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# **Activated Carbon: Prepared from Various Precursors**

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# Activated carbon: prepared from various precursors

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## **PREFACE**

In the present work, preparation of activated carbon from various agricultural wastes was investigated. Activated carbons have a higher adsorption capacity and large surface area. These carbons could be considered as excellent adsorbent in order to remove dyes, heavy metals and different types of pollutants from wastewater. Physical and chemical activation were used to enhance the porosity, surface area and surface chemistry of materials. The equilibrium data were evaluated using Langmuir and Freundlich model. This book is very useful for students, academicians and researchers.

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## Chapter 1

### Agricultural waste materials for activated carbon preparation: review

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#### ABSTRACT

Activated carbon is an amorphous form of carbon, has a high level of porosity and large surface area. In this review, production of activated carbon from some agricultural wastes by physical and chemical treatment has been discussed. Then, the properties of activated carbon produced from them were investigated. Next, the feasibility of adsorbents for heavy metal, dyes and pollutants removal from the liquid phases has been reviewed. Lastly, adsorption capacity was tested using Langmuir and Freundlich model.

Keywords: activated carbon, surface area, agricultural wastes, carbonaceous, adsorbent isotherm and kinetic model

#### INTRODUCTION

Water is a fundamental human need and we all know water quality is important. Heavy metal pollution has become one of the most serious environmental issues today due to the rapid development of industries such as fertilizer industries, paper industries, metal plating facilities, mining operations, and pesticides. The synthetic dyes are favored in printing, paints, leather, cosmetics and textile industry, should be treated to an environmental acceptable limit. Because of they are made up of chemical compounds that can be harmful to humans.

Activated carbon adsorption is the most popular physicochemical treatment for the removal of heavy metal, dye, pollutants from wastewater because of ease of production and as low cost. Texture characteristics of the activated carbon such as surface area, microspore diameter distribution and total pore volume were investigated by many researchers. Changes

in the texture characteristics of the activated carbon prepared under different conditions were monitored. Currently, agricultural wastes and agricultural by-products were employed as raw materials to prepare activated carbon due to their affordability, local availability and efficiency in removing many pollutants. These precursors include Eucalyptus sheathiana bark [1], Parkia Speciosa Pod [2], Tamarind wood [3], oil bean [4], watermelon seeds [5], waste tea [6], walnut shell [7], Phragmites australis [8], peanut shell [9], Persea Americana [10], coffee grounds [11], sugarcane bagasse pith [12], cocoa nibs [13], oil palm shell [14], rice husk [15], waste coffee residues [16], fir wood sawdust [17], corn cob [18], date pits [19], Ceiba Pentradenta wood waste, Ipomea Carnia stem [20], apple waste [21], wood apple shell [22], Jackfruit [23], orange peels [24], Jatropha husk [25], banana peels waste [26], plum stone [27], Macore fruit [28], rambutan peel [29], coconut shell [30], nut shells [31], apricot stones [32], Euphorbia rigida [33].

Activated carbon has a high level of porosity and large surface area. It is a great adsorbent in order to remove dye, heavy metal and pollutant such as copper [34], dye AR 18 [35], reactive blue 19 [36], polycyclic aromatic hydrocarbons [37], safranin-O [38], lead [39], malachite green dye [40], coomassie brilliant blue R-250 dye [41], direct blue-106 dye [42], sodium, magnesium [43], *para*-nitrophenol [44], reactive blue 2 dye [45], reactive dye Remazol Brilliant Blue R [46], dye acid green 1 [47], disperse Orange 30 dye [48], reactive violet 5 dye [49], nickel [50], beryllium [51] and cadmium [52] from the liquid phases.

This review highlights the preparation of activated carbon from carbonaceous agricultural waste using chemical and physical activated method. Adsorption kinetic will be discussed using Langmuir and Freundlich model.

## LITERATURE SURVEY

Activated carbon has been utilized for purification of drinking water, industrial wastewater and municipal waste water for many years [53]. Water pollution has raised severe environmental impacts as a result of different human activities. Adsorption process by adsorbents indicates potential as one of the most efficient methods for the decontamination of water. It has advantages over the other methods because of simple design, low investment, an effective, and eco-friendly treatment technique. Adsorption is basically a mass transfer process by which the metal ion is transferred from the solution to the surface of sorbent, and becomes bound by physical or chemical interaction [54-56].



Characterization and study of adsorption of methylene blue using activated carbon produced from pineapple peel wastes [57]. Researchers found that as the amount of the adsorbent increased, the percentage of methylene blue removal increased accordingly. Results obtained by other scientists [58] show the removal efficiency of methylene blue (99.5 %) for the activated carbon prepared using pineapple crown under chemical activation such as phosphoric acid.

Oil palm shell activated carbon with the surface area (1058 m<sup>2</sup>/g) and average pore diameter (20.6 nm) could be used to remove lead (99.8%), cadmium (99.5%) and copper (25%) ions [59]. Bakhtiar et al. [60] conclude that adsorption capacity of 4-chloro-2-methoxyphenol was 323.6 mg/g and these data were fitted using Langmuir model. Surface area (1571 m<sup>2</sup>/g), total pore volume (0.8 cm<sup>3</sup>/g) and average pore diameter (2.2 nm) were calculated using the adsorption data. The highest removal of lead (100%), iron (99%) and mercury ions (up to 100%) in the experiment by using palm oil empty fruit bunch activated carbon as suggested by Rafeah et al. [61] and Aeslina & Azi [62].

Optimum conditions for the removal of phenol (pH=6, contact time=1 hour) and cadmium ions (pH=4, 0.8 g adsorbent and 25 °C) by banana peel based activated carbon as proposed by Ramakant et al. [63] and Somaia et al. [64], respectively. The adsorption of copper (100%), cadmium ion (70%) and dye Rhodamine-B (87%) onto banana pith based activated carbon was investigated by Azza et al. [65], and Namasivayam et al. [66], respectively. The obtained activated carbon from banana leaves indicates high surface area (798-1227 m<sup>2</sup>/g), large total pore volume (0.83-1.3 cm<sup>3</sup>/g) and the removal of methylene blue varied between 40-90 % within 20 minutes [67].

Activated carbon prepared from bamboo shows high adsorptive capacity in order to remove organic pollutant [68], color of cotton textile mill wastewater [69], Black 5, phenol, Red E in dye effluents [70], colour in ink wastewater [71], nickel, chromium, lead, cadmium, and copper ions [72].

The preparation of activated carbon from apricot stones was carried out under chemical activation with sulfuric acid. Karima et al. [73] point out that adsorption capacity for the safranine dye about 243-294 mg/g and sorption is increased with increased temperatures and concentrations. Mouni et al. [74] highlight capacity of lead ions adsorbed was 21.4 mg/g, match with second order model and Freundlich isotherm. The apricot stones were treated with phosphoric acid with an impregnation ration of 1:1 as suggested by Sahar & Somaia [75]. The results show that adsorption is best fitted in Langmuir model and pseudo second order kinetic and adsorption capacity of the adsorbents was 147 mg/g for oxamyl.

Adsorption of diuron from aqueous solution using grape seed based activated carbon as suggested by Bahri et al. [76]. These carbons have high surface area ( $1139 \text{ m}^2/\text{g}$ ), egg shell structure and mesopore volume ( $0.24 \text{ cm}^3/\text{g}$ ). The obtained activated carbon treated with nitric acid (activating agent) shows surface area about  $1200 \text{ m}^2/\text{g}$  [77]. The removal of lead and copper ions were carried out at 298 K and pH 5 as stated by Nilay & Aysegul [78].

Utilization of papaya seed for activated carbon preparation and application for the removal of copper ions and methylene blue from aqueous solutions. The maximum uptake capacity of copper ions was found 212 mg/g at pH 6, and stirring rate is 350 rpm [79]. Meanwhile, adsorption capacities of methylene blue were found about 555.5 mg/g [80] and 769 mg/g [81] from different researchers.

The percentage of heavy metal reduction by activated carbon produced using watermelon peel and treated with 1M of sulphuric acid was zinc (1.4 %), copper (99 %), iron (91 %) and lead (100 %) ions [82]. On the other hand, adsorption capacity increases with the increase in initial concentration of the sorbate and when the temperature was reduced as reported by Santosh & Kavita [83].

Adsorption of toxic acid blue 25 and methyl violet 2B from dye effluents using cempedak durian peel as an adsorbent [84]. Adsorption kinetic fitted into Langmuir model with adsorption capacity is 0.06 mmol/g. Muhammad and co-workers [85] have confirmed that cempedak durian fruit contains core, peel, seed and flesh. High maximum adsorption capacity was 0.6 mmol/g for 95 % methyl violet 2B.

Mesoporous structure and thermal stability up to  $200 \text{ }^\circ\text{C}$  could be observed for the activated carbon prepared from avocado seeds by chemical activation with sulfuric acid [86]. The adsorption capacity for Cr(VI) ions was approximately 333.3 mg/g at pH 2. Production of high surface area ( $1432 \text{ m}^2/\text{g}$ ) activated carbon as reported by Leite et al. [87]. Adsorption capacity of resorcinol and 3-aminophenol was 407 mg/g and 454 mg/g, respectively at  $50 \text{ }^\circ\text{C}$ . The adsorption behavior of crystal violet dye on the adsorbent indicated a maximum monolayer adsorption capacity at pH 7 and  $55 \text{ }^\circ\text{C}$  as stated by Bazzo et al. [88].

Durian peel based carbon was chemically treated by sulfuric acid [89]. Adsorbent had removed 69% of bisphenol A with adsorption capacity of 4.2 mg/g for 1 day. Activated carbon prepared with potassium hydroxide treatment responsible for the development of new micropores and also for the enlargement of as-existing micropores to mesoporous as well [90]. The surface area and micropore volume were varied from 467-992  $\text{m}^2/\text{g}$  and 0.13-0.37  $\text{cm}^3/\text{g}$  as shown in their work. Removal of methylene blue and  $\text{Cr}^{6+}$  ions from aqueous solution in different experiment conditions as reported by Erny et al. [91] (0.6M hydrogen peroxide at

700 °C for 30 minutes); Phung & Kien [92] (carbonization temperature =760 K, impregnation ratio =1), Phurada [93] (pH=2, contact time=30 minutes, initial concentration of Cr<sup>6+</sup> =75 mg/L).

Mesoporous high surface area (1608 m<sup>2</sup>/g) and pore volume (1.17 cm<sup>3</sup>/g) activated carbon were produced from *Camellia oleifera* [94]. Microporous activated carbons were prepared by steam at 820 °C [95]. These adsorbents have high surface area (1076 m<sup>2</sup>/g), high adsorption capacity for methylene blue (180 mg/g) and iodine (1012 mg/g). Removal of Cr(VI) ions up to 165 mg/g at pH 2, temperature of 293 K and methylene blue (454 mg/g) was investigated by You et al [96] and Lu et al [97], respectively.

Removal of malachite green dye using rambutan seed activated carbon by potassium hydroxide activation and carbon dioxide gasification method was examined [98]. The percentage dye removal obtained was 91.4% under the best conditions such as activation temperature (802 °C), activation time (60 minutes) and impregnation ratio (2.4). The percentage removal of remazol brilliant blue R reactive dye is 78.4 % in activation temperature of 789 °C, activation time of 1.8 h, and impregnation ratio of 3.5 [99].

Up-to-date, activated carbon has been one of the most effective solutions to water purification issues. I believe that global demand for activated carbon is on an upswing with prospects for future growth looking quite healthy. Activated carbon as a potential green adsorbent was intensively investigated from the point of preparation and adsorption capacity.

## CONCLUSION

Activated carbon prepared from agricultural wastes finds its successful application in removal of various constituents of wastewater. The adsorption kinetics data were fitted to Langmuir model and Freundlich isotherm.

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## Chapter 2

### A Sustainable Method for Optimization of Spent Mushroom Compost Activated Carbon Preparation

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#### ABSTRACT

Optimization of spent mushroom compost activated carbon (SMCAC) preparation is investigated in this study. The objectives of this study are to optimize SMCAC using traditional method with analysis of variance (ANOVA) statistical analysis and compare with Response Surface Methodology (RSM) methods. Chemical activation method using furnace involved parameters such as impregnation ratio of KOH: SMC, activation time and activation temperature. The obtained results were further analysed by ANOVA and compared with RSM methods. The optimized parameters for SMCAC were at 0.5 for impregnation ratio of KOH: SMC, 45 minutes for activation time and 500 °C for activation temperature. At optimized conditions, the quantitative output of percentage yield of activated carbon and qualitative output of iodine number were 20 % and 483 mg/g, respectively. The ANOVA analysis showed all parameters were significantly different for percentage yield but not significant different for iodine number. In comparison with RSM methods, this optimization method with ANOVA analysis is not only more reliable but also contributes towards sustainable since involves energy and chemical saving. This information is utmost important in selection of the best method in optimization of activated carbon that ensures a high quantity and quality for prepared activated carbon. It also contributes toward economical sustainable method approach.

