylene blue adsorption capacities, MB/AC-KOH

capacities of I_2/AC-KOH from 412.5 to 729mg/g and the adsorption capacities of MB/AC-KOH ranged from 215 to 418mg/g. The yield and the adsorption capacity of methylene blue of highest values were obtained at 630°C and a ratio of 1/1(experiment 1). However, their lowest values were obtained at 700°C with a higher ratio of 3.4 for the yield(experiment 8) and a lowest temperature of 601°C with a ratio of 2/1 for methylene blue adsorption (experiment 5). Whereas for iodine adsorption, the highest value of 729mg/g was obtained at 700°C corresponding with the lowest ratio of 0.6 (experiment 7). The lowest value of 412.5 mg/g was obtained at the highest temperature of 799°C with a ratio of 2/1 (experiment9). The polynomial model equations in terms of coded factors are given as:

$$Y_1 = 11.005 - 6.104\ X_1 - 4.069\ X_2 + 5.577X_1X_1 + 1.162X_2X_2 + 2.297X_1X_2 \quad \text{…..(4)}$$

$$Y_2 = 445.5 - 25.27\ X_1 - 57.22\ X_2 - 10.5X_1X_1 + 87.13X_2X_2 + 47.38X_1X_2 \quad \text{…….(5)}$$

$$Y_3 = 290.5 - 6.104\ X_1 - 43.573\ X_2 - 29.001X_1X_1 + 40.751X_2X_2 + 29.75X_1X_2 \quad \text{……(6)}$$

A positive sign in front of the coefficients indicates synergistic effects, whereas negative sign indicates antagonistic effects. So, we can see that, for all the three responses, the effects of the two variables (activation temperature and impregnation ratio) were antagonistic on the three responses. So, the increase of any of these factors should result in the reduction of responses studied. From the ANOVA, the suitability of a model equation is evaluated using the correlation coefficients R^2.The proximity of R^2 value to unity, indicated the suitability of the model equation. The R^2 values were 0.837, 0.971 and 0.891 for Y_1, Y_2 and Y_3 respectively. It indicated that 83.7%, 97.1% and 89.1% of the total variation in the activated carbon yield, adsorption capacities of iodine and methylene blue respectively were due to the experimental data analyzed. The R^2 value of 0.971 for Y2 was considered relatively high indicating that there was a good agreement between the experimental and predicted iodine adsorption capacity (I_2/AC-KOH) from the model. The R^2 values of 0.837 and 0.891 were considered as moderate to validate the fit, this can be attributed to larger variation in the activation carbon yield and methylene blue adsorption capacity (MB/AC-KOH) predicted from the model. The ANOVA for Y1 for activated carbon yield is listed in Table 2 below:

From the ANOVA of results obtained, the coefficients of the activation temperature (b_1 = -6.104), of the impregnation ratio (b_2 = -4.069) and of the quadratic term of the activation temperature (b_{11} = 5.577) were found to have significant effects on the activated carbons yield. The coefficient of the activation temperature imposing the greater effect on activated carbons prepared. The coefficient of the interaction term (b_{12} =2.297) was considered moderated, however the coefficient of the quadratic term of the impregnation ratio (b_{22} = 1.162) imposed the least effect on the yield. The ANOVA revealed that, the coefficients of the quadratic term of the impregnation ratio (b_{22} =87.13), of the impregnation ratio (b_2 =-57.22) and of the interaction term (b_{12} =47.38) were found to have significant effects on the iodine number. The coefficient of the quadratic term of the impregnation ratio imposing the greater effect on the iodine number. The coefficients of the activation temperature (b_1 = -25.27) and its quadratic term (b_{11} =-10.50) were considered moderated, with the coefficient of the quadratic term of the activation

Table 2. Analysis of variance of the activated carbon yield, R/AC-KOH (Y_1)

Source of variation	Sum of squares	Degree of freedom	square mean	Rapport	Signif
Regression	650.7137	5	130.1427	302.2592	0.0305 ***
Residual	127.0977	6	21.1829		
Validity	125.8060	3	41.9353	97.3957	0.156 **
Error	1.2917	3	0.4306		
Total	777.8114	11			

Table 3. Statistical Estimations of coefficients: R/AC-KOH(Y_1)

