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Obtención Y Caracterización De Carbón Activado Granular A Partir De Semilla De Nectarina

Tesis que, para completar los requisitos del

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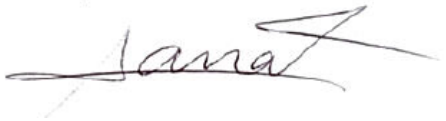

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OBTENTION AND CHARACTERIZATION OF GRANULAR ACTIVATED CARBON FROM NECTARINE SEED

OBTENCIÓN Y CARACTERIZACIÓN DE CARBÓN ACTIVADO GRANULAR A PARTIR DE SEMILLA DE NECTARINA

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Abstract:

Activated Carbon (AC) is an extensively used adsorbant in wastewater treatment for the removal or a wide range of pollutants. Activated Carbon can be obtained from different agricultural wastes that do not have a competitive second use, such as nectarines seeds, which are a byproduct in the jam production or the consumption of the fruit. Nectarine seeds were used as raw material to produce activated carbon through a physical and chemical activation using phosphoric acid (85%) as the activator agent and pyrolysis for the carbonization. Impregnation ratios of 1:1 and 2:1 Different impregnation ratios were used as well as, different maximum temperatures of 450°C and 550°C to test the adsorption capacity. Additionally, the generated activated carbon was characterized through the ASTM D3838-05 to determine the pH value and D4607-14 to determine the iodine number. Furthermore, isotherms of methylene blue were done to obtain the maximum adsorption capacity, fitting the data to Langmuir´s and Freundlich´s model and comparing the isotherm with the IUPAC classification. It was found that activated carbon with the higher impregnation ratio, R=1, and a temperature of 550°C was the most efficient, having an iodine number of 506.87 mg/g and reaching a maximum adsorption capacity of 71 mg/g with a correlation coefficient of R^2=0.73 with the Langmuir model.

Keywords: activated carbon, adsorption, *pyrolysis;* isotherm models, nectarine pit, methylene blue; *ASTM D3838-05; D4607-14*

Resumen:

El carbón activado es un adsorbente ampliamente utilizado en el tratamiento de aguas residuales para la remoción de diversos contaminantes. Se puede obtener de diferentes residuos agrícolas que no tienen un segundo uso competitivo, como las semillas de nectarinas que son un subproducto en la producción de mermelada o el consumo de la fruta. Semillas de nectarina se utilizaron como materia prima para producir carbón activado a través de una activación física y química usando ácido fosfórico (85%) como agente activador y pirólisis para el procedimiento de carbonización. Se utilizaron diferentes relaciones de impregnación, así como diferentes temperaturas máximas para probar la diferencia en la capacidad de adsorción. Además, el carbón activado generado se caracterizó a través de ASTM D3838-05 para determinar el valor de pH y D4607-14 para determinar el número de yodo. Así mismo, se realizaron isotermas de adsorción con azul de metileno para obtener la máxima capacidad de remoción, ajustando los datos con los modelos de Langmuir y Freundlich y comparando la isoterma con la clasificación IUPAC. Se encontró que el carbón activado con la relación de impregnación más alta, R = 1 a una temperatura de activación de 550°C era el más eficiente con un índice de yodo de 506.87 mg /g y alcanzando una capacidad de adsorción máxima de 71 mg / g con un coeficiente de correlación de R^2 = 0.73 en el modelo de Langmuir.

Palabras clave: carbón activado, adsorción, pirolisis, modelos de isotermas, semilla de nectarina, azul de metilo, *ASTM D3838-05; D4607-14*

1.Introduction

Adsorption, widely used for wastewater treatment, is a surface process in which a gas, liquid or dissolved solid substance bind to a solid surface [1]. Therefore, Adsorption technology is used for the removal of pollutants in wastewater [2]. An extensively used adsorbant in wastewater treatment is activated carbon (AC) due to its high adsorption capacity [3]. AC is a crude form of graphite with a non-polar structure which is able to adsorb non-polar organic substances or nonelectrolytes [1]. There are two methods for carbon activation: a) chemical activation, the impregnation of the raw material with an acid activating agent in an inert atmosphere while being heat treated; or b) physical activation, the carbonization of the material followed by steam activation. The method for preparing AC can be physical, chemical or chemical activation followed by physical activation. The activation method affects the AC pore volume and surface area functional characteristics [4]. Moreover, the carbonaceous content in the AC raw material, also influences the development of a high total pore volume and a large surface area. Granulate activated carbo (GAC) is a type of AC with particle size between 0.2 and 2 mm and is mainly used in liquid phase application [3],