#### 1.0 INTRODUCTION

Optimization study in activated carbon preparation plays a vital role in producing high quantity and quality of activated carbon. Quantitative study generally refers to percentage yield of carbon produced. High percentage of yield is important to ensure continues supplies for industry application. Meanwhile, qualitative study involves surface area and porosity of activated carbon that exhibits the efficiency of activated carbon. Iodine number is the easiest and cheapest titration method to estimate the surface area of activated carbon. Thus, percentage

yield and iodine number are considered as significant outputs in activated carbon preparation (Ahmed, 2016).

Recently, optimization study using Response Surface Methodology (RSM) has been addressed by researchers with the aim to reduce experimental number and evaluate significant of involved parameters (Senthilkumar *et al.*, 2017). The well-known optimization parameters involve impregnation ratio of activation agent with precursor, activation time and activation temperature (Theydan and Ahmed, 2012; Tounsadi *et al.*, 2016). The Box-Behnken Design (BBD) and Central Composite Rotatable Design (CCRD) are the two most well-known RSM methods (Mahmood *et al.*, 2016; Md-Desa *et al.*, 2016; Garba and Rahim, 2016). The BBD is based on an independent quadratic design with combination treatments at the centre and at the midpoints of edges of the process space. Meanwhile, the CCRD consists of  $2_k$  factorial runs and each variable is investigated at two levels. These methods have been widely applied in optimization of activated carbon preparation.

There are still a lot of study using optimization tradition method (Saygili and Guzel, 2016; Saygili *et al.*, 2015). However, this method is not further evaluated using statistical analysis. Therefore, this study focuses on optimization of SMCAC through integration of traditional optimization method and statistical analysis. In addition, there is also limited study on the sustainable evaluation on optimization of activated carbon method, not only in term of outputs but also energy and cost saving as well as chemical minimization.

The objectives of this study are to investigate the optimization of the spent mushroom compost activated carbon (SMCAC) using spent mushroom compost (SMC) by traditional method with analysis of variance (ANOVA) and compare with RSM methods in term of sustainable and cost minimization.

## 2.0 METHODOLOGY

This section involves the sample collection of SMC, optimization of SMCAC preparation and comparison of this method to RSM methods. The SMC and potassium hydroxide (KOH) are used as precursor of activated carbon and activation agent, respectively. The optimization parameters include impregnation ratio of KOH: SMC, activation time and activation temperature. The comparison in methodologies is addressed with the purpose to identify the most reliable and economical sustainable method for two outputs evaluation on yield percentage and iodine number of activated carbon.

## 2.1 Sample Collection

Sample of SMC was collected from the Malaysia largest mushroom cultivation farm namely, C & C Mushroom Cultivation Farm Sdn. Bhd. that located in Johor. After sampling, sample was autoclaved under condition of 121 °C at 15 psi for 15 minutes. After that, sample was dried in oven and ground prior to be used in activated carbon preparation.

## 2.2 Optimization of SMCAC Preparation

The optimization parameters of SMCAC preparation include impregnation ratio of KOH: SMC, activation time and activation temperature. All samples were prepared in duplicates and ANOVA analysis for obtained results was conducted.

### 2.2.1 Impregnation ratio of KOH: SMC

A 10 g of SMC was impregnated with 30 ml of 1.5 M KOH solution that corresponded to ratio of 0.25:1 for KOH: SMC (w/w). The slurry was impregnated for 24 hours and dried at 80 °C for 24 hours. After that, char was produced using a furnace at temperature of 600 °C for 60 minutes with set heating rate 10 °C/min. The KOH residual in the sample was removed by washing with 1M hydrochloric acid (HCl) and distilled water until the obtained pH was neutral (pH 7). The sample was dried in an oven at 80 °C until a constant weight. Finally, the prepared activated carbon was sieved to size 150 µm and kept in drying cabinet. The percentage of activated carbon yield was calculated for quantitative estimation as described in Equation 2.1. The iodine number was conducted according to ASTM D4607 standard method.

$$\text{Percentage yield (\%)} = \frac{W_{AC}}{W_{SMC}} \times 100\% \quad (\text{Equation 2.1})$$

where  $W_{AC}$  is weight of activated carbon (g),  $W_{SMFW}$  is weight of dried SMC (g)

The preparation of ratio KOH: SMC was repeated for 0.50:1, 0.75:1, 1:1 and 1.25:1 (w/w). The optimum condition of ratio was selected for the next parameter.

### 2.2.2 Activation time

The sample impregnated ratio selected from Section 2.2.1 was prepared and dried at 80 °C for 24 hours. After that, the sample was burnt using a furnace at temperature of 600 °C and activation time of 30, 45, 60, 75 and 90 minutes. Then, the sample was washed with 1M HCl and distilled water to remove KOH residual until neutral in pH. Lastly, the sample was dried



and sieved to 150  $\mu\text{m}$ . The percentage of activated carbon yield and iodine number were determined as in Section 2.2.1. The optimum condition of activation time was selected for the subsequent experiments.

### 2.2.3 Activation temperature

The selected sample impregnated ratio from Section 2.2.1 was dried at 80  $^{\circ}\text{C}$  for 24 hours. Next, the sample was burnt at selected optimum activation time from Section 2.2.2 using a furnace at various activation temperatures of 500, 600 and 700  $^{\circ}\text{C}$ . Then, the KOH residual of sample was washed using 1M HCl and distilled water. After that, the washed and pH neutral sample was dried for 24 hours and sieved to particle size of 150  $\mu\text{m}$ . The percentage of activated carbon yield was calculated as Equation 2.1 in Section 2.2.1. For iodine number, it was investigated via ASTM D4607 standard method (section 2.2.1).

## 2.3 Comparison of This Study Optimization Method to RSM Methods

The Box-Behnken Design (BBD) of RSM for SMCAC preparation and optimization reported by Md-Desa *et al.* (2016) was assessed. In addition, Central Composite Rotatable Design (CCRD) of RSM was also evaluated (Tay *et al.*, 2015). The literature review on RSM methodologies in optimization study of activated carbon preparation were compared to this study. The three inputs and two outputs evaluation were investigated to identify the most reliable and economical sustainable method.

## 3.0 RESULTS AND DISCUSSION

Results obtained through experimental work and data analysis on optimization of SMCAC preparation are discussed in this section. Identification of the most reliable and economical sustainable method to optimize the SMCAC is evaluated in this section.

### 3.1 Optimization of SMCAC Preparation

The results of impregnation ratio, activation time and activation temperature are discussed in detail. The quantitative analysis for SMCAC was measured by percentage of yield meanwhile qualitative analysis was quantified by iodine number.

#### 3.1.1 Impregnation ratio of KOH with SMC

Figure 3.1 shows percentage yield and iodine number of SMCAC at different impregnation ratio of KOH: SMC. The carbon yields slightly increased 1 % from 17 % to 18 %

by increasing impregnation ratio from 0.25 to 0.50. The carbon yield was then decreased gradually from 18 % to 12 % with IR range from 0.50 to 1.25. Decreased in the carbon yield with an increase of impregnation ratio was due to the weight loss of the volatile matter released through dehydration and elimination reactions during carbonization stage (Tan *et al.* 2008). This observation was supported by Abechi *et al.* (2013) in activated carbon preparation using palm kernel shell.

On the other hand, the iodine number increased from 300 mg/g to 500 mg/g with increased the impregnation ratio from 0.25 to 1.25 (Figure 3.1). Increased in impregnation ratio enhanced the catalytic oxidation during carbonization and widened the activated carbon pore size, more micropores were formed which increased the surface area (Liu *et al.*, 2016). The increased of activated carbon porosity resulted in the raised of iodine number. This was supported by Li *et al.* (2016) and Saka (2012) in preparation of activated carbon from coffee shell and corn shell, respectively.

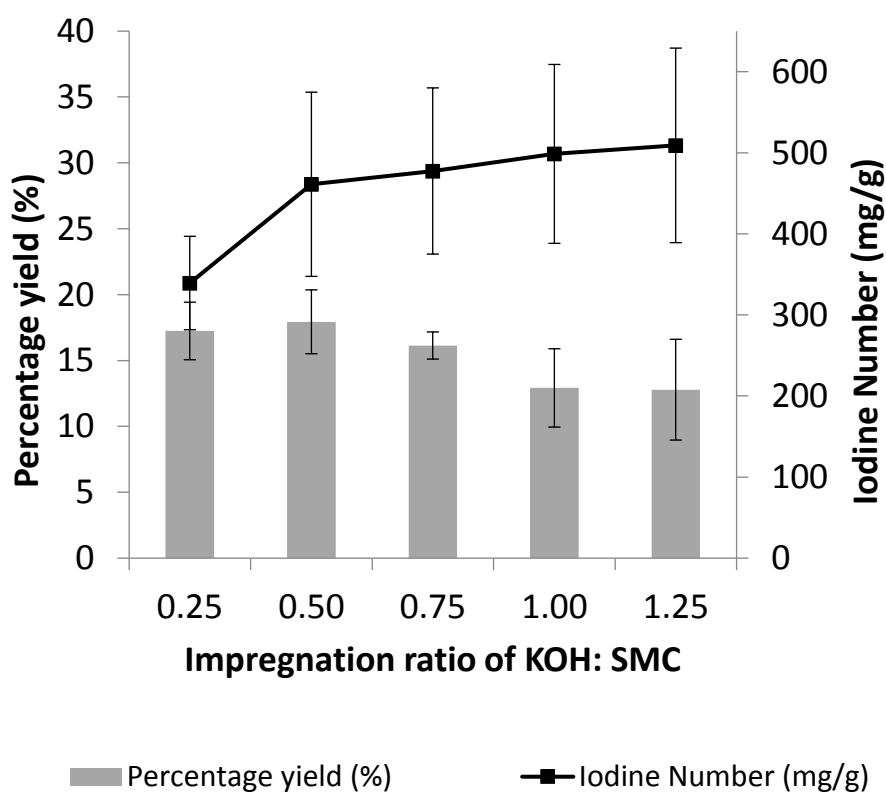


Figure 3.1 The percentage yield and iodine number of SMCAC at different impregnation ratio of KOH: SMC.

In this study, the condition of 0.5 impregnation ratio with carbon yield of 18 % and iodine number of 461 mg/g has been chosen for further studies. This is due to the highest carbon yield which is a crucial parameter compared to iodine number. Carbon yield is essential to provide the continuous supply of materials for industry applications with acceptable pore size indicated by iodine number. The result was supported by ANOVA statistical analysis. The impregnation ratio was a significant parameter ( $p < 0.05$ ) in optimization of carbon yield but not significant ( $p > 0.05$ ) for iodine number. In addition, minimization in use of chemical is in-line with cost effectiveness and sustainable approaches.

### 3.1.2 Activation time

Figure 3.2 shows percentage yield and iodine number of SMCAC at different activation time. The carbon yield was slightly increased from 19 % to 20 % by increasing of activation time from 30 minutes to 45 minutes and generally decreased to 14 % from 45 minutes to 90 minutes. This is consistent with study by Foo & Hameed (2012), that reported as the activation time increased, the percentage of carbon yield decreased in preparation of activated carbon from wood sawdust. Longer activation time led to destruction of carbon structure, decomposition of cellulose components, loss of volatile element and thus produced lower yield (Salman & Abid, 2013).

The highest value of iodine number recorded was 483 mg/g at 90 minutes of activation time. Meanwhile, there is no significant different of the value for iodine number between 30 minutes to 90 minutes. This indicates that surface area stable at elevated carbonization time (Dizbay-Onat *et al.*, 2017). Longer activation time increased the pore structure and showed an inverse relationship with carbon percentage yield (Bouchelte *et al.* 2012; Li *et al.*, 2016).

