



# Preparation and Characterization of Activated Carbon Derived from *Antidesma bunius* L. in Methylene Blue Removal from Wastewater



## ABSTRACT

This study investigated the effect of contact time and methylene blue (MB) solution concentration on the adsorption capacity of granulated activated carbon derived from bignay (*Antidesma bunius* L.) seeds. The raw bignay seeds were subjected to physical activation via oven drying at 120°C and carbonization at 500°C for 30 min. The maximum adsorption capacity of both powdered and granulated activated carbon were determined. The alkyl functional groups of Bignay activated carbon (BAC) were determined using Fourier transform infrared (FTIR) analysis and the surface morphology and composition of the BAC were analyzed using scanning electron microscopy-energy dispersive x-ray (SEM-EDX). Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models were used to analyze the adsorption of isotherm BAC. But the data best fitted with the Freundlich isotherm. The mean energy of the adsorption showed that the adsorption of MB by BAC was physical adsorption implying that MB molecules were trapped in the pores of the BAC. The maximum adsorption capacity was 1.60 mg g<sup>-1</sup>. The rate of adsorption was used to determine if the process is physisorption or chemisorption using pseudo-first order and pseudo-second order adsorption kinetics. The data showed best fit for pseudo-second order, suggesting that the reaction depends on the concentration of both reactants.

**Keywords:** activated carbon, adsorption, Bignay, isotherm, physical activation

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## INTRODUCTION

Organic pollution occurs when osignificant amount of toxic organic substances are released to the environment. most of these organic pollutants are resistant to environmental degradation thus considered a major global environmental problem for the coastal ecosystems. One particular type of organic pollutant comes from the textile industry, where extensive amounts of effluents contaminated with dye are released from the dyeing process. Concerning both volume and composition, effluents from this kind of industry were marked as one of the major sources of water pollution in the world (Abboud-Abi Saab and Hassoun 2017).

Dyes are generally utilized in numerous industries and businesses such as textile, leather tanning, cosmetics, metal finishing, paper printing, plastic, food, corrective, and others (Noorimotlagh et al. 2019; Katheresan et al. 2018; Yaseen and Scholz 2018). In fact, there are 10,000 t in excess of economically available dyes of more than 700,000 t dyestuff being produced every year all over the world (Han et al. 2013). The total dye utilization of the textile industries worldwide is in excess of 10,000,000 kg yr<sup>-1</sup>, and

around 90% winding up on textures (Mulugeta and Lelisa 2014; Abboud-Abi Saab and Hassoun 2017). Dye makers and buyers are focused in the firmness and fastness of dyes and thus manufactured dyestuffs are harder to degrade. It has been reported that 10-15% of the dye is lost during the coloring procedure and discharged in the effluent (Mulugeta and Lelisa 2014).

In searching for solutions to these concerns, there are several chemical and physical strategies in removing dyestuffs in effluent. One of it is the adsorption onto activated carbon (AC) that has been observed to be better than any other method of removing dyes from wastewaters. As far as the methodology is concerned, it has the capacity in adsorbing a wide scope of various kinds of adsorbates, and it will have a simplicity of design for adsorber (Hameed et al. 2007). Adsorption is one of the most effective technology applications due to its non-toxicity in both water and wastewater treatment facility. (Venkat-Mohan et al. 2000; Noorimotlagh et al. 2019). One of the main functions of activated carbon is an adsorbent for gas and water purification processes via adsorption process.

Adsorption, one of the procedures being used in dye removal, is a process where molecules attach to a surface of a material called adsorbent or substrate and the substance that adsorbs is called the adsorbate (Atkins and de Paula 2010). The process can be done through physical or chemical adsorption. Steam activation method is preferred in other studies over chemical activation methods since it is least expensive. The concept of water-shift reaction is accustomed with water vapor system as carrier in order to improve the carbon matrix porosity making them high value AC (Shoaib and Al-Swaidan 2014). In chemical activation,  $\text{ZnCl}_2$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{KOH}$ , and several types of chemicals are used as the activating agents. Properties of the produced AC are dependent on what type of activating agent. A study found that AC obtained from the carbonization temperature of  $600^\circ\text{C}$  with  $\text{ZnCl}_2$  and activation of  $\text{H}_3\text{PO}_4$  had the excellent specific surface areas. On the other hand, AC obtained at the carbonization temperature of  $800^\circ\text{C}$  with alkali metal ( $\text{KOH}$ ,  $\text{NaOH}$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ ) treatment obtained the maximum surface areas (Hayashi et al. 2000).

In adsorption process, AC is one of the most important microporous adsorbents because of its extremely large surface area that suits to a specific application such as food and beverage processing, odor removal, industrial pollution control, and filters at home (Ismadji et al. 2005). Some of the most commonly used agricultural wastes in producing AC are the coconut shell, pistachio shell, saw dust, walnut shell, tropical wood, and almond shell (Adinata et al. 2007). A study was conducted using plane tree seed biomass on the preparation of AC derived through pyrolysis. Plane tree seed is a good source of carbon in preparing for AC of various uses most likely for sorption. It focused on the use of AC for carbon dioxide capture and storage (CCS) technology. The major applications of AC are in wastewater treatment, water and gas purification, desulfurization, and mercury removal (Dodevski et al. 2017).

Fitting isotherms to the adsorption mechanism are another effective way to characterize the AC produced and describe the adsorption phenomena that occurs. There are multiple adsorption isotherm models that are being used in adsorption studies. However, in the study for the *bignay*-derived activated carbon, the isotherm models used were the four most common in AC studies today. In Freundlich isotherm, the sorption is independent on the concentration if the constant  $n$  is in unity. If  $n > 1$ , a normal adsorption will be observed. However, if  $n < 1$ , it indicates cooperative adsorption (Mohan and Karthikeyan 1997). The equilibrium parameter of Langmuir isotherm declares if the monolayer

adsorption is favorable. If  $R_L > 1$ , then monolayer adsorption is not favorable. If  $R_L = 1$  the adsorption is linear and if the  $0 < R_L < 1$  the monolayer adsorption process is favorable and will most likely be the sole characteristic of the adsorption occurrences. The mean energy of Dubinin-Radushkevich isotherm determines if the adsorption is physisorption or chemisorption. If the mean energy,  $E$  is lesser than  $8 \text{ kJ mol}^{-1}$ , the process indicates physical adsorption, and if the  $E$  value is between  $8$  and  $16 \text{ kJ mol}^{-1}$ , the process indicates chemical adsorption. Otherwise, the process is unfavorable. Adsorption is described through the use of isotherms because the effect of temperature has significance with the process. The adsorbate quantity that bounds to the adsorbent at constant temperature is expressed as a function of pressure and concentration. Several isotherm models, including the linear, Freundlich, Langmuir, BET (Brunauer, Emmett, and Teller), and Kisiuk theories have been developed to describe adsorption (Helmenstine 2017).