The use of GAC facilitates an efficient adsorption process, however, the treatment with GAC expensive. An approach to make the process more efficient regenerating the processes but also the generation of low-cost GAC using different carbonaceous materials [5]. A viable alternative is to use agricultural waste that are a naturally abundant, renewable and cost effective [6]. Activated carbon can be obtained from residues that do not have a second use like coconut shell [1], oily sludge [2], rice straw [3], rice bran residues [4] or walnut shell [6].

Additionally, recent research has established that the lignocellulosic composition influences the solid yield of the GAC, specifically, the greater the lignin proportion, the higher the pore volume and the heterogeneity distribution of pores, because lignin is least reactive substance compared to hemicellulose and cellulose [7]. In this regard, peach stones have proven to be an appropriate lignocellulosic starting material for GAC with a high adsorption capacity when subjected to the right activation treatment [8].

Peach is a stone fruit with a hard-inner stone from the genus Prunus family [9]. Nectarine is a variety of peach; both share similar leaves and flowers, but vary in fruit size, firmness and shapes, including the stones shape [10]. Both fruits are also mainly used to produce juice and jams or consumed directly. However, the seeds are not consumed and represent the main a by-product of the juice and jam. In a production plant of juice and jam, approximately, 15 to 25 kg of seeds are disposed every month [9]. In Mexico, peach and nectarine production has been constantly around two thousand tons per year and still the demand is not covered, resulting in imports of the fruit at a significant price increment [11]. Therefore, valorizing the waste production for this agricultural activity is a viable option.

This work aims to study the adsorption capacity of nectarine stones (NS) since there are few related research, being the main focus peach from the genus Prunus. NS was activated through a combined

physical and chemical process, using activating temperatures of 450°C and 550°C and as activating agent H_3PO_4 with activation ratios R (mass ratio of activator to raw material) of 1:1 and 2:1. The effects of the quality of the GAC produced was tested through adsorption isotherms of methylene blue (MB) and a characterization of the GAC produced was made by determining the iodine number and the pH of the obtained samples.

2.Materials and methods

2.1. Nectarine Seed preparation

Nectarines were selected and the whole pulp was removed to use the center stone of the fruit, which was splitted and the inner seed was removed. The remaining stone was washed with abundant tap water to remove any pulp residual or dust for 10 minutes. The seeds were dried in an oven at a temperature of 110°C for 24 hours to eliminate humidity content.

2.2 Impregnation and activation

In 25 mL of distilled water, the activating agent, phosphoric acid (85%) was dissolved. The amount of acid used was determined by the R selected for each sample, with a mass ratio of activator to raw material of 2:1 and 1:1. The phosphoric acid solution was added to the dry and clean NS in a 250 mL covered flask. The flasks were stirred at 150 rpm while being heated at 85°C for 5 hours. After this, the excess liquid was eliminated, and the stones were dried in an oven at 110°C for 24 hours to eliminate humidity.

2.3 Pyrolysis

The dried NS were put in in a porcelain crucible into a furnace, to carbonize with a constant carbonization time of 3 hours and at two different maximum temperatures (mT) 450 and 550°C according to the samples. Heating and cooling ramps of 10°C/min were used. After the pyrolysis process, the samples were left to cool to 100°C and placed in a desiccator for storage.

2.4 Washing and packing

To remove the acid activator from the GAC, each sample was returned to their respective beakers. From each sample, 0.2 g of the activated material were placed in a 250 mL beaker with 25 mL of a previously prepared 0.1M solution of hydroxide Sodium (NaOH) for 30 mins at a stirring of 150 rpm. The material was then filtered twice by gravity using a Whatman-1 filter and 175 mL of distilled water were added to the beaker to wash the GAC. A final third rinse was done with 200 mL, following the same procedure. The value of pH from the last filtered solution was measured to reach a value near 7. If one wash was not enough to reach the desired pH value, another wash was done. After reaching the desired range of pH the AC was dried in an oven for 12 hours at 110°C to remove all humidity.