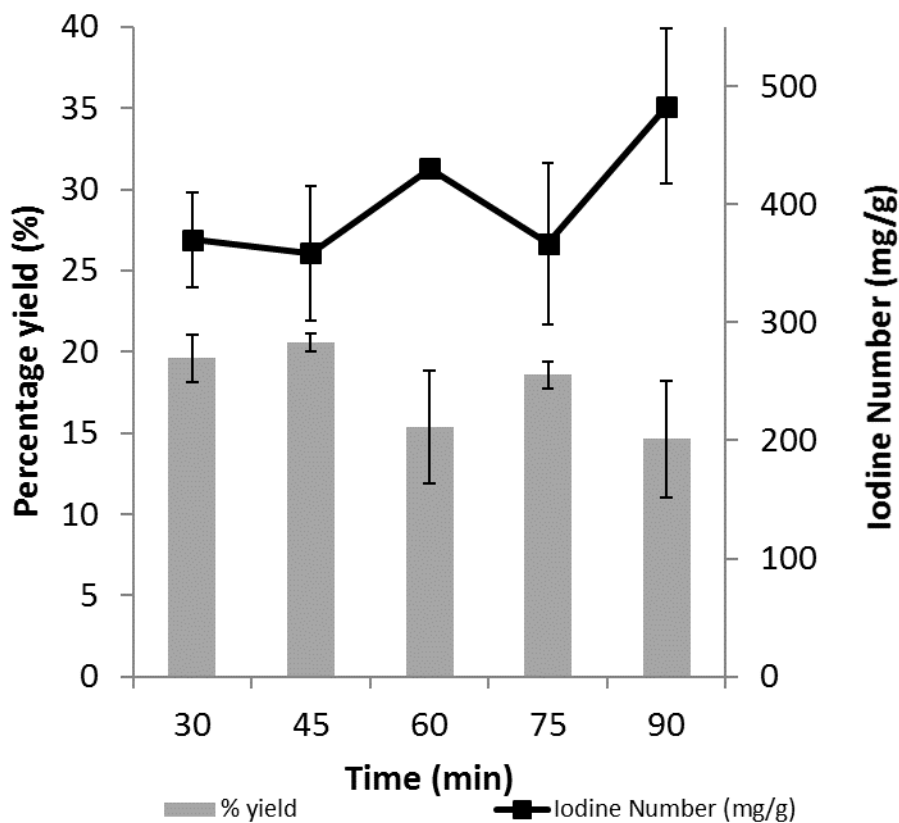


Figure 3.2 The percentage yield and iodine number of SMCAC at different activation time.

In this study, the 45 minutes of activation time at carbon yield of 21 % and iodine number of 358 mg/g has been chosen due to the highest carbon yield obtained with acceptable iodine number which suitable for industrial application. The selected condition also is considered as the most economic interest due to energy consumption minimization in order to reduce production cost of activated carbon. The result was supported statistically by ANOVA analysis that showed activation time was a significant parameter in carbon yield ( $p < 0.05$ ) but not for iodine number ( $p > 0.05$ ).

### 3.1.3 Activation temperature

Figure 3.3 shows the percentage yield and iodine number of activated carbon at different activation temperatures. The carbon yield decreased from 21 % to 10 % by increased of activation temperature from 400 ° C to 700 ° C. This was due to the loss of volatile matter as temperature increased during carbonization stage. Meanwhile, the iodine number was almost constant from 400 ° C to 600 ° C but increased at 700 ° C. Increased of the temperature resulted in increasing devolatilization which further developed the pore structure and increased the iodine number (Liu *et al.*, 2016). The trend of carbon yield and iodine number in this study

had been supported by Danish *et al.* (2014) and Sentorun-Shalaby *et al.* (2006). Such study reported that at higher activation temperature, activation of precursor became more extensive and resulted in a lower carbon yield.

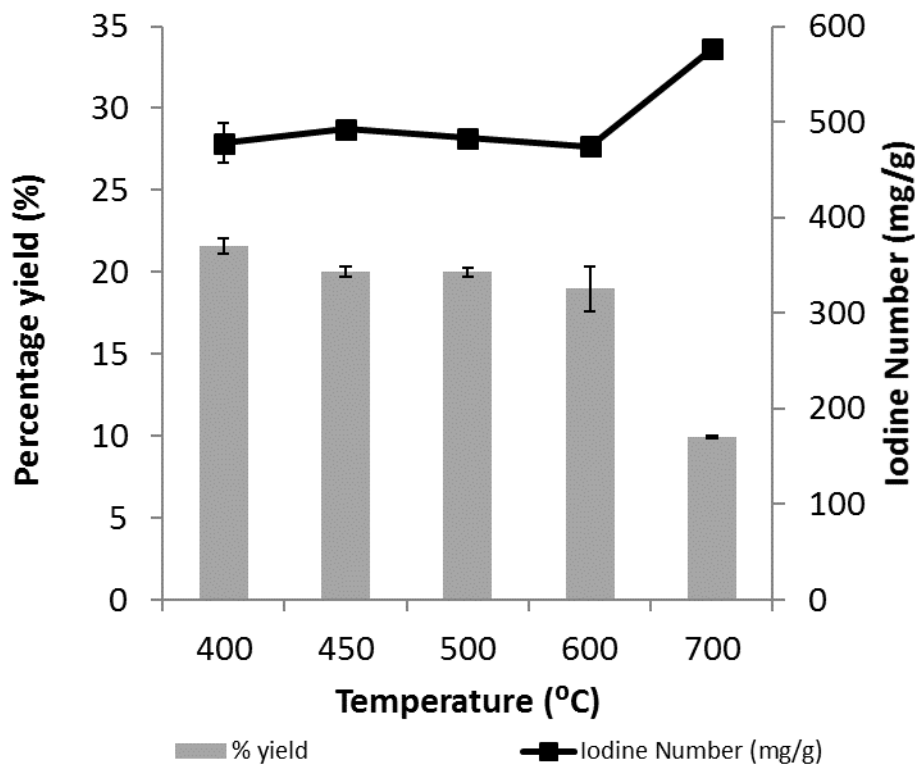


Figure 3.3 The percentage yield and iodine number of activated carbon at different activation temperatures.

The 500 ° C was chosen as activation temperature at 20 % of carbon yield and 483 mg/g of iodine number due to acceptable value determination of carbon yield. The highest value of carbon yield at 400 - 450 ° C was not relevant as the carbonization process of precursor was not completed. The optimization of carbon yield was statistically significant in activation temperature according to ANOVA analysis ( $p < 0.05$ ) but not for iodine number ( $p > 0.05$ ). The activation temperature of 500 ° C is beneficial for energy conservation and suitable for industrial applications.

### 3.2 Comparison of This Study Optimization Method to RSM Methods

Table 4.1(a) and (b) summarize statistical analysis for method comparison between RSM and this study. For percentage yield (Table 4.1(a)), BBD of RSM method and this study shared the similar statistical analysis result where all parameters showed significant different and played major roles in activated carbon preparation. CCRD of RSM method also

demonstrated significant different in impregnation ratio KOH: SMC and activation temperature parameters. However, CCRD of RSM method showed not significantly different in activation time parameter. This indicates that BBD and this method are reliable methods to optimize and interpret the percentage of carbon yield in activated carbon preparation.

Table 4.1 Statistical analysis for comparison of methods between RSM and this study (a) percentage yield (b) iodine number

(a)

Methods	Statistical analysis for percentage yield		
	Ratio KOH: SMC	Activation time, minutes	Activation temperature, °C
This study	Significant	Significant	Significant
BBD, RSM	Significant	Significant	Significant
CCRD, RSM	Significant	Not significant	Significant

(b)

Methods	Statistical analysis for iodine number		
	Ratio KOH: SMC	Activation time, minutes	Activation temperature, °C
This study	Not significant	Not significant	Not significant
BBD, RSM	Significant	Significant	Significant
CCRD, RSM	Not significant	Not significant	Significant

This study showed not significantly different for all investigated parameters in iodine number output (Table 4.1(b)). Meanwhile, BBD of RSM method showed significant different for all investigated parameters for iodine number output. On the other hand, CCRD of RSM method shared partial similar result with this study that limited to impregnation ratio KOH: SMC and activation time only. There was significant different in activation temperature parameter for CCRD of RSM method. This reveals that CCRD and this method are more reliable for iodine number evaluation in activated carbon preparation.

It could be suggested that this study is better than the BBD and CCRD of RSM methods as it is a reliable method to evaluate two outputs in optimization of activated carbon preparation. These includes quantitative output of percentage yield and quality output of iodine number.

Table 4.2 presents the method comparison study on optimized conditions and outputs among BBD, CRD and this study. This study method is an excellent method when compared to BBD of RSM method. This is because this study exhibited 10 – 33 % in energy saving and

50 % in chemical minimization with increased of outputs 15 % for percentage yield and 10% for iodine number. On the other hand, this study is comparable to CCRD of RSM method as this method reduced 20 - 50 % energy consumption and 60 % chemical usage with increased percentage yield output 25 % but decreased 11 % in iodine number. Therefore, this study is a reliable and sustainable method as it contributes towards energy and chemical minimization as well as cost effectiveness in order to produce a high quantity and quality activated carbon.

Table 4.2 Comparison study on optimized conditions and outputs among BBD of RSM, CCRD of RSM and this study

Optimized conditions/ outputs	Methods			Comparison	
	This study (A)	BBD, RSM (B)	CCRD, RSM (C)	A VS B, %	A VS C, %
Optimized conditions					
Ratio KOH: SMC	0.5	0.75	0.8	-50	-60
Activation time, minutes	45	60	67.5	-33	-50
Activation temperature, °C	500	550	600	-10	-20
Outputs					
Percentage yield, %	20	17	15	15	25
Iodine number, mg/g	483	433	537	10	-11

#### 4.0 CONCLUSION

This study focuses on optimization of SMCAC with ANOVA statistical analysis in order to produce high quantity and quality activated carbon. Furthermore, comparison to RSM methods were evaluated with purpose to identify the most efficient and sustainable methodology. Chemical activation for activated carbon preparation with optimization parameters of impregnation ratio KOH: SMC, activation time and activation temperature were conducted. Results of percentage of carbon yield and iodine number were analysed using ANOVA analysis. Comparison to RSM methods was conducted with purpose to identify the most economical, effective and sustainable method in activated carbon preparation. The optimized parameters for SMCAC preparation were found to be 0.5 impregnation ratio KOH: SMC, 45 minutes activation time and 500 °C activation temperature. Such optimized conditions yielded 20 % percentage of activated carbon and 483 mg/g iodine number. The ANOVA for optimized parameters are significantly different for percentage yield while not significantly

different for iodine number. For comparison study, the percentage yield statistical analysis of this study is consistent with BBD of RSM method where all parameters are significant. However, such comparison study showed an opposite result for iodine number. On the other hand, CCRD of RSM method showed inconsistent results when compared to this study. This study exhibited a high reliability and contribute in economical, effective and sustainable methodology development in activated carbon preparation. This study leads to integration of economical and sustainable approaches in production of high quantity and quality of activated carbon to ensure excellent performance of activated carbon in removal of contaminants.

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### Chapter 3

## PANDANUS AMARYLLIFOLIUS WASTE-BASED ACTIVATED CARBON FOR COLOR AND COD REDUCTIONS IN TEXTILE WASTEWATER

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### ABSTRACT

The synthesis of activated carbons from *pandanus amaryllifolius* stem (PSAC) through physicochemical activation have been successfully investigated. The physicochemical activation was carried out by using potassium hydroxide (KOH) impregnation and carbon dioxide (CO<sub>2</sub>) gasification. The adsorption performance of the PSAC was evaluated through the reduction of color and COD of industrial textile effluent. By using an experimental design, the results revealed that the activation temperature, activation time and KOH impregnation ratio (IR) were significant factors influencing the adsorption performance for all pollutants. The optimum preparation conditions of PSAC were 794°C, 1.19 h and 2.75 for activation temperature, activation time and IR, respectively. PSAC gave reduction color and COD of 75.40 % and 61.10 %, respectively. Adsorption of all adsorbates onto PSAC was best fitted by Langmuir model.