This research could benefit the industry by treating wastewater using alternative adsorbent sources like *bignay* seeds. It decreases the amount of pollutants discharge from the effluents of the industry in order to lessen the harmful effects in the environment especially the aquatic life. A study about nano porous AC prepared from *karanj* (*Pongamia pinnata*) fruit hulls, which involves adsorption of the target pollutant, showed an excellent performance in MB removal (Azharul Islam et al. 2017). There were similarities between *bignay* and *karanj* including seed and tree sizes, and both are endemic to tropical countries like Philippines. They are both small fruits, therefore their seeds and hulls are about the same size. *Karanj* fruit hull is another example of a low-cost source of AC which can be used in MB adsorption. Since *karanj* exhibited outstanding properties as an AC precursor, this study came up with an idea of looking for similar raw materials that exhibits the same characteristics as *karanj* and is endemic to the Philippines. There were no previous researches about the potential use of *bignay* seeds as an AC precursor, thus it was selected as the material for this study.

The general objective of this study was to synthesize an AC derived from *bignay* (*Antidesma bunius* L.) seeds. The specific objectives of the study included the following: to identify the morphology and composition of BAC using SEM-EDX analysis; to determine the functional alkyl groups of BAC using FTIR; to determine the adsorption equilibrium of AC produced by testing the varying contact time; to determine the effect in adsorption capacity of the activated produced by testing in varying concentration; to determine if the

rate of adsorption is either proportional or based on the square of number of vacant sites on the adsorbent using pseudo-first and pseudo-second order kinetics; and to determine the best fit model, interaction of adsorbent-adsorbate of process, and if the adsorption process is either physisorption or chemisorption at equilibrium using Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms. The experimental research study was conducted in the Chemistry Laboratory of Malayan Colleges Laguna at Laguna, Philippines in July 2017-March 2018.

## MATERIALS AND METHODS

### Preparation of activated carbon

The *bignay* seeds were obtained from the Institute of Food Science and Technology, College of Agriculture and Food Science, University of the Philippines Los Baños, Laguna. The *bignay* seeds were washed using tap water followed by distilled water for final rinsing to remove soil and impurities then dried in a drying oven at around 120°C for 12 h to remove moisture content. The dried *bignay* seeds was passed through a 2-mm sieve to remove the remaining pulp, soil, and impurities and to obtain seeds that were almost similar in size. The seeds were carbonized and activated using box resistance furnace at 500°C for 30 min. The produced activated carbon was stored in the desiccator. The resulting product was the *bignay* activated carbon (BAC).

### Preparation of Methylene Blue (MB) test solution

Methylene blue (MB) was used as the adsorbate in this study. Approximately 10 mg of MB dye (LabChem, Inc., 100%, MW = 319.85 g mol<sup>-1</sup>) was dissolved in a 1000 mL volumetric flask with distilled water. The solution was allowed to stand for 6 hr then diluted to 1000 mL volumetric flask. The solution stood for 6 h and diluted to 20, 15, 8, and 6 mg L<sup>-1</sup> solutions. The calibration curve was generated by measuring the absorbance using visible spectrophotometer at 666 nm.

### Determination of adsorption capacity of BAC

Approximately 0.5 g of BAC sample was added in a flask with 25 mL MB solution. The MB solution was prepared in different concentrations (0.006, 0.008, 0.015 and 0.02 mg mL<sup>-1</sup>). The sample MB was analyzed for initial concentration and then the flask was shaken for 5 min. After shaking, the collected samples were filtered and final MB concentration was determined. Then, the final concentration of the solution was determined using

### Activated Carbon Derived from *Antidesma bunius* L.

spectrophotometer. The procedure was repeated in different time (10, 20, 30, 45, 60, 90, 120, 150, 180, 210, and 240 min.) and different MB concentrations (0.006, 0.008, 0.015 and 0.02 mg mL<sup>-1</sup>).

The amount of MB adsorbed per unit mass of adsorbent at equilibrium conditions,  $q_e$  (mg g<sup>-1</sup>), was calculated using Equation 1:

$$\text{Equilibrium Absorbance Equation } q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where  $C_0$  is the initial concentration of MB (mg mL<sup>-1</sup>),  $C_e$  is the concentration of MB at equilibrium (mg mL<sup>-1</sup>),  $V$  is the volume of the solution (mL) and  $m$  is the mass of BAC (g).

The MB removal efficiency of prepared BAC was calculated using Equation 2:

$$\text{Removal Efficiency Equation A (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

### Characterization Techniques

The characterization of BAC involved Fourier transform infrared (FTIR) analysis for determination of alkyl functional groups, scanning electron microscopy (SEM) analysis for surface morphology of the sample, and energy dispersive x-ray (EDX) spectroscopy for the elemental composition of the sample. ImageJ Analysis software was used to estimate the pore diameter and surface area of the BAC. The image in SEM was divided into two 4 quadrants and generated at least 10 random measurements in each quadrants to calculate and estimate the average pore size and total surface area.

### Adsorption Kinetics

Adsorption kinetics was used to determine if the rate of adsorption is either directly proportional or based on the square of the number of vacant sites using pseudo-first order and pseudo-second order kinetic models. The kinetic studies were conducted by adding 25 mL of MB solution under varying time. In this study, the orders of the reaction were used in assessing the experimental results. The rate of adsorption is directly proportional to the number of vacant sites when the plotted curve of the given equation is linear (Moussout *et al.* 2018). Pseudo-first order kinetic equation could be expressed as Equation 3.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where  $q_e$  is the amount of MB adsorbed at equilibrium (mg g<sup>-1</sup>),  $q_t$  is the amount of MB adsorbed at time  $t$  (mg

$g^{-1}$ ), and  $k_1$  is the pseudo-first order rate constant ( $mg\ g^{-1}\ min^{-1}$ ).

The rate of adsorption is based on the square of number of vacant sites when the plot curve of the equation is linear (Ho and McKay 1999). The linear form of pseudo second-order is expressed in Equation 4.

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (4)$$

where  $k_2$  is the pseudo-second order rate constant ( $mg\ g^{-1}\ min^{-1}$ ).