2.5. Granulometry

The desired mesh size of AC is 8x30 from 0.6 mm to 2.36 mm [12]. To achieve this size, each NS sample was crushed in a mortar. Additionally, each sample was classified using a tower of 8 sieves with mesh sizes from 8 to 30. The produced AC had to go through the first sieve and not through the last one. The AC was classified in percentage at each sieve and the maximum desire percentage at the last sieve was 10%. After this the AC produced could be classified as granular activated carbon (GAC).

2.6 Experimental design

With the objective of evaluating the efficiency of adsorption of the GAC obtained, the resulting material was characterized and tested for contaminant removal efficiency. The characterization was tested according to ASTM D3838-05 to determine the pH number [13] and D4607-14 to determine the iodine number [14]. Additionally, the test to remove contaminants was made with methylene blue (MB); altering the GAC yield by changing two variables, (mT) and (R).

2.7 Adsorption Isotherm determination

A solution of 25 ppm of MB was prepared and mixed with different masses of GAC (10, 20, 30, 40 and 50 mg). Each sample was mixed with 100 ml of a 25 ppm of MB solution in a 250 mL Erlenmeyer flask, which was covered and wrapped with aluminum to avoid photodegradation of the sample. The dynamic equilibrium of the adsorption process for the concentrations used was reached at 72 hours, as established in other experiment previously made [15]; therefore, the flasks were stirred at 150rpm for this period. Absorbency from each flask was taken at the beginning of the experiment and after 72 h using a Hach Spectrophotometer (model DR6000) at 660 nm wavelength. Each run included a control sample of MB without GAC. To determine the remnant $C_e$concentration, an absorbancy-concentration calibration curve was made using values below 25 ppm, in order to remain within the linear range, according to Beer´s Law. Finally, the obtained data was fitted to the Langmuir and Freundlich adsorption isotherm models.

3. Results and discussion

The results and discussion will be made only from the GACs obtained from a mT of 550°C. The procedure used was not adequate for GAC obtained from a mT of 450°C, since after washing, a more than 10% of the sample was pulverized and could not be considered granulated carbon size [12]. The tests performed with the sample left, had poor results compared to samples with an mT of 550 °C. Therefore, the results presented in the following sections correspond only to the mT of 550°C.

3.1 Pyrolysis yield

The pyrolysis yield is the mass of GAC obtained per mass of the raw material used. Table 1 shows the yield calculated at different ratios, using the same original mass of seeds, 7 g. The sample of GAC were weighted after washing away the phosphoric acid and drying them to avoid any humid content interference.

Table 1. Pyrolysis yield of R=1 & R=2 for GAC.

R	M_f, g	Yield %
1	2.11	30
2	2.30	33

It can be observed that the yield increased with R in a non-linear way, however the carbon yields are relatively low. Factors such as washing GAC have an influence in such a low yield because the filter retained carbon particles. Agricultural byproducts such as NS, have low organic content, between 30 to 4 5 %w/w. Therefore, NS is expected to have a low pyrolysis yield [16].

3.2 Determination of GAC pH (T=50°C)

The average pH of GAC R=1 is 6.43 and for GAC R=2 is 7.53, Table 2. A neutral pH was desired because it affects the surface of the adsorbant, with a higher pH the surface becomes more negatively charged and therefore, it favors the MB adsorption, but when pH gets higher, the diffusion through the pores is more difficult [17].

Table 2. GAC pH determination for R=1 and R=2.

	R=1			R=2	
m, g	pH	Stan. Dev.	m, g	pH	Stan. Dev.
0.5	6.3		0.5	7.4	
0.5	6.4	0.153	0.5	7.6	0.115
0.5	6.6		0.5	7.6	
Avg. pH	6.43		Avg. pH	7.53	

3.3 Determination of iodine number

The iodine number of GAC is related to its surface area and porosity. A typical value of iodine number for ACs with good adsorption capacity is between 500 and 1200 mg/g [18]. For NC GAC The average

iodine for R=1 is 506.9 and for R=2 is 513.1, both within the range; while the commercial GAC tested was of 838.5. Table 3 shows the results, where C is the residual iodine in the filtrated, and X/M the adsorbed iodine per gram of AC used [14].