Keyword: Activated carbon, textile waste water, physicochemical activation, textile waste water

### 1.0 Introduction

Textile industries contributed a part in the economy activity of several countries around the world, including Malaysia. Total numbers of textile manufacturer in Malaysia about 1500 and these amounts keep increasing with the demand of textile products (Ismail *et al.*, 2015a). Most textile industries deal with several processing stages; fiber manufacturing, processing and spinning, preparation of yarn, fabric manufacturing, bleaching process, coloring and printing and finishing (Hayat *et al.*, 2015). However, each process produces by productions in which appropriate treatments are required. As a matter of fact, textile industry uses various kinds of solvents and chemicals in the wet processes throughout the whole production lines. Therefore, the textile industry produces wastewater that contain high concentration of salts, dye color, chemical oxygen demand (COD), nutrients (nitrogen and phosphorous) and toxic compounds (Ahmad *et al.*, 2015). Textile industry also exposed to continuous demand in term of quality, innovation and durability. This results in further increase in chemicals usage in order to cope with the market demand. Continuous demand in term of quality, innovation and durability has caused textile operators searching for fastness, rapid and durable chemicals products in order to meet the market supply. Consequently, further increased in chemicals usage in order to cope with the market demand have led to excessive wastewater generation which need to be treated efficiently. Textile wastewater that directly released into the environment can induce potential risk to water bodies as the effluent is toxic to the environment and living organisms (Freitas *et al.*, 2015). Therefore, these wastes need to be treated before discharging it into the environment. In Malaysia, the wastewater containing dyes have been classified as schedule wastes under the Environmental Quality Regulation 1989 (Ismail *et al.*, 2015b). In response to such event, stringent legislation on discharge quality as per requirement of Environmental Quality Act of Malaysia further constrains the industry to comply. Therefore, continuous study and research on the textile wastewater treatment is needed for sustainable the environment.

## 2.0 Pollutants Removal

### 2.1 Colorant

Color is a detectable pollutant and its presence damages the aesthetic quality of surface waters, affects and changes the aquatic ecosystem by hindering the penetration of light (Hayat *et al.*, 2015). There are three large groups of colorant, which are natural, organic and inorganic (Verma *et al.*, 2015). The most important differentiation of colorant is that colorant is either dyes or pigments. These terms are often used indiscriminately, in particular, pigments are quite

often considered to be a group of dyes. Ideal pigments are characterized by being practically insoluble in the media in which they are applied, for example, by a polymer in paint, in a plastic or in a melt (Pang *et al.*, 2013).

## 2.2 Chemical Oxygen Demand (COD)

The chemical oxygen demand (COD) is an indirect measurement of the amount of organic compounds presence in water/wastewater. As COD can determine the amount of organic pollutants found in surface water, it is a critical tool in describing the quality of water. It is expressed in milligrams per liter (mg/L) or parts per million (ppm), which indicates the mass of oxygen consumed per liter of solution (Yadav *et al.*, 2013). In other words, the COD determine the presence of potential overall oxygen in wastewater sample which also includes the oxidizable components not excluded in the BOD analysis (Zhen *et al.*, 2013).

Untreated wastewater discharged from fabric processing, yarn printing, and coloring using dye are dangerous to environment because of their color. Biological treatment process is usually efficient for the removal of BOD<sub>5</sub> and suspended solids, but its low efficiency and low reaction rate of treatment are unsatisfactory. With different types of activated sludge treatment methods, the following removals are normally achieved: about 90 % of BOD<sub>5</sub>, 40–50 % of COD and 10–30 % of color (Yadav, *et al.*, 2013). Whereas for color and COD removal, textile wastewater is generally treated with lime or ferrous sulphate and very effective with 70–90 % and 50–60 %, respectively (Pang *et al.*, 2013). Another treatment are ozone process and Fenton's oxidation which are used to remove the COD in range of 33 % and 59 % while color removal was 91 % and 89 %, respectively (Ismail, *et al.*, 2015a).

## 2.3 Pandanus Amaryllifolius Waste-Based Activated Carbon (PSAC)

*Pandanus amaryllifolius* originates from Pandanus (screwpine) genus, a tropical plant, known as pandan leaves (Han *et al.*, 2014). It functions as an extra flavor in Southeast Asian cooking (Bhattacharjee *et al.*, 2005). The pleasant smell comes from aroma compound of 2-acetyl-1-pyrroline. In general, the genus Pandanus is belonging to the family Pandanaceae which comprises about 600 species and widely distributed in tropical and subtropical regions. The leaves have been used as traditional medicine as reported by Takayama *et al.*, (2001) for many years. The plant can be found in the wild, but also widely cultivated. The *pandanus*

*amaryllifolius* left some residues after cultivation such as their stems. The plant also possess several medicinal properties such as antispasmodic, diuretic, and stimulant properties .

Nowadays the main challenges for waste utilization especially from pandanus genus, is the development of specific properties and the reduction of processing costs. Previous literature has shown that pandanus leaves have been employed for natural repellent, cancer anti-oxidant), anti-fungal and biosorben (Ismail *et al.*, 2013). However, it is important that optimum operating criteria and processing conditions be established to ensure prime quality of pandanus based activated carbon is determined. In this work, pandanus amaryllifolius stem was utilized as precursor for AC production for color and COD removal.

#### 2.4 Preparation Method of Pandanus Amaryllifolius Waste-Based Activated Carbon (PSAC)

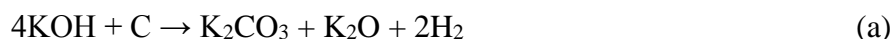
Activated carbon can be prepared either by using only single step pyrolysis or two step pyrolysis. In single step pyrolysis, the carbonization and activation step are simultaneous, whereas the latter, the activation is after the carbonization (Djilani *et al.*, 2015).

Carbonization is a non-oxidized thermal process for the conversion of raw material into solid char. This process enriches the carbon content and creates initial porosity in the char. The carbonization temperature commonly ranges between 400 to 850°C. During the carbonization process, components in agricultural waste (hemicelluloses, cellulose and lignin) would undergo dehydration reaction and linkage breaking to form solid char.

Activation is a process to enhance of char porosity and removal of tar residing and clogging the pores. There are three types of activation of char; physical, chemical and physiochemical. In physical activation, the char is pyrolyzed at elevated temperature under oxidizing atmosphere using gases such as, oxygen (O<sub>2</sub>), carbon dioxide (CO<sub>2</sub>), and steam. CO<sub>2</sub> is preferable since it is easy to handle and clean. The activation temperature is normally set higher than 900 °C to sustain high reaction rate. The reaction between carbon atom and the oxidizing gas gives rise to the pore creation and enlarge the existing pores (Njoku *et al.*, 2014)

On the other hand, chemical activation is normally carried out with char being impregnated with chemical activating agents such as ZnCl<sub>2</sub>, KOH, H<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub> and NaCO<sub>3</sub> (Nowicki et al, 2015)). Chemical activation has advantages over physical activation as it can be performed at lower temperatures (450 °C - 900 °C) and shorter times. The impregnation

ratio (IR) is calculated by the weight ratio of the char sample to the chemical used. Optimum IR is important for the development of porous structure of the adsorbent, particularly the surface area. It leads to the formation of large surface area and high adsorption capacity. KOH is an effective activating agent due to its selectiveness in activation process. The chemical reaction between KOH and carbon material are as follows.



However, excessive IR can insulate the adsorbent in a form of layer, resulting pore blockage. Yadav *et al.*, 2013 found that at very high IR of KOH, white spheres and fluffy materials were appeared which indicated the presence of  $\text{K}_2\text{O}$  and  $\text{K}_2\text{CO}_3$  or K residues accumulated on the porous surface. Hence, optimum IR is required to achieve a highly porous characteristics of AC.

Physicochemical activation consists of both physical and chemical treatment. The sample was first impregnated with chemical agent similar as chemical activation technique, before undergo  $\text{CO}_2$  activation to produce AC. This chemical interferes with the pyrolytic decomposition and retards the tars formation during the activation process. The presence of chemical raises the pore size and porosity of AC in addition to  $\text{CO}_2$  gasification (Ismail *et al.*, 2015a). The combination of chemical and physical treatment has the potential to improve pore development at lower activation temperature, ranging from  $600\text{ }^\circ\text{C}$ - $900\text{ }^\circ\text{C}$  due to the effect of chemicals (Hameed *et al.*, 2009). Therefore, it will reduce the consumption of energy by aids of chemical treatment for production of AC.

## 2.5 Adsorption Isotherm

Adsorption is usually described by the quantity of adsorbate settling onto the adsorbent against pressure (if gas) or concentration (if liquid) isothermally. The isotherm describes the distribution of adsorbed molecules between the liquid and solid phase at equilibrium state. It is necessary to establish the most appropriate adsorption isotherm for different adsorbent system for purpose of designing the adsorption system (Ismail *et al.*, 2015b).

Common isotherm models such as Langmuir and Freundlich are used to interpret the adsorption data. The isotherm models are utilized to fit the experimental equilibrium data. Linear regression method had been chosen to estimate the isotherm parameters. The analysis of fitting degree of isotherm with the experimental data was represents by coefficient of determination,  $R^2$ . The values vary from 0 to 1, whereas the closest  $R^2$  to unity and the lowest %

error values represents suitable parameter to correlate the adsorption behavior (Ismail *et al.*, 2015a).

### 2.5.1 Langmuir Isotherm

The Langmuir adsorption isotherm has been most widely used sorption isotherm for the sorption of a solute from a liquid solution. This model depends on the assumption that intermolecular forces decrease rapidly with distance and consequently help to predict the existence of monolayer coverage of the adsorbate on the outer surface of adsorbent. The Langmuir model is expressed as:

$$q_e = \frac{Q_o K_L C_e}{1 + K_L C_e} \quad (1)$$

The linear form of Langmuir isotherm equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{1}{Q_o} C_e \quad (2)$$

where  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g),  $Q_o$  is the maximum monolayer adsorption capacity of the adsorbent (mg/g) and  $K_L$  is the Langmuir adsorption constant related to the free energy adsorption (L/mg). The constant value can be evaluated from intercept and slope of the linear plot of experimental data of  $(C_e/q_e)$  versus  $C_e$ . The essential characteristics of Langmuir equation can be expressed in terms of dimensionless separation factor,  $R_L$ , defined as:

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (3)$$

Where  $C_o$  is the highest initial solute concentration whereas  $R_L$  value implies the adsorption to be unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ) (Ismail *et al.*, 2015a).

### 2.5.2 Freundlich Isotherm

The Freundlich model is an empirical equation based on adsorption of heterogeneous surface or surface supporting sites of varied affinities. It is assumed the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. Freundlich isotherm is expressed as:



$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

where  $q_e$  is amount of adsorbate adsorbed per unit mass of adsorbent (mg/g);  $K_f$  is Freundlich isotherm constant (mg/g).(L/mg)<sup>1/n</sup>; which indicate the relative adsorption capacity of the adsorbent related to the bonding energy;  $C_e$  is equilibrium concentration of the adsorbate (mg/L) and  $n_F$  is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. The equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log q_e = \log K_f + (1/n) \log C_e \quad (5)$$

A plot of ( $\log q_e$ ) against ( $\log C_e$ ) yielding a straight line indicates the confirmation of the Freundlich isotherm for adsorption. The constant can be obtained from the slope ( $1/n$ ) and intercept ( $\log K_f$ ) of the linear plot of experimental data. The  $n_F$  parameter indicates whether the adsorption is linear ( $n_F = 1$ ), chemical process ( $n_F < 1$ ) or physical process ( $n_F > 1$ ). The slope of  $1/n$  ranging between 0 and 1 is a measure of adsorption intensity, becoming more heterogeneous as its value gets closer to zero (Hameed *et al.*, 2009).

### 3.0 Analytical Methods

All tests (color and COD) were conducted in accordance with the Standard Methods for the Examination of Water and Wastewater (APHA, 2009). Color concentration was measured as apparent color by DR 6000 (HACH, USA) spectrophotometer and the wavelength was fixed at 455 nm (Program number 120) based on Method No. 8025. The sample cells used were strictly following manufacturer recommendation 2495402, whereby the fill line faces right of the cell orientation. COD test was done according to Method 8000 (Program number 435) for high range concentrations (20-1500 mg/L). The COD reagent was obtained from HACH. Prior to measurement, the COD vial was first filled with 2.5 mL of sample and preheated on a reactor for 2 h at 150 °C. The wavelength was set at 620 nm while pH of the textile wastewater was measured by a bench top pH meter PC 2700 (Thermo Scientific, USA).

### 3.1 Activated Carbon Preparation

The experimental setup to prepare the activated carbon (AC) is shown in Figure 3.3. The AC preparation rig consists of stainless steel (SS) vertical tubular reactor equipped with

programmable temperature controller. The gas flow meter was used to control the flow rates of  $N_2$  and  $CO_2$  supplied to the reactor. The piping system was mainly made of Teflon and SS fittings and pipes. The vertical stainless steel reactor with dimension of 150 mm long and 25 mm inner diameter were used to carry out carbonization and activation processes. A SS wire mesh was positioned at the bottom part of the tubular reactor to hold the sample intact.