### Adsorption Isotherm

Adsorption isotherm was used to determine the interaction of adsorbent-adsorbate when the process reaches the equilibrium. The adsorption of Bignay AC was analyzed by Langmuir, Freundlich, Temkin, Dubinin-Radushkevich isotherms. The Freundlich isotherm model is used to describe the adsorption phenomena for the heterogeneous surfaces. The linearized Freundlich equation is given by Equation 5.

$$\log q_e = \frac{\log C_e}{n} + \log K_f \quad (5)$$

where  $q_e$  is the equilibrium adsorption capacity of the adsorbent ( $mg\ g^{-1}$ ),  $K_f$  is the Freundlich isotherm constant, and  $n$  is the adsorption intensity.

The constant  $K_f$  is an indicator for the estimated adsorption capacity, and the slope  $1/n$  determines the strength of the adsorption process (Kuang et al. 2020). On the other hand, the Langmuir isotherm model distinguishes if the adsorption is a monolayer adsorption, or otherwise a multilayer adsorption. This model can be used to predict the affinity of the sorbate to sorbent (Desta 2013; Faria and Young 2010). It determines if the adsorbate is uniformly distributed in the surface of the adsorbent in a single layer system. The linearized Langmuir equation is expressed by Equation 6.

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max} C_e} \quad (6)$$

where  $q_{max}$  is the maximum adsorption capacity ( $mg\ g^{-1}$ ) and  $K_L$  is the Langmuir isotherm constant. The favorability of the monolayer adsorption is given by the equilibrium parameter,  $R_L$  as expressed below.

$$R_L = \frac{1}{1 + (1 + K_L C_0)} \quad (7)$$

$R_L$  value describes the nature of the adsorption

process. Another model isotherm used is Temkin which describes the interactions between the adsorbent and the adsorbate. This model assumes that heat of adsorption would decrease linearly with the increase in coverage of the adsorbent surface (Calagui et al. 2014). Such that adsorption is characterized by equal distribution of binding energies, up to a maximum binding energy. Temkin isotherm and heat of sorption equations are expressed in Equations 8 and 9, respectively.

$$q_e = B \ln C_e + B \ln A_T \quad (8)$$

$$B = \frac{RT}{K_T} \quad (9)$$

where  $B$  is the heat of sorption ( $J\ mol^{-1}$ ),  $R$  is the universal gas constant ( $8.314\ J\ mol^{-1}\ K^{-1}$ ),  $T$  is the temperature ( $K$ ), and  $K_T$  is the Temkin isotherm constant. The last isotherm model used is the Dubinin-Radushkevich isotherm model which is used to distinguish between physical and chemical adsorption. The linearized form is represented by Equation 10.

$$\ln q_e = \ln q_{max} - K_{DR} \varepsilon^2 \quad (10)$$

where  $K_{DR}$  is the Dubinin-Radushkevich isotherm constant and  $\varepsilon$  is the Polanyi potential. The parameter  $\varepsilon$  can be calculated using Equation 11.

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (11)$$

The Dubinin-Radushkevich isotherm also gives the mean energy of adsorption, given by Equation 12:

$$E = \sqrt{-2K_{DR}} \quad (12)$$

## RESULTS AND DISCUSSION

### Characterization of BAC

The SEM images of granulated BAC and powdered BAC were captured at 1000x and 3000x magnifications (Figure 1). The image for granulated BAC has large pore size (Figure 1a and 1b). Based on the analysis using the ImageJ software, the results show that it has a larger surface area of approximately  $44.08\ \mu m^2$ . The larger surface area is due to larger pore sizes generated using the ImageJ with an average diameter of  $3.87\ \mu m$ . The SEM shows the finer pores with an average diameter generated of about  $2.82\ \mu m$ . The powdered BAC sample generates a smaller surface area measuring about  $24.90\ \mu m^2$  compared with the granulated sample (Figures 1c and 1d). Since the contaminant dye has a large molecular size and structure about  $13.82\ \text{\AA}$  (Macedo et al. 2006),