Name	Coefficient	F.Inflation	Ecart-Type	t.exp.	Signif. %
b_0	11.005		0.328	33.54	< 0.01 ***
b_1	-6.104	1.00	0.232	-26.31	< 0.01 ***
b_2	-4.069	1.00	0.232	-17.54	0.0253 ***
b_{11}	5.577	1.04	0.259	21.50	0.0141 ***
b_{22}	1.162	1.04	0.259	4.48	1.91 *
b_{12}	2.297	1.00	0.328	7.00	0.479 **

Table 4. Analysis of variance of iodine adsorption, I_2/AC-KOH (Y2)

Source of variation	Sum of square	Degree of freedom	square mean	Rapport	Signif
Regression	9.406E+0004	5	1.881E+0004	39.9158	0.0361 ***
Residual	2.827E+0003	6	4.713E+0002		
Total	9.688E+0004	11			

Table 5. Statistical Estimations of coefficients: I_2/AC-H_3PO_4 (Y_2)

Name	Coefficient	F.Inflation	Ecart-Type	t.exp.	Signif. %
b_0	445.50		10.85	41.04	< 0.01 ***
b_1	-25.27	1.00	7.68	-3.29	1.66 *
b_2	-57.22	1.00	7.68	-7.46	0.0451 ***
b_{11}	-10.50	1.04	8.58	-1.22	26.7
b_{22}	87.13	1.04	8.58	10.15	0.0121 ***
b_{12}	47.38	1.00	10.85	4.36	0.505 **

Table 6. Analysis of variance of methylene blue adsorption, MB/AC-KOH (Y_3)

Source of variation	Sum of squares	Degree of freedom	Square mean	Rapport	Signif
Regression	3.8718E+0004	5	7.7436E+0003	93.2971	0.166 **
Residual	4.7327E+0003	6	7.8872E+0002		
Validity	4.4837E+0003	3	1.4944E+0003	18.0055	2.00 *
Error	2.4900E+0002	3	8.3000E+0001		
Total	4.34507E+0004	11			

Table 7. Statistical Estimations of coefficients: MB/AC-H_3PO_4 (Y_3)

Name	Coefficient	F.Inflation	Ecart-Type	t.exp.	Signif. %
b_0	290.500		4.555	63.77	< 0.01 ***
b_1	-4.486	1.00	3.221	-1.39	25.8
b_2	-43.573	1.00	3.221	-13.53	0.0561 ***
b_{11}	-29.001	1.04	3.601	-8.05	0.304 **
b_{22}	40.751	1.04	3.601	11.32	0.0995 ***
b_{12}	29.750	1.00	4.555	6.53	0.600 **

temperature imposing the least effect on the iodine number. The ANOVA for MB/AC-KOH (Y3) is listed in the following Table 6: Based on the ANOVA, the coefficients of the impregnation ratio (b_2 =-43.573) and its quadratic term (b_{22} = 40.751) were found to have significant effects on the BM/AC-KOH. The coefficient of the impregnation ratio revealed to impose the greatest effect on activated carbons prepared. The coefficients of the quadratic term of activation temperature (b_{11} =-29.001) and of the interaction term (b_{12} = 29.750) were found to have same and opposite values which were found to have moderated effect. Whereas the coefficient of the activation temperature (b_1 =-4.486) have the least effect on the BM/AC-KOH.

Activated carbon Yield: R/AC-KOH (Y_1)

The Figures 1 below presented the two and three dimensional responses surface constructed to show the most important variable on the response Y_1.

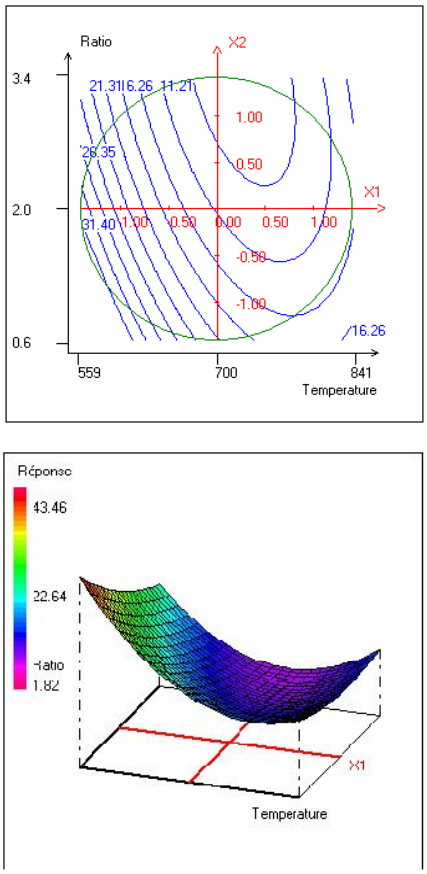

Figure 1. Variation of the activated carbon yield (Y_1) in the plan Temperature-Ratio