The reactor was stand and placed inside a vertical tubular furnace with programmable controller (Model Carbolite, USA). The dimension of the furnace was 500 mm length and 82 mm inner diameter. A K-type thermocouple was used to measure the temperature of the sample inside the reactor. The maximum tolerance of the thermocouple is  $1000\text{ }^\circ\text{C}$ . The excess flue gas was released to a condenser.

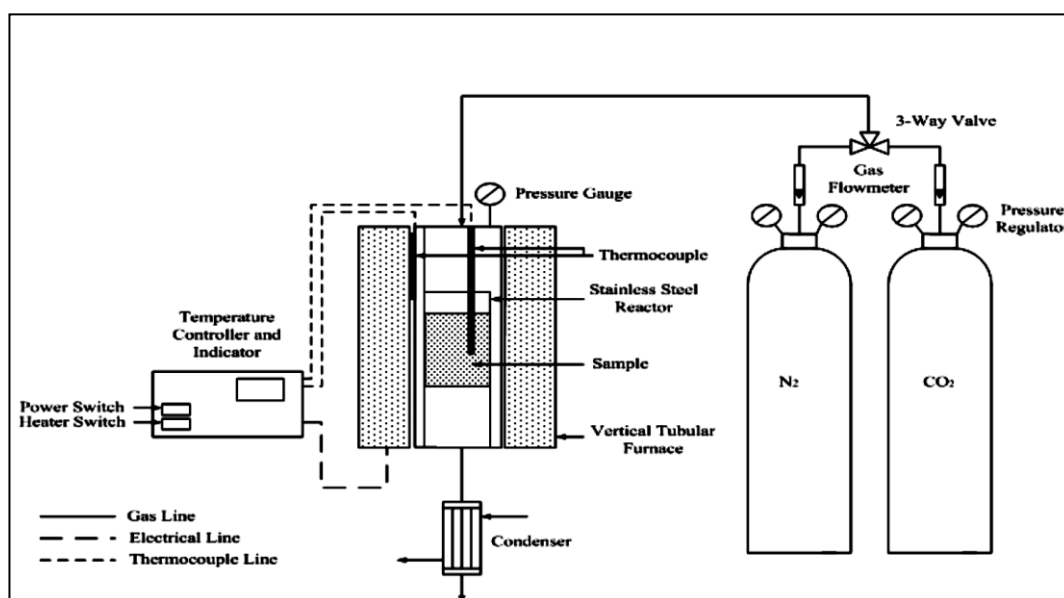


Figure 1.0: Schematic diagram of the experimental setup for activated carbon production

### 3.2 Precursor Preparation

The Pandan stems (PS) samples were washed and cleaned dried in an oven (Model Heraeus Series 6000 Oven, Germany) at temperature of  $120\text{ }^\circ\text{C}$  for 2 hours. The dried samples were cut into 2-3 cm and kept in a hermetic container.



Plate 1.0: Precursors a) *Pandanus amaryllifolius* stems

### 3.2.1 Activated Carbon Synthesis

The activated carbon preparation procedures were divided into three main stages consists of:

- i. Carbonization of the precursors
- ii. KOH impregnation of char
- iii. CO<sub>2</sub> gasification of the KOH-impregnated chars

#### 3.2.1(a) Carbonization

A thirty gram (30 g) of precursor was put inside a vertical reactor (Figure 3.3) continuously purged with nitrogen gas at 150 mL/min. The reactor temperature was ramped to 400 °C and held for 2 h. After that, the char produced was cooled down to room temperature. Then they were stored inside a dessicator about 2 h for further treatment.

#### 3.2.2(b) KOH Impregnation

The impregnation of char in powder form (250 μm) with potassium hydroxide (KOH) was done in various impregnation ratio (IR) calculated in Eq. 3.2; 
$$IR = \frac{w_{KOH}}{w_{char}} \quad (3.2)$$

where  $w_{KOH}$  is the dry weight (g) of KOH pellet and  $w_{char}$  is the dry weight (g) of char. A specific amount of char and KOH pellet (depending on the IR) was mixed together with deionized water in a 250 mL beaker. The mixture was stirred thoroughly until completely dissolved and have been put in oven overnight at temperature 105 °C for dehydration.

### 3.2.2(c) Carbon Dioxide Gasification

The KOH-impregnated char was then heat-treated with continuous flow of nitrogen at 150 mL/min. The required temperature was increased at 10 °C/min. Once the desired activation temperature was reached, the nitrogen was switched to carbon dioxide (CO<sub>2</sub>) at 150 mL/min and held for a time duration which suggested by Response Surface Methodology (RSM) analysis. The CO<sub>2</sub> was switched back to N<sub>2</sub> (1 h) for the sample to cool to room temperature.

The AC was then washed with deionized water and hydrochloric acid to obtain the neutral value of pH. It was measured by using pH meter (Model Delta 320, Mettler Toledo, China). The AC was dried in oven at 105 °C for 24 hours. The dried AC was stored in dessicator for characterization and further adsorption studies.

### 3.2.2(d) Experimental Design

This study utilized response surface methodology (RSM) with central composite design (CCD) analysis to optimize the studied parameters. The independent variables include;

- i.  $x_1$ , Activation temperature (°C)
- ii.  $x_2$ , Activation time (h)
- iii.  $x_3$ , KOH: char (IR)

These variables and their respective ranges were selected based on the literature and the results obtained from the preliminary studies. As a matter of facts, this analysis used Design Expert software version 7.1.5 (STAT-EASE Inc., Minneapolis, USA) to develop regression model and evaluate the significance of responses. Table 1.0 shows the range levels of each factor (variable) studied.

Table 1.0: Independent variables and their coded levels for the CCD

Variables (factors)	Coded variables level				
	$-\alpha$	-1	0	+1	$+\alpha$
Activation temperature (°C)	514	600	725	850	935
Activation time (hour)	0.32	1.00	2.00	3.00	3.68
IR	0.07	0.75	1.75	2.75	3.43

In this study, *Pandanus amaryllifolius* stems were successfully used to produce PSAC using physiochemical activation method. The optimum preparation conditions of PSAC were 794°C, 1.19 h and 2.75 for activation temperature, activation time and IR, respectively.

#### 4.0 Adsorption on Equilibrium for Textile Wastewater

Figures 2.0 - 3.0 show the effect of contact time on the removal of color and COD from textile wastewater. From the figures, both ACs exhibited similar pattern to the synthetic dyes removal. Color percent removal increased with time and reached an equilibrium value signifying saturated adsorption. As it reaches equilibrium, the adsorption rate decrease as the remaining vacant site requires higher repulsive force between the adsorbate on the solid and bulk phase (Shoaib et al, 2015).

Color removal at optimum condition were found at 75.40 % while COD maximum removal were found at 61.10 % for PSAC. In general, the adsorption performance at different concentration varied with the type of adsorbate and adsorbent used. In this case, the characteristics of the ACs influence the adsorption performance.

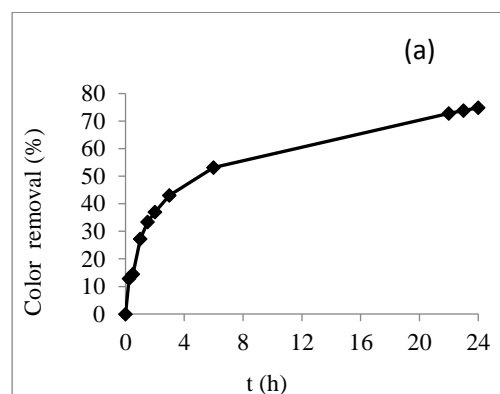


Figure 2.0: Color percent removal versus adsorption time at 30°C for PSAC

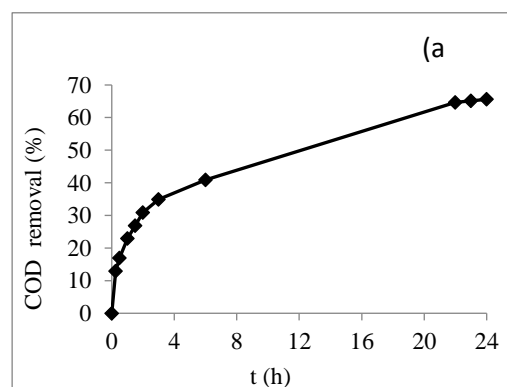


Figure 3.0: COD percent removal versus adsorption time at 30°C for PSAC

#### 4.1 Adsorption Isotherms for Textile Wastewater

Industrial wastewater adsorption isotherm data for color and COD isotherms at the different adsorbent was fitted with Langmuir and Freundlich models. Tables 2.0 - 3.0 showed that the isotherms model were well fitted to the experimental data for removal color and COD on PSAC. The Langmuir isotherm gave slightly closer fittings than other models as it was obvious from a comparison of the coefficient of determination ( $R^2 > 0.98$ ) within the range of adsorbent doses considered. The well fitted isotherm data by the Langmuir suggested that monolayer coverage of COD and color on PSAC. Value of  $1/n$  and  $K_F$  with  $R^2$  values calculated using linear equation. The value of  $1/n$  was found below 1.0 for PSAC, suggesting that the adsorption condition was favourable.

Table 2.0: Isotherm parameters for PSAC (color) at temperature 30°C

Sample	Langmuir			Freundlich		
	$Q_m$	$K_L$	$R^2$	$1/n_F$	$K_F$	$R^2$
PSAC	96.72	0.0433	0.999	0.743	0.163	0.996

Table 3.0: Isotherm parameters for PSAC (COD) at temperature 30°C

Sample	Langmuir			Freundlich		
	$Q_m$	$K_L$	$R^2$	$1/n_F$	$K_F$	$R^2$
PSAC	64.34	0.0268	0.997	0.724	0.19	0.994

In terms of actual textile wastewater, The Langmuir isotherm gave slightly closer fittings than other models as it was obvious from a comparison of the coefficient of determination ( $R^2 > 0.98$ ) within the range of adsorbent doses considered. The well fitted isotherm data by the Langmuir suggested that monolayer coverage of COD and color on both ACs, respectively. Higher  $R^2$  values suggested that the rate limiting step was controlled by chemisorptions that involves the valency forces or electron exchange between adsorbent and adsorbate.

In terms of economic benefit, regeneration of activated carbon is highly recommended. Consequently, the results ethanol regenerability revealed that the pollutant removal reduced from the first cycle to the third because of the decreased in adsorbent weight, due to losses by

washing and drying, which affects the adsorption capacity and desorption percentage for both activated carbons.

## 5.0 CONCLUSION

In conclusion, *Pandanus amaryllifolius* stems were successfully used to produce PSAC using physiochemical activation method. The optimum preparation conditions of PSAC were 794°C, 1.19 h and 2.75 for activation temperature, activation time and IR, respectively. PSAC gave reduction color and COD of 75.40 % and 61.10 % respectively. The adsorption uptakes of the PSAC increased with increased in adsorbates initial concentration and contact time. Adsorptions equilibrium followed Langmuir isotherm model.

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## Chapter 4

# Optimization and Characterization Study of Preparation Factors of Activated Carbon Derived from Coconut shell to Remove of H<sub>2</sub>S from Wastewater

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## ABSTRACT

The main point of this work is to investigate the preparations variables of activated carbon derived from coconut shell (CSAC) for removal of hydrogen sulfide (H<sub>2</sub>S) from wastewater. The CSAC was chemically modified with potassium hydroxide (KOH). The central composite design (CCD) under response surface methodology (RSM) was employed to prepare the CSAC. The three preparation variables impact on the removal efficiency (%) of H<sub>2</sub>S were examined. The preparation parameters to the responses were correlated by developing a quadratic model. The analysis of variance shows the significant impact of variable on each experimental design responses. The results show that the temperature of 857°C, chemical impregnation ratio of 3.4 wt% and activation time of 66 min were the optimum conditions for CSAC preparation of with removal efficiency of 88.8%.