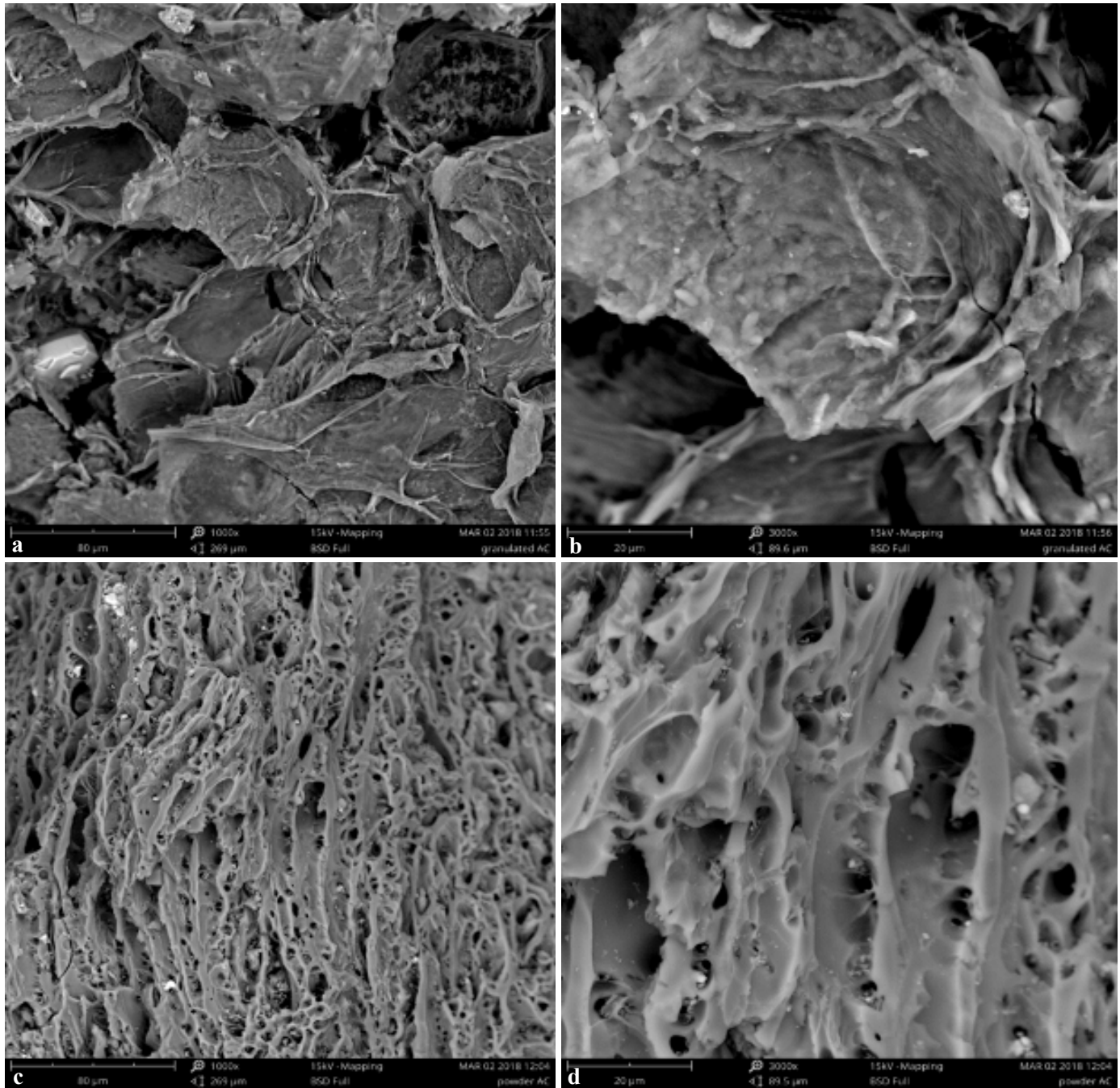


Figure 1. Scanning Electron Microscope image of granulated *Bignay* Activated Carbon at (a) 1000x magnification, (b) 3000x magnification, and powdered BAC at (c) 1000x magnification, (d) 3000x magnification.

itis necessary for the activated carbon to have large pores to be able to catch methylene blue molecules easier and more effectively.

The Energy Dispersive X-ray Spectroscopy (EDS) results for the granulated and powdered activated carbon will determine the most abundant element present in the sample (**Figures 2a** and **2b**). The five abundant chemical component of the *Bignay* AC were Oxygen, Carbon, Silicon, Calcium and Potassium. In the granulated BAC, Carbon was found to be 26.95% and

that Oxygen, Silicon, Calcium and Potassium were found to be 48.29%, 8.75%, 11.95% and 4.06%, respectively. Carbon found in powdered BAC was 32.83% and that of Oxygen, Silicon, Calcium and Potassium were found to be 46.77%, 6.12%, 10.79% and 3.49%, respectively. The result of elemental analysis for granulated BAC compared with the powdered sample has significant difference and this is due to the surface area of the sample used during the analysis. This is obvious since the samples tested were different from each other and expected to have different carbon and oxygen content.

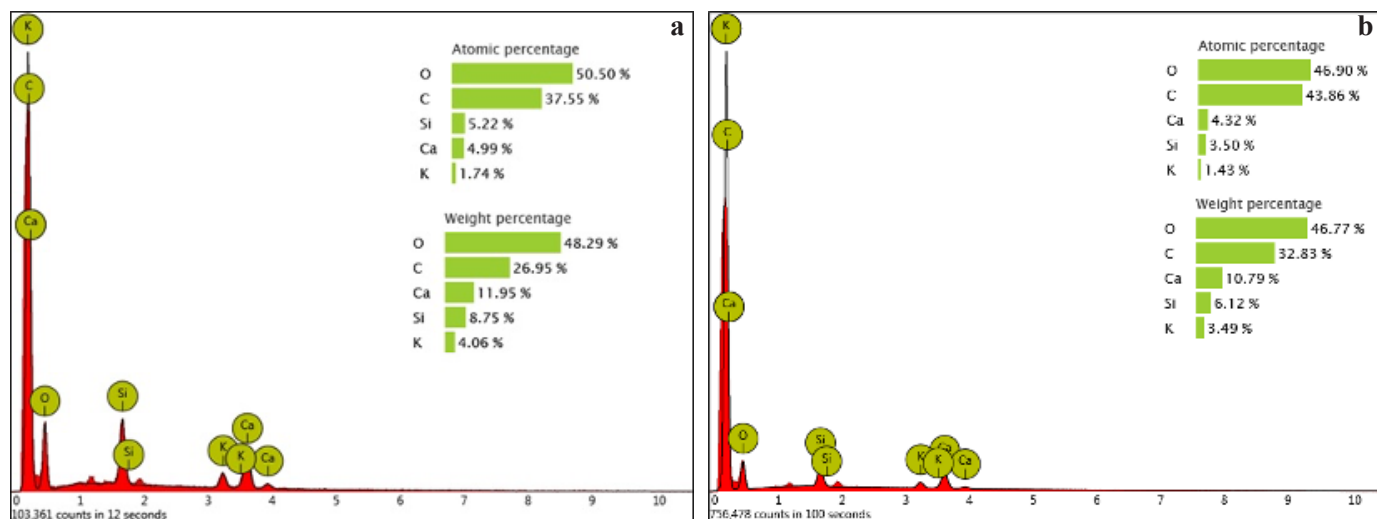


Figure 2. Energy dispersive X-ray plot for (a) granulated *Bignay* Activated Carbon (BAC), and (b) powdered BAC.

FTIR analysis of BAC was conducted to identify surface functional groups involved in binding to MB cations (**Figure 3a**). The first peak at 2,980.83  $\text{cm}^{-1}$  indicates the C-H stretch representing the alkyl group in the BAC. Other peaks at 1,382.14, 1,157.52, and 953.25  $\text{cm}^{-1}$  are characteristics of the C-H bend of alkyl groups, C-O stretch of ethers, and C-H bend of alkenes (*Silverstein et al. 1981*). The first peak at 2,943.16  $\text{cm}^{-1}$  indicated C-H stretch (**Figure 3b**). Other peak is at 1,605.67  $\text{cm}^{-1}$  which corresponds to C=C or alkene. The peaks at 1,466.22  $\text{cm}^{-1}$  and 880.93  $\text{cm}^{-1}$  correspond to C-H bending. After MB adsorption (**Figure 3c**), some peaks shifted from 2,980.93-3,361.67  $\text{cm}^{-1}$ , which corresponds to O-H stretching and disappearance of peak at 1,157.52  $\text{cm}^{-1}$ , which corresponds to C-O stretch. Therefore, O-H and C-O functional groups were involved in the possible interaction of BAC-MB, which attribute to *bignay* seeds as potential AC.

### Adsorption Studies

The adsorption capacity of the granulated BAC was determined using different initial MB concentrations (**Figure 4**). It can be observed that at 0.02  $\text{mg mL}^{-1}$ , adsorption took place quickly, increasing by 0.42  $\text{mg g}^{-1}$  during the first 30 min of contact with the BAC. However, it slowly decreased with time as the quasi-equilibrium phenomena occurred in about 120 min because the MB was closely reaching its equilibrium. In equilibrium, the adsorption capacity becomes constant which reflects to the maximum adsorption capacity of BAC. The same with the initial concentration of 0.006  $\text{mg mL}^{-1}$ , the quasi-equilibrium occurred in about 60 min, which means the surface of BAC is already saturated with MB. Upon increasing the initial MB concentration on the adsorption to BAC, the maximum adsorption capacity also increases.