The analysis of the Figures 1 above showed that, the activated carbon yield was found to decrease from 31.40 to 11.21% when the activation temperature increased from 559 to 841°C. This was expected because, the increase in activation temperature would involved the release of volatiles compounds as the result of intensifying dehydration and elimination reactions as well as increasing the C-KOH reaction rate, thus the decrease in activated carbons yield (Yang and Lua, 2003; Lua and Yang, 2004; Donni Adinata *et al.*, 2007(b)). The yield was also affected by the impregnation ratio. We noticed that, when the ratio increased from 0.6 to the values up to 2/1, the yield also decreased from 31.40 to 11.21%. The increase of the impregnation ratio decreased the yield and increased the burn-off of oil palm shells. Donni Adinata et al., have observed the same trend with activation of palm shells with K_2CO_3 (Donni Adinata *et al.*, 2007(b)). This same observation was carried out by Sudaryanto et al. (Sudaryanto *et al.*, 2006) which reported that the pore structure of activated carbon produced from cassava peel, changed significantly with the activation temperature and also with the KOH impregnation ratio. We also saw that, for higher ratio and temperature up or equal to 700°C, the yield had very low values (experiments 4 and 8). It can be justify by the fact that, at higher impregnation ratio, the movement of volatiles compounds towards the pores is facilitated. Juan Yang et al. (Juan Yang *et al.*, 2010) observed the similar effect with the walnut shells. The ANOVA above shown that, the activation temperature had an antagonistic effect on the yield. Juan Yang et al. (Juan Yang *et al.*, 2010) also revealed that, the activation temperature had a negative influence on the yield of activated carbons from walnut shells. This can be owing to the fact that, when the activation temperature increased, it intensified the gasification reactions of carbon which liberate the entrances of the pores blocked by amorphous components, thus the decrease in the activated carbons yield (Baçaoui *et al.*, 2001). Both, increasing activation temperature and impregnation ratio conducted to increase the carbon burn off, this weight loss were attributed to huge elimination reactions (Donni Adinata *et al.*, 2007 (b)), which affected significantly our materials and reduced the yield.

Iodine adsorption capacities: I_2 /AC-KOH (Y2)

The Figures 2 below presented the two and three dimensional responses surface constructed to show the most important variable on the response Y_2.'

The quality of our activated carbon, AC-KOH, was examined in terms of his iodine adsorption capacity, which is related to the surface area available for adsorption. From the analysis of our graphs above, we found that, the iodine adsorption on AC-KOH decreased from 613.9 to 441.3mg/g when the impregnation ratio increased from 1/1 to 3/1. This implies that the impregnation of the raw materials with KOH affected the adsorption characteristics of the oil palm shell based activated carbons. It can be attributed to the increased in potassium ion provide to the sample during impregnation process. Achaw and Osei-Wu have observed the same trend with the coconut shell based

activated carbons (Afrane *et al.*, 2008). It was noticed that, for the lowest values of the impregnation ratio (0.6 and 1/1), their adsorption capacities of iodine were found to be have the higher values (experiments 1 and 7). The high impregnation ratio seems to high occupation of the pores sites by potassium ion, hence reduced adsorption of the iodine molecules, used to measure adsorptive capacity of the activated carbon materials. This observation was consistent with the work done by Afrane (Afrane et al., 2008). We also had known from recent work that, the impregnation with KOH, permit the intercalation of potassium ion within the materials network. Since potassium is the most dominant mineral in the sample, its influence will be to overshadow the free sites and therefore reduce the surface area, thus decrease the iodine adsorption. Achaw revealed that there was a definite relationship between the iodine adsorption characteristics of activated carbons and the levels of potassium in the sample. Consequently, samples with lower impregnation ratio recorded higher iodine adsorption capacities (Afrane et al., 2008). From the polynomial equation (Y_2) above, we saw that, the activation temperature and the impregnation ratio have antagonistic effects on the iodine adsorption.