*Key Words: Coconut shell, Activated carbon, wastewater, hydrogen sulfide, Response surface methodology.*

## 1.0 INTRODUCTION

Hydrogen sulfide (H<sub>2</sub>S) is a very toxic and dangerous gas. There are many sources that contributed to the emission of H<sub>2</sub>S to the environment. The petroleum refinery is considered as the main source contributor of H<sub>2</sub>S. It is produced during the processing of crude oil to useful product. The crude oil normally contains sulfur component and to remove the sulfur, process

such as desulfurization, liquefied petroleum gases and distillation units in used in the crude oil refinery. Therefore, these processing procedures will generate many wastes which are dissolved inevitably in the water to produce hazardous sour water which consist of  $H_2S$ . Hence, it is a must the water to be treated before being discharge for reuse or discard to swamp (Kazmierczak-Razna *et al.* 2015). There are many methods to remove  $H_2S$  from wastewater, such as biological, chemical and physiochemical (adsorption) methods (Siefers *et al.* 2010). Amongst these methods, adsorption is the most effective method due to its excellent performance and low cost (Foo and Hameed 2010).

Activated carbons (ACs) from agricultural wastes, such as date stones (Sekirifa *et al.* 2013), sugar canes (Castro *et al.* 2000), nut shell (Hu and Vansant 1995), coconut shell (Yang *et al.* 2010), and sunflower straw (Foo and Hameed 2011) are the most widely used to remove the different types of pollutants from wastewater. ACs have large adsorption capacity due to its great permeability and large surface area which is created during the activation of carbonaceous substances and carbonization. ACs are commonly used in industries as well. The two common forms of ACs are granular forms with sizes ranging from 0.5 to 2.5mm to be used in adsorption and columns, while powder forms with a size predominantly less than 0.15 mm to be used in batch adsorption followed by filtration (Allen and Koumanova 2005) ; (Dabrowski *et al.* 2005). Adsorption using ACs has been reported to be an effective method for the removal of pollutants from water and air (Bansal and Goyal 2005). Availability, cost, low inorganic matter content, low degradation during storage and ease of activation are the criteria needed to be considered in the selection of the precursors (Dabrowski *et al.* 2005). Physical and chemical activation methods are normally used for activation of chosen precursor. Physical activation is used to activate the precursor to enhance the porosity, surface area and surface chemistry of materials. It consist of two steps: thermal carbonization and activation. The carbonization process of raw materials under high temperature is to increase the carbon content and reduced the other component in the materials used. The activation process is conducted under gasified with an oxidizing agent such as steam or carbon dioxide to enhance the porosity, surface area and functional groups on the carbon surfaces. Chemical activation is done by chemical agents such as alkaline hydroxides, zinc chloride, or phosphoric acid, and followed by carbonization under inert gas and high temperature. The impregnated product must be washed to remove excess chemical agent (Zhang, Shao, and Karanfil 2010). The chemical nature of ACs surface is very important to determine the textural properties and of the adsorption capacity ACs. The activated carbon surface is heterogeneous, consisting multiple faces/edges and layers of

graphite sheets. The located some of elements such as halogen hydrogen, nitrogen, and particularly oxygen on the edges are consisted of the chemisorbed foreign heteroatom (El-Sayed and Bandoz 2004). In the interior of the graphite sheets, the edge sites seem to be more reactive than the residing atoms. There are many processes that forms of surface chemical functional groups such as the activation process of precursor like heat treatment and chemical treatment (Moreno-Castilla 2004) ; (Derylo-Marczewska *et al.* 2008). There are two categories of surface functional groups. First, basic groups consisting of pyrone, chromene, ethers and carbonyls (Boehm 1994). Second, acidic groups which are mainly consisting of carboxylic, lactones and phenols.

Moreover, the caustic carbon surface could help to immobilize the H<sub>2</sub>S species on the adsorbent surface and would allow for greater removal efficiency due to the H<sub>2</sub>S is acidic. The caustic materials such as NaOH or KOH is capable to improve the pH level of the carbon surface which result an attractive adsorbent toward H<sub>2</sub>S. In this study, the preparation factors of ACs produced from coconut shell are investigated. The design of experiment is implemented to optimize the preparations factors of ACs to remove of H<sub>2</sub>S from wastewater. All the activities of experimental planning, conducting experiments, and fitting models to the out puts responses are involved in this method. Response surface methodology (RSM) is the useful tool for optimizing the factors using center composite design (CCD). The objectives on this work are to investigate the optimum preparation factors conditions needed to maximize the removal efficiency (RE) (%) to remove dissolved H<sub>2</sub>S from wastewater.

## 2.0 METHODS AND MATERIALS

### 2.1. Preparation of activated carbon

Coconut shell is used to produce CSAC. The details of raw material preparation method of precursors are detailed in our previous work (Habeeb *et al.*, 2016). In this study, the precursor was activated with KOH at different temperature and time with a constant heating rate of 10 °C/min. The KOH to precursor ratio was varied from 2:1 - 4:1. The precursor was blended with KOH at different fertilization proportion (IR), using equation (1):

$$IR = \frac{W_{KOH}}{W_c} \quad (1)$$

Where, W<sub>KOH</sub> is the weight (g) of KOH pallets and W<sub>C</sub> is the weight (g) of precursor.

The procedures for activation process are explained in details in our previous study (Omar Abed Habeeb, Ramesh Kanthasamy, Gomaa A.M. Ali and Yunus 2017). After activation process, the samples are rinsed with hot distillate water and 1.0 M hydrochloric acid until the pH of the washing solution achieved 6–7. The preparation factors ranges are shown in Table 1.

## 2.2. Modeling and optimization

### 2.2.1. Experiment design

Response surface methodology (RSM) is an accumulation of numerical and statistical methods that are important for illustrating, examination, demonstrating and investigation of problems in which a response of interest effected by a couple factors (Montgomery 2001). Central composite design (CCD), three-level factorial design and Box–Behnken design are considered the several classes of designs under RSM and they are the most common designs utilized by the scholars. However, in current study the CCD was employed to study optimization and the effect of factors toward their responses(Montgomery 2001). This method is suitable for fitting a quadratic surface and it spreads to enhance the influential parameters with a minimum number of experiments as well as examine the association between the parameters. The three parameters investigated were the activation temperatures (T), mass ratio of KOH to Precursor (IR) and the duration of time activation (t) and their related extends were 724– 1000 °C, 2:1– 4:1 and 60-120 min, respectively with response of removal efficiency.

The residual error was estimated by replicating the central point and based on the extend of each elements (factor), the independent factors are coded to the (-1, 1) interval. The different levels, that is to say, high and low, are coded +1 and -1 separately. The axial points are situated at  $(0, 0, \pm\alpha)$ ,  $(\pm\alpha, 0, 0)$ ,  $(0, \pm\alpha, 0)$ , what makes the design rotatable is the  $\alpha$  which represents the axial point from the center. In order to set up an empirical model the responses were used which in turn correlate the responses to three preparation elements using a second degree polynomial equation as given by equation (2) (Zainudin et al. 2005):

$$Y = b_o + \sum_{i=1}^n b_i x_i + \left( \sum_{i=1}^n b_{ii} x_i^2 \right) + \sum_{i=1}^{n-1} \sum_{j=i+1}^n b_{ij} x_i x_j \quad (2)$$

where  $Y$  is the predicted response,  $b_0$  the constant coefficient,  $b_i$  the linear coefficients,  $b_{ij}$  the interaction coefficients,  $b_{ii}$  the quadratic coefficients and  $x_i, x_j$  are the coded values of the activated carbon preparation variables.

Model fitting and statistical analysis are conducted using ANOVA statistical techniques. A coefficient of determination ( $R$ -squared), Fisher value ( $F$ -value), probability ( $P$  value), and residual were used as a standard of significance of the model equations (Hassani et al. 2014). Finally, optimization and validation are also conducted to find the optimum preparation factors conditions to enhance the removal of  $H_2S$  from wastewater.

## 2.2 Characterization of adsorbent

The surface structure morphology of CSAC adsorbent are characterized using scanning electron microscopy (SEM). Moreover, the elements of the adsorbent before and after adsorption process are examined by Energy-dispersive X-ray spectroscopy (EDX).

## 3.0 RESULT AND DISCUSSION

### 3.1 Model analysis of central composite design (CCD)

The independent variables such as activation temperature (724-1000 °C), activation mass ratio KOH: Precursor (2:1-4:1 w %), and activation contact time (60-120 min) are investigated. The factors names, coded, and ranges, are demonstrated in Table 1. The dependent response is the removal efficiency of  $H_2S$  from wastewater. The correlations between independent variables and dependent response are developed using quadratic polynomial model.

**Table 1:** The code, unit and ranges for optimization of independent variables of (CSAC)

Variables	code	Unit	Coded variable levels				
			$-\alpha$	-1	0	+1	$+\alpha$
Activation temperature	A	°C	630	724	862	1000	1094
KOH: Precursor ratio	B	Wt%	1.3	2	3	4	4.5
Activation contact time	C	min	39.5	60	90	120	140.5

### 3.2. Statistical Analysis

The interactions between three parameters (activation temperature, KOH: precursor ration, and activation contact time) for the removal efficiency of dissolved H<sub>2</sub>S are analysed using response surface methodology (RSM). The central composite design results are allowed to develop a mathematic equation that can predict the response value. Moreover, the analysis of variance (ANOVA) is used to analysis obtained results as represented in Table 2. The goodness of fit and lack-of-fit are estimated from ANOVA Table. The ANOVA test is successfully conducted as seen in Table 2. The quadratic model is significant. While the lack of fit was not significant. The lack of fit describes the variation of the data around the fitted model. Thus, this is an indicated to prove the statistically corrected the relation between the factors and response. Moreover, the F-value of the quadratic model is (44.9). Consequently, the terms of significant model are A, B, C, A<sup>2</sup>, B<sup>2</sup>, C<sup>2</sup>, AC and BC. While AB is the insignificant model terms. It can be observed that factors of KOH: Precursor ration has high contribution to the response of removal efficiency as seen in Table 2. This is attributed to the important of impregnation ratio that might be enhanced the surface chemistry of the adsorbent and it also provides the basic environment that could be attractive to acidic pollutant such H<sub>2</sub>S. In addition, the residual value is very low that another indicator that shows the goodness fitted of the model.

**Table 2:** Analysis of variance (ANOVA) and lack-of-fit test for response surface quadratic model for removal efficiency (RE %).

Sources	Sum of squares	df	Mean square	F-value	P value	Comment
Model	110.89	9	12.32	44.95	< 0.0001	significant
A-activation temperature	2.83	1	2.83	10.31	0.0037	significant
B-KOH:AC ratio	11.12	1	11.12	40.57	< 0.0001	significant
C-Activation contact time	1.35	1	1.35	4.94	0.0359	significant
AB	2.500E-003	1	2.500E-003	9.121E-003	0.9247	insignificant
AC	7.29	1	7.29	26.60	< 0.0001	significant

BC	3.24	1	3.24	11.82	0.0021	significant
A <sup>2</sup>	75.64	1	75.64	275.94	< 0.0001	significant
B <sup>2</sup>	25.46	1	25.46	92.87	< 0.0001	significant
C <sup>2</sup>	2.57	1	2.57	9.39	0.0053	significant
Residual	6.58	24	0.27			
Lack of Fit	2.12	5	0.42	1.80	0.1609	not significant

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### 3.3 Development of the equation of regression model

In addition, the CCD software is implemented to improve the empirical model. The correlation coefficient and standard deviation were used to obviate the model developed fitness. The better the model in forecasting the response is the smaller the standard deviation and the closer the  $R^2$  value is to unity (Alam *et al.* 2009). The statistical analysis of quadratic model for removal efficiency is demonstrated in Table 3. It can be seen clearly that the  $R^2$  value of 0.944 with small standard deviation 0.52. Moreover, the predicted  $R^2$  is in agreement with the adjusted  $R^2$  with only small differences between them. Therefore, the quadratic model is successfully developed. The quadratic model equation suggested by the software can be written as shown in equation (3). This equation can be used to predict the value of response (removal efficiency).