The adsorption capacity of BAC is increased from 0.27 to 0.58  $\text{mg g}^{-1}$  because the ions were adsorbed by active sites of BAC at low concentration and active sites of BAC at higher concentrations are occupied due to its saturation resulting in decrease of adsorption rate (**Figure 5**). Then the removal efficiency of granulated BAC decreases from 92.49-78.00% at equilibrium seeing that the active sites of BAC that is occupied easily in increase of MB concentration (**Figure 6**). Therefore, the saturation of the solution takes effect on the adsorption capacity and removal efficiency of BAC due to the active sites that it occupies. There was an obvious trend from which increasing the initial concentration of the MB, there was a possibility that will decrease the removal efficiency of BAC. The equal distribution of MB on the surface of the BAC will lead to saturation of active sites which may contribute to low removal efficiency (*Calagui et al. 2014*). The pseudo first and second order kinetic models for the adsorption of different MB concentrations on the granulated BAC are also presented (**Figures 7 and 8**).

The process favored pseudo-second order adsorption kinetics, which has correlation coefficient value higher than the pseudo-first order adsorption kinetics. Meaning, it implies that adsorption mechanism is chemisorption (**Tables 1 and 2**). Chemisorption, on the other hand, alters the chemical structure of the adsorbent or adsorbate because reaction occurs between the two surfaces. Favoring chemisorption implies that reactions occur on the functional groups of MB forming covalent bonds with BAC, which causes for the adsorption of the dye as well. These reactions cause ionic or covalent bonds to form and thus attaching the adsorbate's atoms to the adsorbent based on the comparison done by *Simonin (2016)* on his study about pseudo-first order and pseudo-second order rate laws. The rate of adsorption depends on

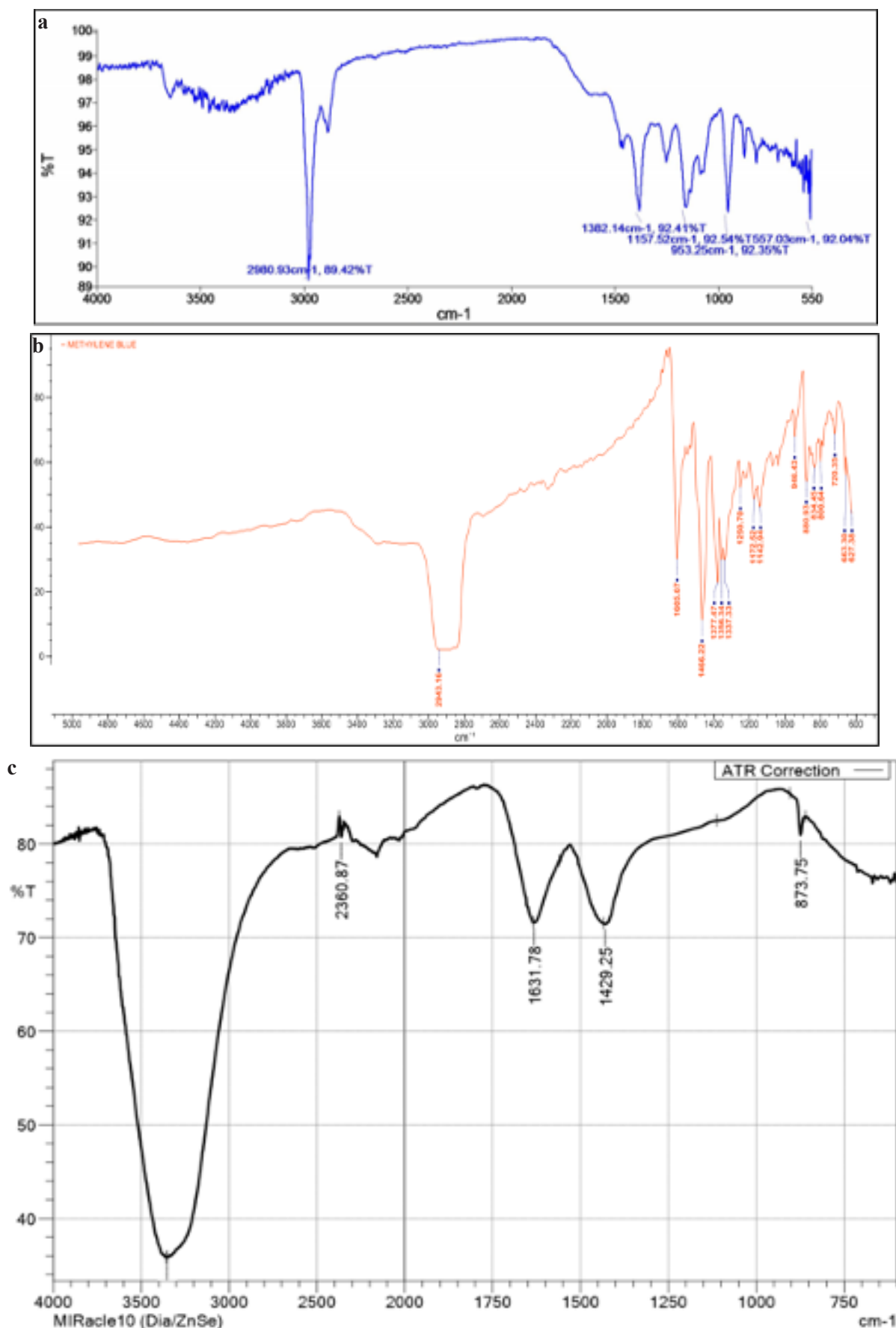


Figure 3. Founier Transform Infrared (FTIR) Spectra of (a) *Bignay* Activated Carbon (BAC), (b) MB (Tarik 2014), and (c) BAC-MB

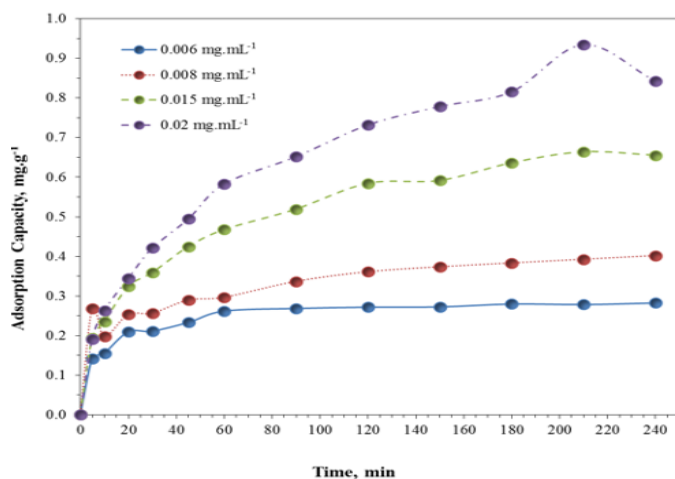


Figure 4. Adsorption capacity plot of granulated *Bignay* Activated Carbon at different contact times.