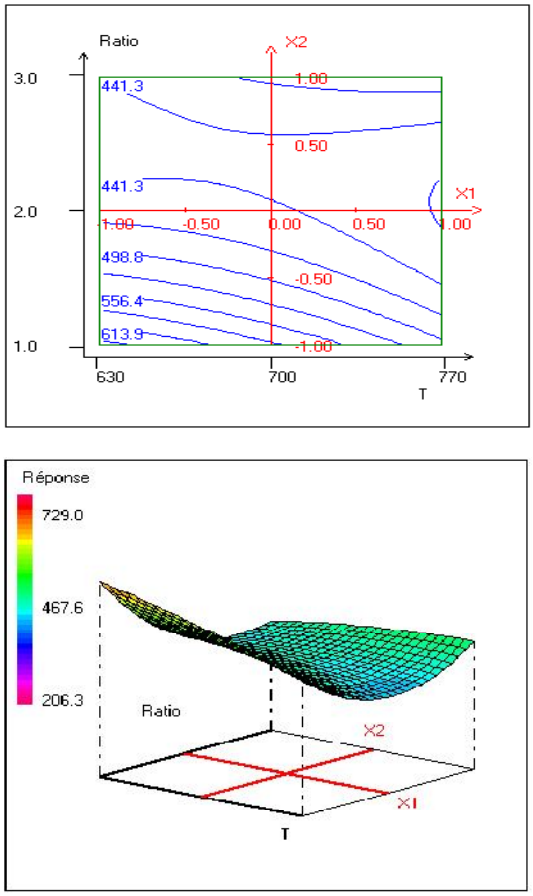

Figure 2. Variation of the iodine adsorption, I_2/AC-KOH (Y_2) in the plan Temperature-Ratio

This can be attributed to the fact that, as well as the activation temperature increased, the devolatization rate and the decomposition of the materials increased, thus the specific surface area decreased and consequently, the iodine adsorption decreased. Currently, a higher iodine adsorption indicated a higher surface area and also a largely micro and mesopores structure (Gergova *et al.*, 1993). In the present work, the increased length of activation temperature probably caused a decrease in the microporous volume, thus the decreased of the iodine adsorption. This might be due to the conversion of micropores to mesopores or macropores. In the adsorption procedure, we know that, macropores are used as access ways to micropores, where the effective adsorption took place. Chemical activation with KOH, the influence of the activation temperature and the impregnation ratio used to modify the structure of the sample and this had been observed by many authors (Baocheng Jiang *et al.*, 2008). Activated carbons that can remove a high quantity of iodine normally have a high surface area and subsequently a microporous structure. The iodine adsorption by an activated carbon is an indicative of its ability to adsorb low-molecular weight compounds. So, we can suppose that, there was a widening of micropores to meso and macropores, to justify the decreased in iodine adsorption with an increased in the activation temperature.

Methylene blue adsorption capacities: MB/AC-KOH (Y_3)

Figures show the two and three dimensional response surface which were constructed to present the most important factors on the BM/AC-KOH

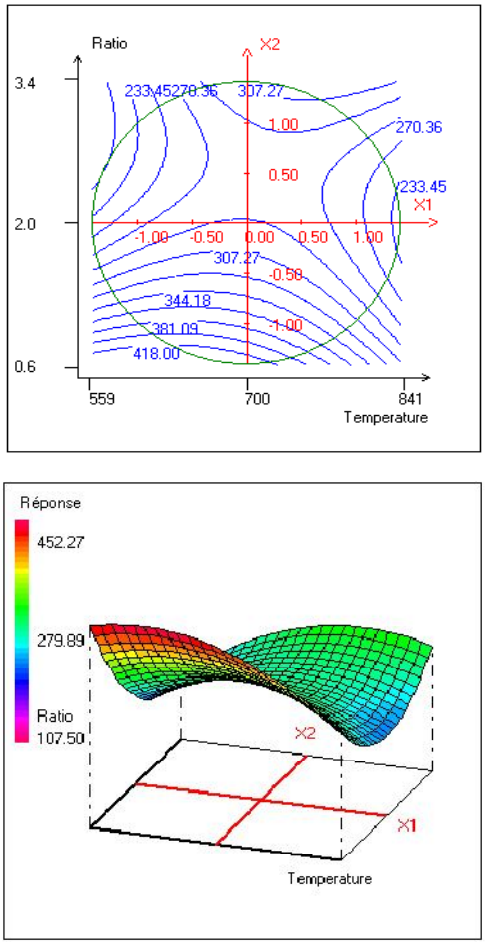

Figure 3. Variation of the methylene blue adsorption, MB/AC-KOH (Y_3) in the plan Temperature-Ratio.