Table 3. Iodine number from GAC for R=1, R=2 and commercial GAC.

R=1		R=2		Commercial GAC	
C, N	X/M mg/g	C, N	X/M mg/g	C, N	X/M mg/g
0.079	508.734	0.079	510.686	0.055	862.567
0.077	547.789	0.079	508.734	0.055	840.027
0.081	464.099	0.078	519.892	0.057	812.751
Avg. Iodine Number: 506.874		Avg. Iodine Number: 513.104		Avg. Iodine Number: 838.448	

Although the iodine number of the GAC samples was lower than commercial GAC, Table 4 shows a comparison of the iodine numbers of GAC obtained from different agricultural waste. The value obtained from NS, is low comparing it with the iodine number of coconut shell [1], which can be due to the low mass aveilable of GAC used for the test. However, NC GAC is high compared to oily sludge [2] and similar to rice straw [3], this makes it a competent activated carbon from agricultural waste.

Table 4. Iodine number comparison of GAC from different agricultural waste

Reference Raw material	mg/g	Reference
Nectarine stone	513	This work (R=2)
Coconut shell	975	[1]
Oily Sludge	248	[2]
Rice straw	510	[3]

3.4 Effect of agitation in MB adsorption

In the adsorption process, agitation is important to provide a proper interaction between the binding sites in GAC and the molecules of MB. It influences the way molecules will be distributed in order to have a high interfacial area of contact [19]. Additionally, agitation reduces the boundary layer in the GAC, lowering the external mass transfer resistance and promoting molecular diffusion as the speed of agitation increases, providing, therefore, a better adsorption capacity [20].

During the determination of adsorption isotherm determination for MB, the importance of agitation was noted. When using different stirring hot plates each sample reached equilibrium at different times and results were unreliable. To ensure a constant agitation rate, a Multipoint Stirrer (model 50088077) was used so that samples reached equitable equilibrium times and the results were reliable.

3.5 Adsorption isotherm determination for MB

To compare the adsorption capacity of GAC R=1 and R=2, two different models were used for the MB adsorption isotherm. Langmuir is the mostly used two-parameter equation (equation 1 [22]) because it is a simple form to quantify an adsorption process by modeling the equilibrium between the adsorbate and the adsorption system or surface [21],

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \qquad \text{(equation 1)}$$

Where:

C_e is the equilibrium concentration of MB remaining in the solution (mg/g);

q_e is amount of MB adsorbed per mass of GAC at equilibrium (mg/g);

q_{max} is the maximum adsorption capacity;

and K_L defines the MB and GAC affinity.

The Freundlich isotherm (equation 2 [23]) is satisfactory when using low concentrations [23].

$$logq_e = logK_F + \frac{1}{n}logC_e \qquad \text{(equation 2)}$$

Where:

KF is the Freundlich constant related to sorption capacity;

and 1/n is the Freundlich constant related to intensity of adsorption.

The results obtained from R=1 GAC are shown in figure 1, graph for equation 1 (a) and 2 (b). Figure 2 shows the results for R=2 GAC, graph for equation 1 (a) and 2 (b).