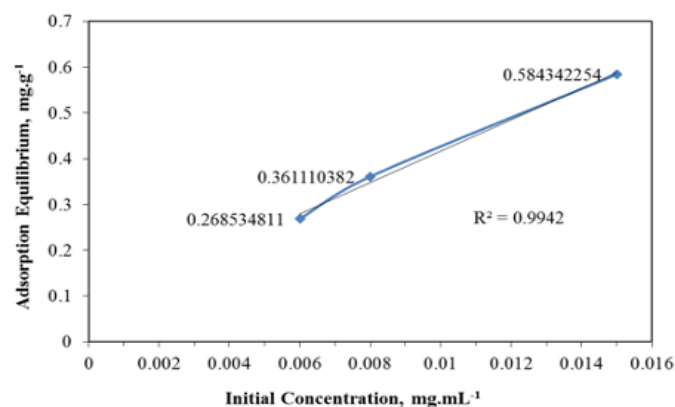


Figure 5. Adsorption capacity plot of granulated *Bignay* Activated Carbon at different initial concentrations of dye.

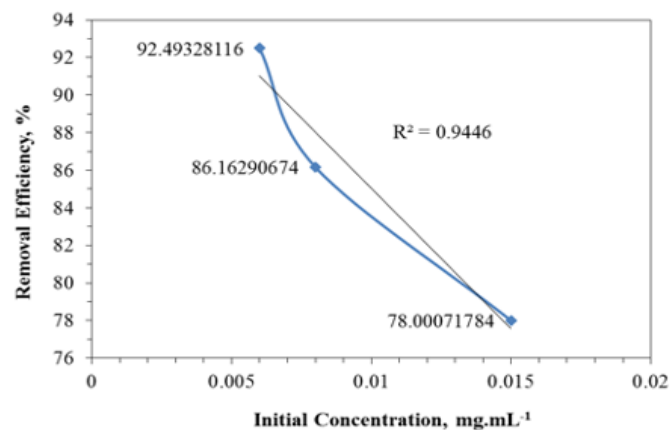


Figure 6. Removal efficiency plot of methylene blue dye at different initial concentrations using granulated *Bignay* Activated Carbon.

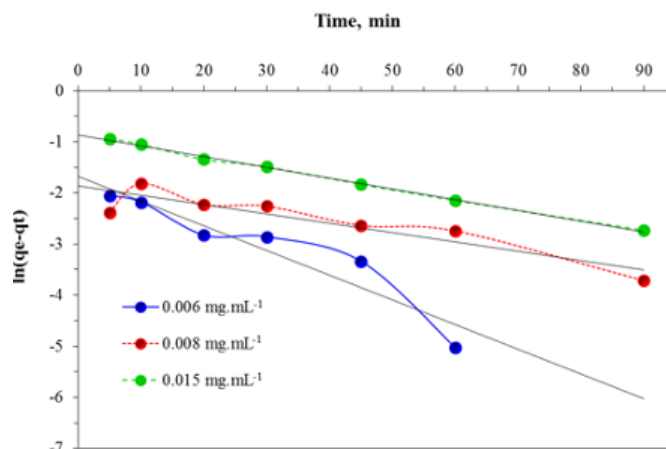


Figure 7. Pseudo-first order kinetic model for MB adsorption on granulated *Bignay* Activated Carbon.

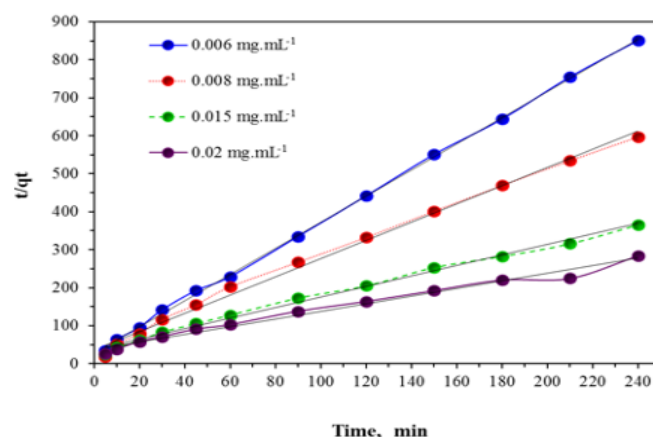


Figure 8. Pseudo-second order kinetic model for MB adsorption on granulated *Bignay* Activated Carbon.

Table 1. Data for Pseudo-first Order Kinetics.

Initial Concentration	R <sup>2</sup>	q <sub>e</sub>	K <sub>1</sub>
0.006	0.898585015	0.186323138	0.048333311
0.008	0.837826598	0.155078129	0.018193957
0.015	0.997404588	0.419995478	0.021022718

Table 2. Data for Pseudo-second Order Kinetics.

Initial Concentration	R <sup>2</sup>	q <sub>e</sub>	K <sub>1</sub>
0.006	0.999504099	0.290916014	0.408721537
0.008	0.994743677	0.41732624	0.154622707
0.015	0.993611817	0.721807377	0.052485488
0.02	0.983783089	0.994153314	0.027283229



the active sites on the surface of BAC. On the average, the granulated BAC has a pore count of  $13.21 \mu\text{m}^2$  and the powdered BAC has an average pore count of  $22.65 \mu\text{m}^2$ .