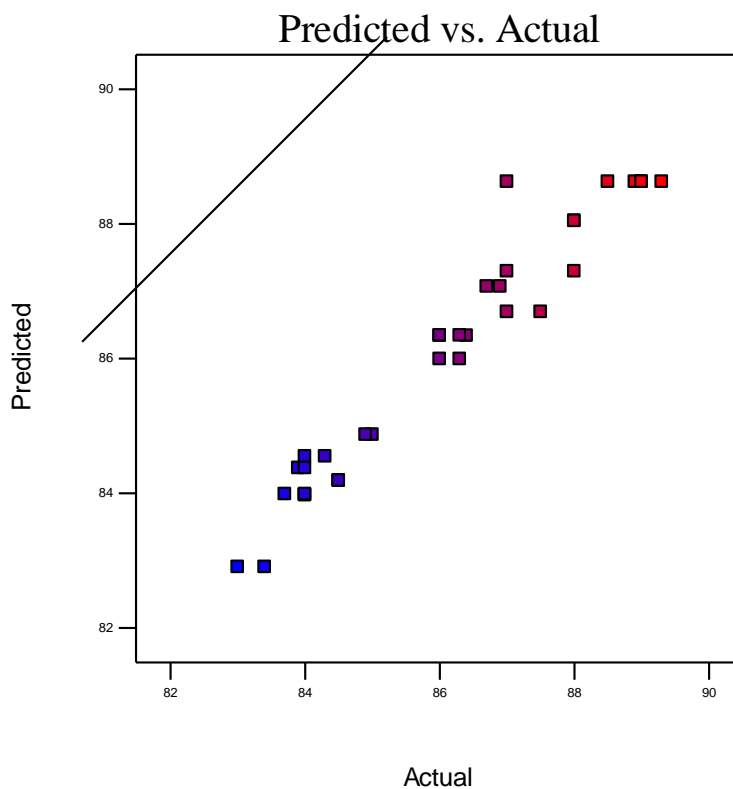
Furthermore, predicted vs actual values and normal plot of residual graphs are shown in Figure 1 (a, b) respectively. Figure 1 (a) represents the predicted vs actual values. This figure shows a sufficient agreement between the predicted data from the mode and the ones obtained from experiments. It is observed that the values are very close to the line which indicated the experimental values are closed to predict one. Figure 1 (b) shows the normal plot of residual error which demonstrated the residual error deviation from the model.



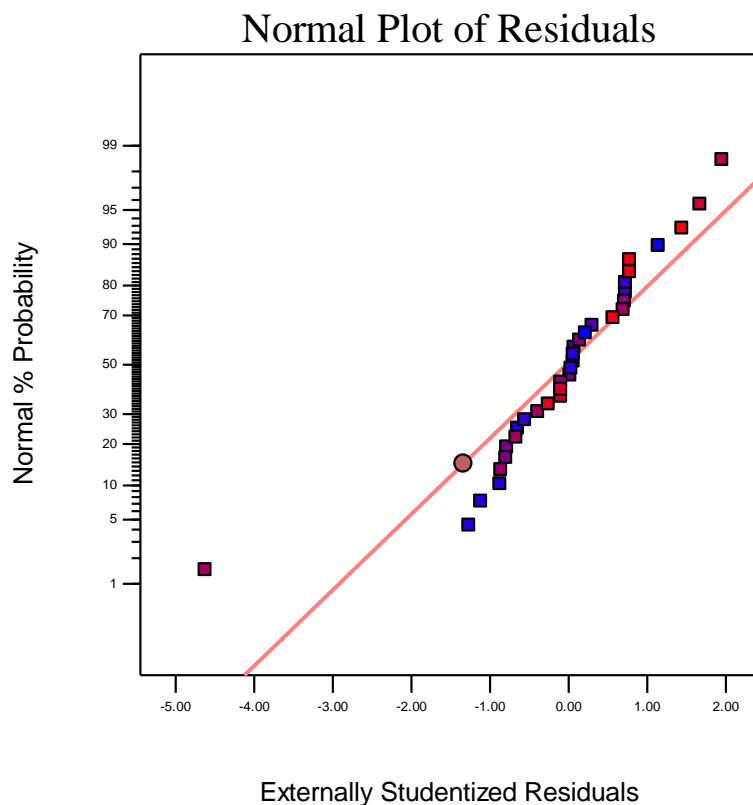
**Table 3:** Regression statistics for removal efficiency RE (%) at equilibrium.

Source	Standard deviation	R <sup>2</sup>	Adjusted R <sup>2</sup>	Predicted R <sup>2</sup>	Comment
Linear	1.85	0.1302	0.0433	-0.0604	
2FI	1.84	0.2199	0.0465	-0.0027	
<b><u>Quadratic</u></b>	<b><u>0.52</u></b>	<b><u>0.9440</u></b>	<b><u>0.9230</u></b>	<b><u>0.9011</u></b>	<b><u>Suggested</u></b>
Cubic	0.48	0.9609	0.9355	0.9253	Aliased

$$\text{Removal efficiency} = 88.6 + 0.32A + 0.638B - 0.2226C - 0.0125AB + 0.675AC - 0.45BC - 1.83A^2 - 1.0625B^2 - 0.337C^2 \quad (3)$$



(a)



(b)

Figure1 (a) Actual and predicted curve. (b) Normal plot of residual

### 3.4 Effect of interaction factors

The effect of the factors interaction on the removal efficiency is demonstrated in Figure 2 (a, b, & c). The interaction between activation temperature and KOH: Precursor ratio are represented in Figure 2 (a). The two factors have affected the removal efficiency. It can be seen there is no interaction as the activated temperature increasing, the impregnation ration increased. However, the impact of the activation agent ratio has more significant effect on removal efficiency than activation temperature. While, the Figure 2 (b) represents the effect of interaction between activation temperature and activation contact time. The activation temperature has a significant effect on the removal efficiency of H<sub>2</sub>S. The removal efficiency was low at lower temperature of 724 °C and higher activation contact time of 120 min. Then, it start increasing when the temperature increased and the time decreased until reach the optimum removal efficiency of 88.8 % at activation temperature of 857 °C and activation contact time of 70 min.

Figure 2 (c) shows the interactions between activation time and the impregnation ratio. The interaction plot shows the removal efficiency was very low at lower impregnation ratio and activation contact time. In fact, the graph demonstrated that high contact time of 120 min and low contact time of 60 min with low impregnation ratio are negatively affected the removal efficiency (as seen from Figure 2 (c)). After that, the removal of H<sub>2</sub>S increasing with increased of impregnation ratio and activation contact time until reach the optimum removal efficiency of 88.8 % with impregnation ratio of 3.4 wt% and activation contact time of 70 min.

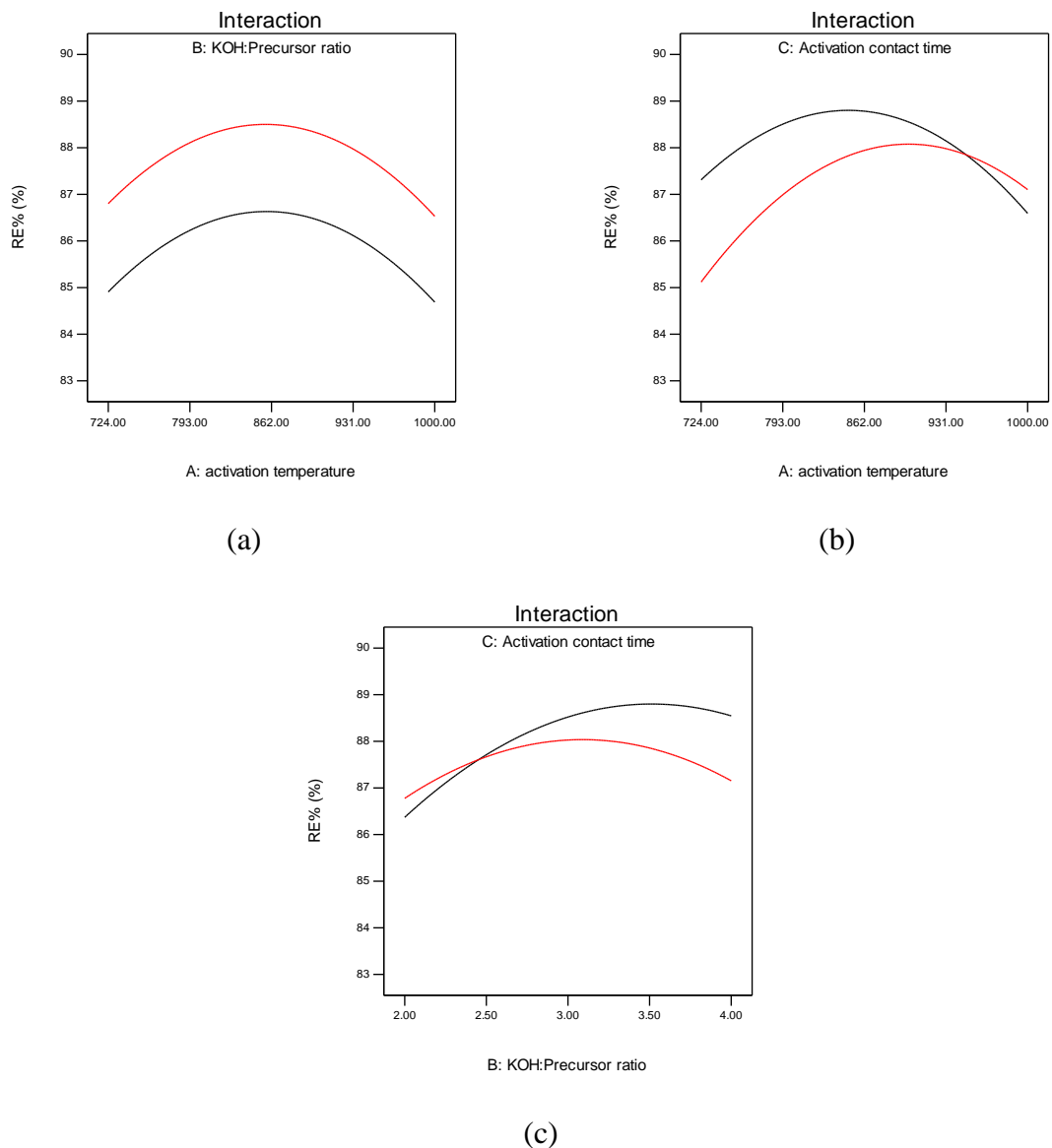


Figure 2. The effect of interactions between factors on the removal efficiency

### 3.5 Effect of combined factors

The effect of activation temperature and KOH: Precursor ratio on the removal efficiency show in Figure 3. The 3D plot presents impact of activation temperature with range between 724 to 1000 °C and activation agent mass ratio (KOH: Precursor) with range of (2:1-4:1 w%) on removal efficiency. From the trend of plot, it can be observed that, impregnation ratio and activation temperature have parallel contribution on removal efficiency. As increased in activation temperature and impregnation ratio, the removal efficiency increased. At the low activation temperature around 724 °C, the value of removal efficiency was very low. After that, the removal efficiency start increased with increasing the activation temperature and impregnation ratio until reach the optimum requirement of activation temperature and impregnation ration for getting the optimum removal efficiency.

Moreover, the effect on the interaction between activation temperature and contact time on the removal efficiency are demonstrated in Figure 4. The activation temperature with range (724-1000 °C) and activation contact time range (60-120 min) have a significant effect on response removal of H<sub>2</sub>S. The temperature of activated of adsorbent has more effect on removal of H<sub>2</sub>S than activation time as seen in Figure 4. From the trend of 3D plot was observed that H<sub>2</sub>S experienced lowest residual at a preparation conditions of activation temperature of 857 °C and activation contact time of 66 min. Furthermore, the 3D plot of the interaction effect between activation time and KOH: Precursors on the removal efficiency are shown in Figure 5. It can be observed that the KOH: Precursors has a significant impact compared with the activation time which has less contribution on the removal of H<sub>2</sub>S. The same trend was reported by Chaudhary (Chaudhary and Balomajumder 2014) As can be concluded that all the preparation factors of CSAC have a significant effect in different percentage that could contribute to enhance the removal of H<sub>2</sub>S from synthetic wastewater.