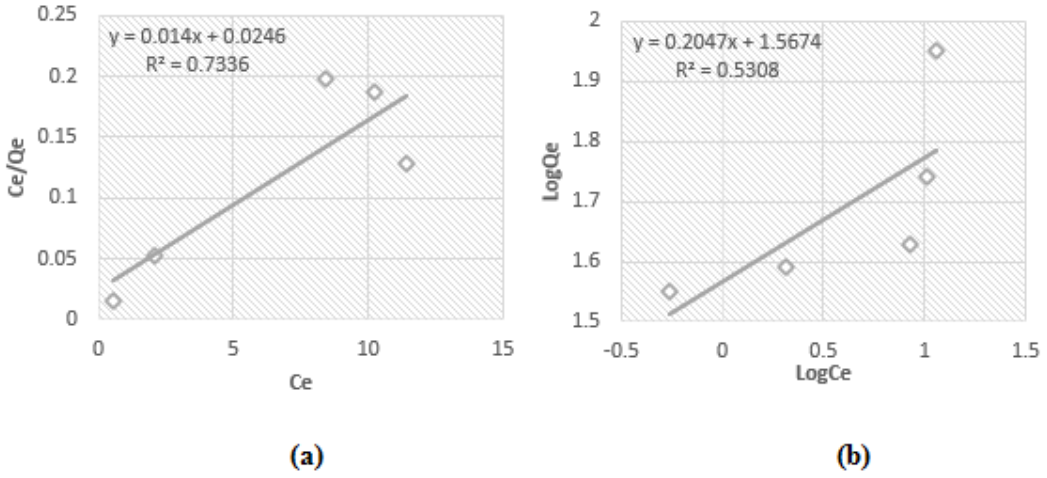

Figure 1. Linear transformations of the adsorption isotherm for MB R=1 using Langmuir´s (a) and Freundlich´s (b) model.

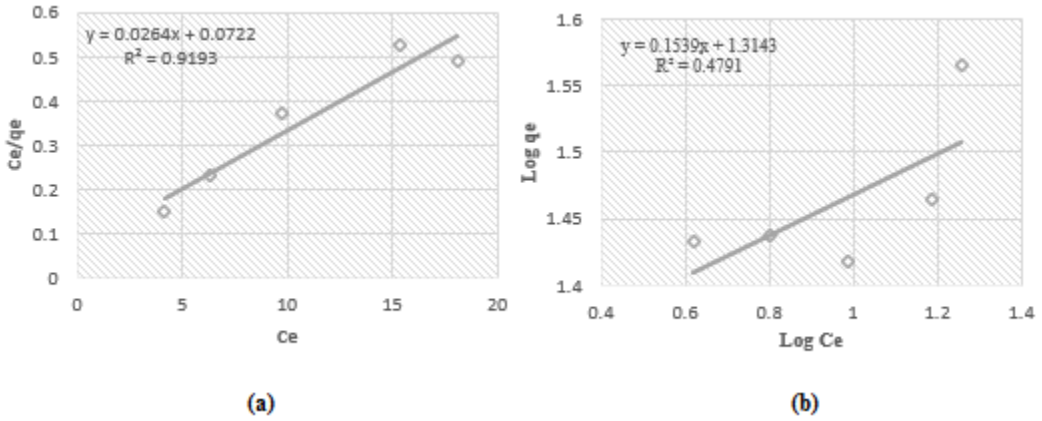

Figure 2. Linear transformations of the adsorption isotherm for MB R=2 using Langmuir´s (a) and Freundlich´s (b) model.

The data fitting to the isotherm model was evaluated with the correlation coefficient, R^2. Langmuir model had a better fitting than Freundlich. This suggests that adsorption of MB was homogeneous [24], meaning that all sites have the same probability to become occupied by MB molecules [25]. It can be noted that R=1 GAC had a correlation coefficient R^2=0.734 while R=2 GAC had a correlation coefficient R^2= 0.919 which only indicates a better fitting to the Langmuir model, however the remotion efficiency is higher with the sample R=1 than the sample R=2 as shown in Figure 3.

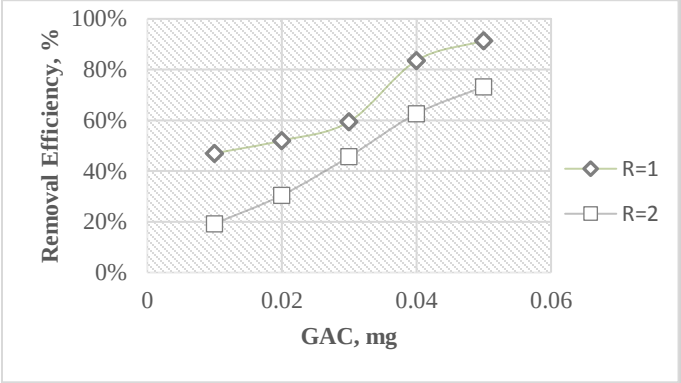

Figure 3. Remotion efficiency of MB of GAC R=1 and R=2.