### Adsorption Isotherms

The coefficient of determination ( $R^2$ ) value is considered as a measure of goodness-of-fit of isotherm

data. The data showed that the best fit model isotherm is Freundlich isotherm, which has an  $R^2$  value of 0.993, followed by Temkin, Langmuir, and Dubinin-Radushkevich isotherm, which has an  $R^2$  value of 0.968, 0.942, and 0.847, respectively (Table 3). The equilibrium parameter ( $R_L$ ) from the Langmuir isotherm was found to be 0.123, which is less than 1. Meaning, the adsorption process is favorable. From the Freundlich isotherm,  $1/n$  was found to be 0.392, which is less than 1. Therefore,

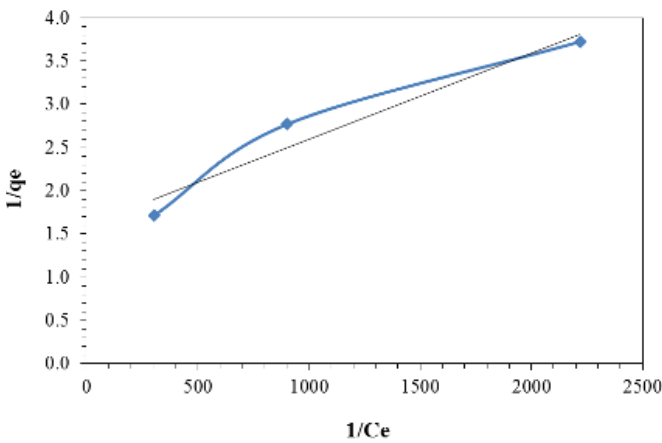


Figure 9. Adsorption isotherm of Langmuir for MB adsorption on granulated *Bignay* Activated Carbon.

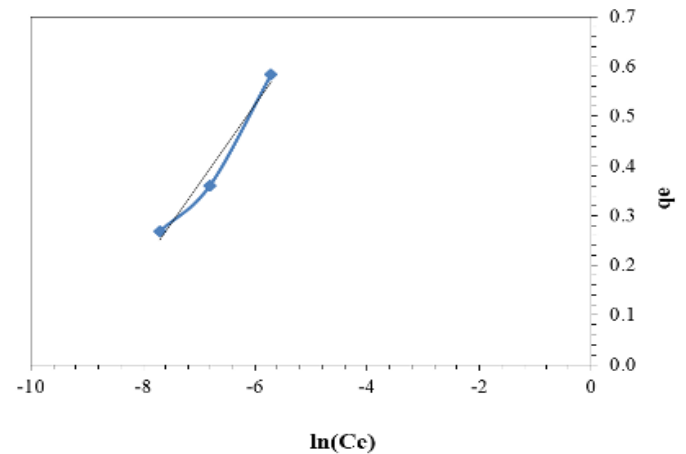


Figure 11. Adsorption isotherm of Temkin for MB adsorption on granulated *Bignay* Activated Carbon.

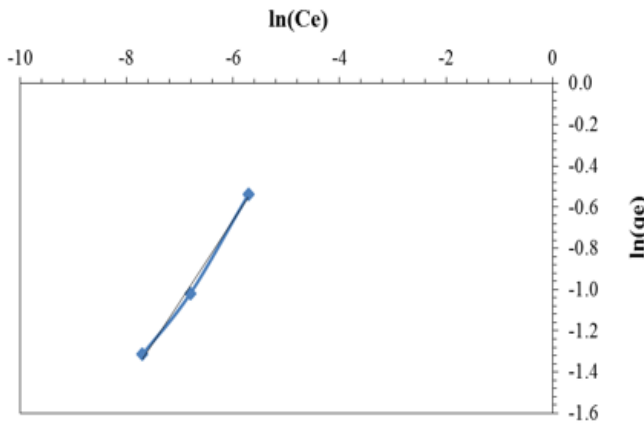


Figure 10. Adsorption isotherm of Langmuir for MB adsorption on granulated *Bignay* Activated Carbon .

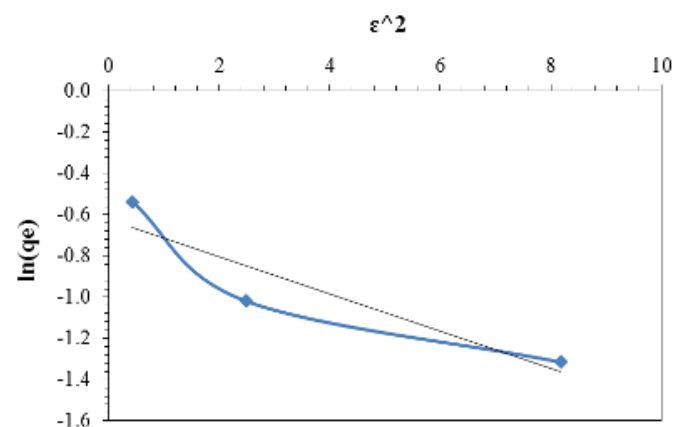


Figure 12. Adsorption isotherm of Dubinin-Radushkevich for MB adsorption on granulated *Bignay* Activated Carbon.

Table 3. Isotherm Constants for Langmuir, Freundlich, Temkin, Dubinin-Radushkevich Isotherm for the adsorption of MB by *Bignay* Activated Carbon .

Langmuir Isotherm				Freundlich Isotherm			
R <sup>2</sup>	q <sub>max</sub> (mg g <sup>-1</sup> )	KL (L g <sup>-1</sup> )	R <sub>L</sub>	R <sup>2</sup>	1/n	Kf (mg g <sup>-1</sup> )	
0.942	1.596	0.629	0.123	0.993	0.392	48.659	
Temkin Isotherm			Dubinin-Radushkevich Isotherm				
R <sup>2</sup>	A <sub>T</sub> (L g <sup>-1</sup> )	B	K <sub>T</sub> (mg g <sup>-1</sup> )	R <sup>2</sup>	q <sub>max</sub> (mg g <sup>-1</sup> )	E	K <sub>DR</sub>
0.968	10.591	0.160	15.266	0.847	0.535	2.356	-0.090

the process indicates normal adsorption. The mean energy (E) from the Dubinin-Radushkevich isotherm was found to be 2.36 kJ mol<sup>-1</sup> which is lesser than 8 kJ mol<sup>-1</sup>. Thus, the adsorption of Bignay Activated Carbon was physical adsorption.

## CONCLUSIONS

The pore size, with a diameter of 3.87 µm, and carbon content of 26.95%<sub>weight</sub> of granulated BAC is high, compared to powdered BAC with a pore size diameter of 2.82 µm and 32.83% carbon content by weight. The Freundlich isotherm model best fitted the adsorption with an R<sup>2</sup> value of 0.993, suggesting a multilayer adsorption on the AC surface. From the Langmuir isotherm, the adsorption process was favorable (RL = 0.123). From the Freundlich isotherm, normal adsorption occurred (1/n = 0.392). The adsorption of BAC was via physical adsorption (E = 2.36 kJ mol<sup>-1</sup>). The best fitted model of adsorption kinetics was pseudo-second order. The adsorption studies show that the maximum adsorption capacity of BAC is 1.60 mg g<sup>-1</sup>. Therefore, BAC is a precursor to activated carbon.