The analysis of the curves above showed that, when the ratio varied from 0.6 to 2/1, the methylene blue adsorption decreased from 418 to 307 mg/g. Usually when a material is impregnated with a reagent, such as KOH, it penetrated inside the particle. So the presence of KOH in the interior of the precursor restricted the formation of tar as well as other liquids such as acetic acid and methanol by formation of cross-links, and inhibited the shrinkage of the precursor particle by occupying certain substantial volumes (Guo *et al.*, 2003). By so doing, it conducted to the intercalation of metallic potassium which appeared to be responsible for the drastic expansion of the carbon material and the creation of large surface area and high porosity, leading to the high BM adsorption (Zabaniotou *et al.*, 2008). Donni Adinata et al., also revealed it with K_2CO_3 activation (Donni Adinata *et al.*, 2007 (b)) and also Guo and Lua confirmed this observation (Guo *et al.*, 2003). The response Y_3 had shown well the negative effect of the impregnation ratio. This can be attributed to the excessive amount of KOH, which could cause further reaction between KOH and carbon, with the destruction of the micropore structure formed at previous

stage. The excessive KOH molecules might also be decomposed into water, causing the following gasification process under high temperature (Guo *et al*., 2003):

$2KOH \rightarrow K_2O + H_2O$ …….. (7)

Currently, the activation with steam water favourised the reaction between C-H_2O:

$H_2O + C \rightarrow CO + H_2$ …… (8)

It conducted to the elimination of atoms of carbons and caused the burn off of the material, and consequently a decrease in BM/AC-KOH adsorption. Hakan Demiral et al. has observed the same trend with olive bagasse (Hakan Demiral *et al.,* 2011). Therefore, over gasification might occur with the detrimental effect of reducing the surface area and porosity, hence the reduction in BM adsorption of the activated carbons (Stavropoulos *et al.,* 2005). In this work all the two variables studied were found to have antagonistic effects on the methylene blue adsorption. As far as our knowledge in adsorption procedure, the macropores didn't participate in the adsorption properly. They served as access roads to the mesopores and micropores, which are more responsible of the adsorption capacity of an adsorbent. Adsorption capacity of activated carbon largely depend on the amount of micropores that are present in the activated carbon. Additionally, the chemical activation with KOH, improves the production of micropores, which seems to be block by the large molecules of MB, and limited the adsorption procedure, thus the decrease in the methylene blue adsorption.

Optimization

In the manufacture of commercial activated carbons, relatively high quantity and quality are expected. Therefore, in practical manufacture, a compromise should be made between the activated carbon yield and the adsorption performance of the product for economical viability. However, to optimize activated carbon yield, the iodine and the methylene blue adsorption capacities under the same condition is difficult because the interest region of factors is different. The activated carbon yield, the iodine adsorption and the methylene blue adsorption capacities varied differently. Therefore, in order to compromise between these three responses, the function of desirability was applied using the software NEMROD (New Efficient Methodology of Research using Optimal Design). In order to optimize the preparation conditions of activated carbon prepared from oil palm shells, the targeted criteria was set as maximum values for activated carbon yield (*Y*1), the iodine adsorption capacity (*Y*2) and the methylene blue adsorption capacity(Y3) while the values of the two variables (activation temperature and impregnation ratio) were set in the ranges being studied. The model which showed the highest desirability from the software NEMROD was selected to be verified. The predicted and experimental values for the three responses obtained were also presented. The optimal activated carbon was obtained using preparation condition of 630°C activation temperature and impregnation ratio of 1/1, which resulted in 38.78% of activated carbon yield 803.72 mg/g of I_2/AC-KOH and 457.36mg/g of MB/AC-KOH. It was observed that the experimental values obtained were in good agreement with the values predicted from the models. This indicated that the models developed were suitable and sufficient to predict the responses from the operating variables fixed. Through process optimization, oil palm shells activated with KOH and steam was proved to be a promising precursor for production of activated carbons with high carbon yield, iodine and methylene blue adsorption capacities.

Conclusion

The Methodology of Experimental Design was used to evaluate the effects of activation temperature and impregnation ratio on the yield, the iodine and methylene blue adsorption capacities of the activated carbons prepared. The adequacy of the polynomial model was effectively verified by the validation of experimental data. The process optimization was carried out and the experimental values obtained for the responses were found to agree satisfactory with the predicted values. Through analysis of the response surface, derived from the models, activation temperature, and impregnation ratio were found to have significant effects on the responses. The R^2 values of the responses showed a good fit of the models with experimental data. The activated carbon prepared under the optimum conditions were found to have well-developed pores on its surface according to their adsorption capacities of iodine and methylene blue. The activated carbons so prepared are potential adsorbent in the removal of pollutants in surface water.

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