The sample R=2 had a higher iodine number, which indicates higher surface area and porosity that enables a higher adsorption rate. However, it also had a higher pH number. Therefore, although the sample has a higher surface area, the diffusion of MB through the pores was more difficult, possibly due to a higher pH (as mentioned before), which caused a lower removal efficiency compared to the sample of R=1. Additionally, the values of maximum adsorption capacity were 71.4 and 37.9 mg/g for GAC R=1 and R=2 respectively, and the values for Langmuir´s constant 0.57 and 0.37. A comparison of MB adsorption with different organic material is shown in Table 5, were it can be noted that value is low, compared with similar procedures; however, there is a high affinity between the adsorbant and MB, as seen due to the high K_L values. This result might be related to the low organic content of NS since higher organic content result in higher adsorption capacities [26].

Table 5. Comparison of maximum adsorption capacity for MB on GAC from different agricultural waste.

Reference Raw Material	q_{max}, mg/g	K_L, L/mg	Refence
Nectarine seed (R=1)	71	0.57	This work
Rice Husk	41	0.13	[28]
Walnut Shells	79	0.06	[6]
Peach shells	184	0.38	[27]
Black cherry stone	322	0.035	[15]

Additionally, the isotherm for MB was plotted to determine the type of isotherm according to the IUPAC classification (Figure 4). The isotherms tend to follow the Type III classification, a reversible isotherm [29] and typical of macroporous adsorbents of 50nm or higher [30].

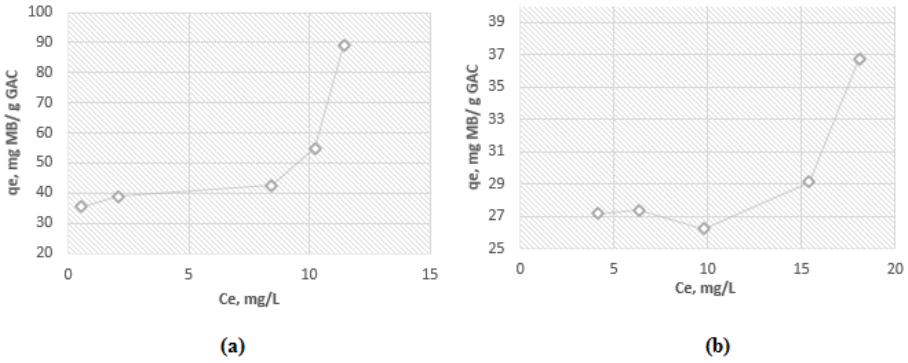

Figure 4. Isotherm for MB R=1 (a) and R=2 (b).

4. Conclusion

The best results in terms of adsorption capacity from the MB adsorption isotherm, iodine number and pH determination tests made were obtained from the impregnation ratio of 1 of GAC prepared from NS, meaning that the amount of activating agent, phosphoric acid, applied to the raw material influences the GAC adsorption performance. GAC activated with R=1 at 550°C had an iodine number of 506, a value within the range of 500 t0 1200 mg/g of AC with good adsorption capacities [18&21]. The results of iodine number obtained are similar to the reported values of rice straw (510 mg/g) [3], but lower than coconut shell (975 mg/g) [1]. Additionally, the adsorption isotherm of MB showed a Type III isotherm behavior according to the IUPAC classification and it fitted better in the Langmuir model with a correlation coefficient of 0.7336, a maximum adsorption capacity of 71 mg/g and a Langmuir constant (K_L) of 0.57. The adsorption capacity is considerably low comparing it to the characteristics of GAC prepared with a similar procedure such as cherry stone [15] which had an adsorption capacity of 321.7 mg/g of MB. This can be explained by the weak interactions between adsorbate and adsorbent that characterize Type III isotherms [31]. However, it was also low compared to the capacity of peach seeds [27], a similar raw material that reached an adsorption capacity of 184 mg/g of MB. Therefore, these results suggested the need to modify the activation method to seek an improvement in the adsorption capacity of GAC obtained from NS. Maximum activation temperature and activating agent concentrations are factors that affect the surface area of ACs, increasing them can generate a higher adsorption capacity; however, increasing them has a negative effect in the hardness of GAC [32]. Additionally, the agitation rate also influences, increasing the capacity with a higher rate, but destruction of the carbon structure may happen, as it happened with samples with maximum activating temperature of 450°C [33]. Finally, the high production of NS as byproducts makes it possible to generate profit by synthesizing it to generate GAC, improving its adsorption capacity with optimum activating agent concentration, maximum activating temperature and agitation rate values which can be further studied.

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