## REFERENCES

- Abboud-Abi Saab, M. and Hassoun, A.E.R. 2017. "Effects of Organic Pollution on Environmental Conditions and the Phytoplankton Community in the Central Lebanese Coastal Waters with Special Attention to Toxic Algae." *Regional Studies in Marine Science* 10: 38-51.
- Adinata, D., Wan Daud, W.M.A., and Aroua, M.K. 2007. "Preparation and characterization of activated carbon from palm shell by chemical activation with K<sub>2</sub>CO<sub>3</sub>." *Bioresource Technology* 98: 145.
- Atkins, P., and de Paula, J. 2010. "The Extent of Adsorption." In: *Physical Chemistry*. (eds. Atkins, P., de Paula, J.). Great Britain: Oxford University Press. pp. 888-889.
- Azharul Islam, M.D., Sabar, S., Benhouria, A., Khanday, W.A., Asif, M. and Hameed, B.H. 2017. "Nanoporous activated carbon prepared from karanj (*Pongamia pinnata*) fruit hulls for methylene blue adsorption." *Journal of the Taiwan Institute of Chemical Engineers* 74: 96-104.
- Calagui, M.J.C., Senoro, D.B., Kan, C.-C., Salvacion, J.W.L., Futralan, C.M. and Wan, M.-W. 2014. "Adsorption of indium (III) ions from aqueous solution using chitosan-coated bentonite beads." *Journal of Hazardous Materials* 277: 120-126.
- Desta, M.B. 2013. "Batch sorption experiments: Langmuir and Freundlich isotherm studies for adsorption of textile metal ions onto Teff straw (*Eragrostis tef*) agricultural waste." *Journal of Thermodynamics* DOI: 10.1155/2013/375830.
- Dodevski, V., Jankovic, B., Stojmenovic, M., Krstic, S., Popovic, J., Pagnacco, M.C., Popovic, M. and Pasalic, S. 2017. "Plane tree seed biomass used for preparation of activated carbons (AC) derived from pyrolysis. Modeling the activation process." *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 522: 83-96.
- Faria, I.R. and Young, T.M. 2010. "Modeling and predicting competitive sorption of organic compounds in soil." *Environmental Toxicology and Chemistry* 29(12): 2676-2684. DOI:10.1002/stc.343.
- Hameed, B.H., Ahmad, A.L. and Latiff, K.N.A. 2007. "Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust." *Dyes and Pigments* 75(1): 143-149.
- Han, X., Yuan, J. and Ma, X. 2013. "Adsorption of malachite green from aqueous solutions onto lotus leaf: Equilibrium, kinetic, and thermodynamic studies." *Desalination and Water Treatment* 52 (28-30): 5563-5574. DOI: 10.1080/19443994.2013.813102.
- Hayashi, J., Kazchaya, A., Muroyama, K. and Watkinson, A.P. 2000. "Preparation of activated carbon from lignin by chemical activation." *Carbon* 38: 1873-1878.
- Helmenstine, A. M. 2017. "Adsorption Definition: How to Define Adsorption." Retrieved from <https://www.thoughtco.com/definition-of-adsorption-605820>.
- Ho, Y.S. and McKay, G. 1999. "Pseudo-second order model for sorption processes." *Process Biochemistry* 34(5): 35-742. doi:10.1016/S0032-9592(98)00112-5
- Ismadji, S., Sudaryanto, Y., Hartono, S.B., Setiawan, L.E.K. and Ayucitra, A. 2005. "Activated carbon from char obtained from vacuum pyrolysis of teak sawdust: pore structure development and characterization." *Bioresource Technology* 96: 1364-1369.
- Macedo, J.S., Júnior, N.B.C., Almeida, L.E., Vieira, E.F.S., Cestari, A.R., Gimenez, I.F., Carreño, N.L.V. and Barreto, L.S. 2006. "Kinetic and calorimetric study of the adsorption of dyes on mesoporous activated carbon prepared from coconut coir dust." *Journal of Colloid and Interface Science* 298: 515-522.
- Mohan, S. and Karthikeyan, J. 1997. "Removal of lignin and tannin color from aqueous solution by adsorption on to a solution by adsorption on to activated charcoal." *Environmental Pollution* 97: 183-187.
- Moussout, H., Ahlafi, H., Aazza, M., and Maghat, H. 2018.

- “Critical of linear and nonlinear equations of pseudo-first order and pseudo-second order kinetic models”. *Karbala International Journal of Modern Science* 4: 244-254.
- Mulugeta, M., and Lelisa, B. 2014. “Removal of methylene blue (MB) dye from aqueous solution by bioadsorption onto untreated *Parthenium hysterophorus* weed.” *Modern Chemistry and Applications* 2: 146. doi:10.4172/2329-6798.1000146.
- Noorimotlagh, Z., Mirzaee, S.A., Martinez, S.S., Alavi, S. Ahmadi, M., and Jaafarzadeh, N. 2019. “Adsorption of textile dye in activated carbons prepared from DVD and CD wastes modified with multi-wall carbon nanotubes: Equilibrium isotherms, kinetics and thermodynamic study.” *Chemical Engineering Research and Design* 141: 290-301.
- Silverstein, R.M., Bassler, G.C., and Morrill, T.C. 1981. *Spectrometric Identification of Organic Compounds* (4th ed.). New York: John Wiley and Sons.
- Simonin, J. 2016. “On the comparison of pseudo-first order and pseudo-second order rate laws in the modeling of adsorption kinetics.” *Chemical Engineering Journal* 300: 254 – 263. doi:10.1016/j.cej.2016.04.079.
- Shoaib, M. and Al-Swaidan 2014. “Effect of CO<sub>2</sub> flow rate on the synthesis of sliced activated carbon from date palm tree fronds (Agro waste) by physical activation.” *Asian Journal of Chemistry* 26(20): 7025-7028.
- Tarik, A. Khammour, F., Talbi, M. and Elkouali, M. 2014. “A Novel Bio-adsorbent of Mint Waste for Dyes Remediation in Aqueous Environments: Study and Modeling of Isotherms for Removal of Methylene Blue.” *Oriental Journal of Chemistry* 30(3): 1817. doi: 10.13005/ojc/300332.
- Venkat-Mohan S., Krishna-Mohan S., and Karthikeyan J. 2000. “Adsorption mechanism of acid azo dye from aqueous solution on to coal/coal based sorbents and activated carbon: A mechanist study”. In: *Analytical techniques in monitoring the environment*. (ed. S. Jayarama Reddy). Student offset printers, Tirupathi, India. pp. 97-103.
- Yaseen, D.A. and Scholz, M. 2018. “Treatment of synthetic textile wastewater containing dye mixtures with microcosms”. *Environmental Science and Pollution Research* 25: 1980-1997. <https://doi.org/10.1007/s11356-017-0633-7>