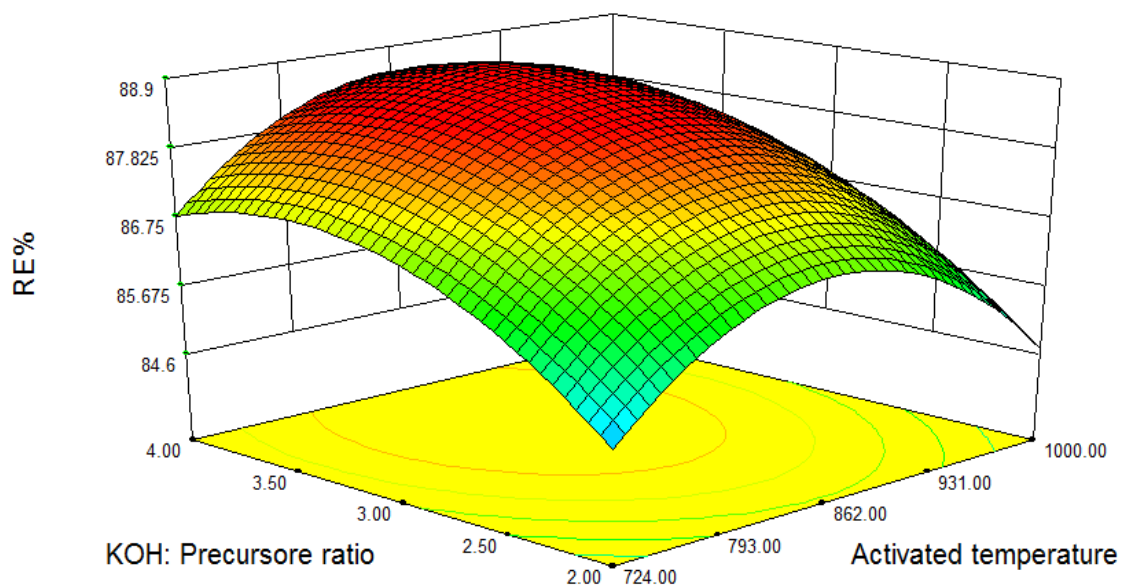


Figure 3: Combined impact of activation temperature and KOH: Precursor ratio on RE (%).

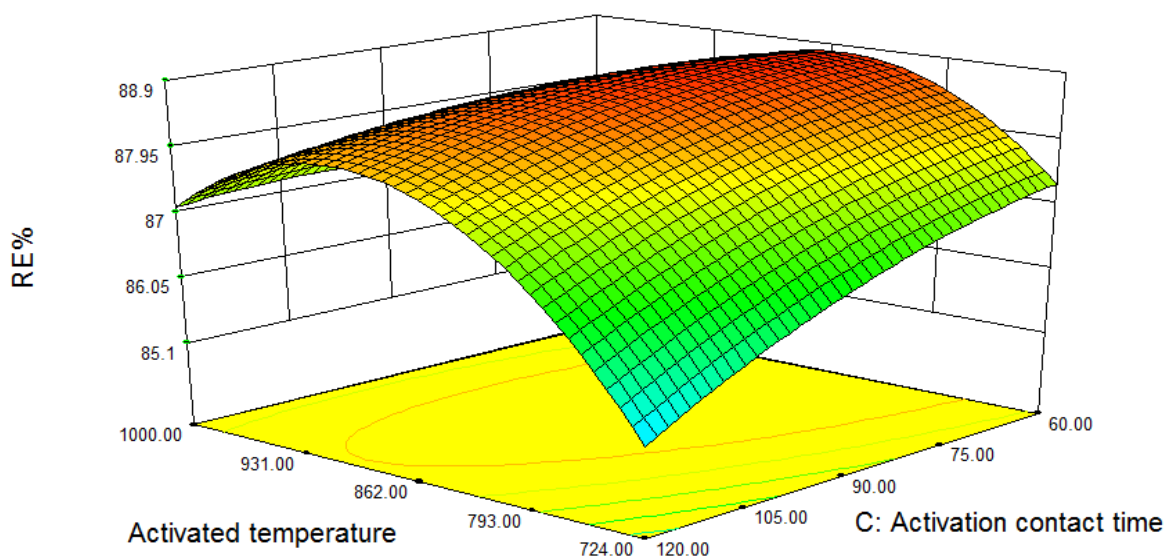


Figure4: Combined impact of activation time and activation temperature of AC on of RE (%).

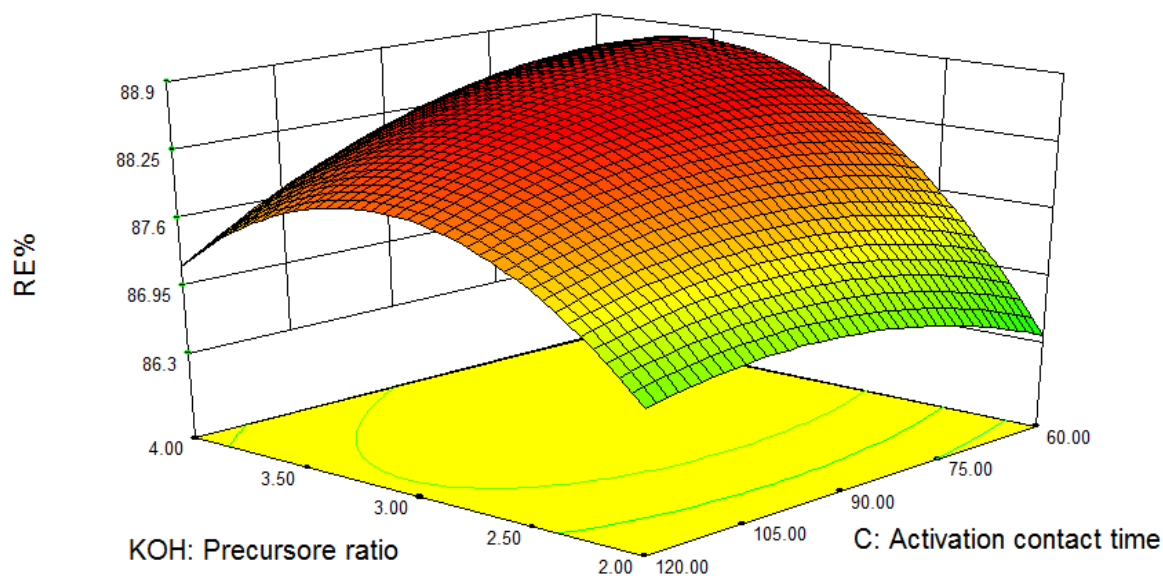


Figure 5: Combined impact of activation contact time and KOH: Precursor (IR) on RE (%)

### 3.6. Characterization of the optimally prepared activated carbon

#### 3.6.1. Surface morphology (SEM / EDX)

Figure 6 (a, b) represent the SEM test for fresh and spent CSAC adsorbent respectively. As can be observed from Figure 6 (a) the chemical activation process with KOH was effective in creating well-developed pores on the surfaces of the activated carbon leading to produce activated carbon with a huge porous structure as seen in Figure 6 (a). The well-developed porosity on the surface of CSAC is attributed to the preparation factors such as activation temperature, activation contact time and KOH: Precursor ratio. The impregnation ratio with temperature have a significant contributed on developing the pore structure of the adsorbent due to during combustion of raw materials. It is attributed to chemical activations using of KOH. It possibly create more pores in CSAC structure due to the reaction between carbon and KOH as shown in equation (4). Pore generation is based on dehydration of KOH to  $K_2CO_3$ , which reacts with  $CO_2$  produced by the water-shift reaction, affording  $K_2CO_3$  as well as promoting the diffusion of KOH and  $CO_2$  molecules into the pores, thereby increasing its porosity (Stavropoulos and Zabaniotou 2005). As seen in Figure 6 (a).

However, the image of SEM in Figure (b) indicating the morphology of adsorbent surface after adsorption process which could be seen that there is some blocked in porosity due to stick of

sulfur on the pore hole and also can be seen the some white particle on the surface which indicated that the sulfur already stick on porous area.

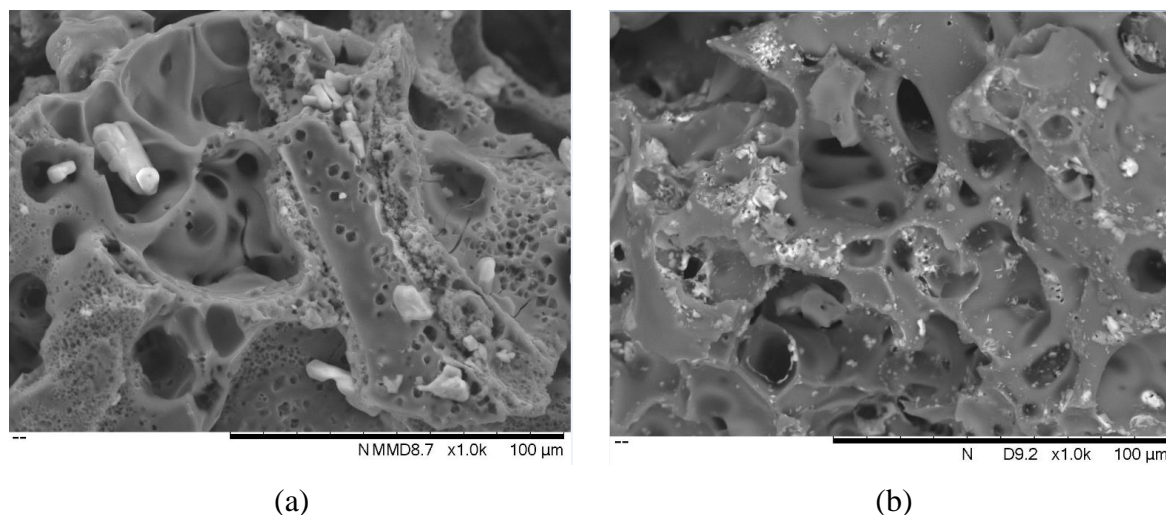
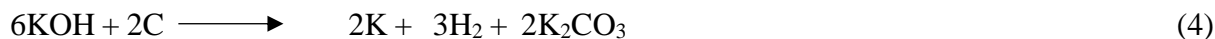
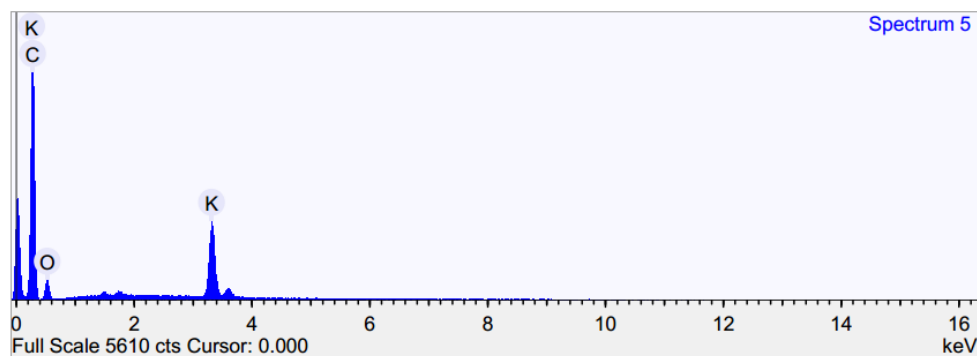


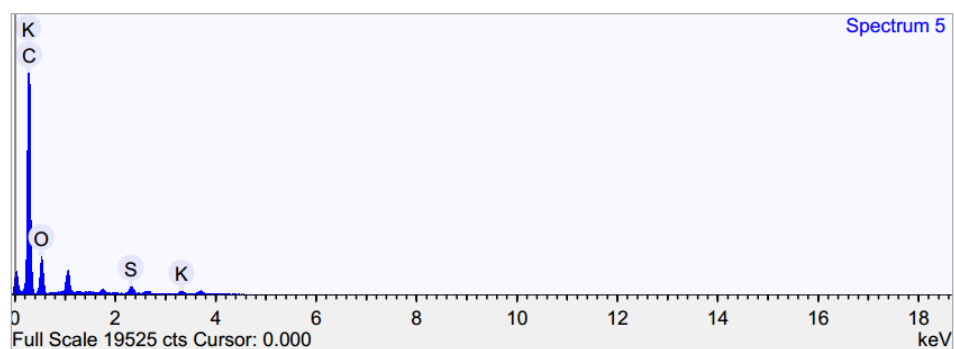
Figure 6 SEM image of (a) fresh (b) spent CSAC adsorbent

Moreover, the EDX test for the CSAC before and after adsorption process are shown in Figure 7 (a, b). As can be seen the peaks for the fresh CSAC represents the adsorbent components which is (C, O and K). However, the peaks for the spent CSAC is representing the adsorbent components after adsorption process which is shown clearly that there more peaks which is represent the different components such as (C, O, K, and S). All composite components of the adsorbent before and after adsorption process shown in Table 4. It can be seen that the percentage of C, O, and K are decreased after the adsorption process. In fact, the most interesting finding was that the percentage of K decreased to around 0.93 % after adsorption, indicating that acid–base reaction occurs. Moreover, S content detected as 0.724, which is another indicator for the possible occurrence of oxidation. In fact, during the adsorption process, the acid/base reaction is occurred. The KOH provides a basic environment on the active sites on the adsorbent which attracted the acidic dissolved  $\text{H}_2\text{S}$  and its ions to produce the sulfide salt and water as seen in equation (5). The reactions occurred on the surface of CSAC. From that the percentage of C, O, and K are decreased as noticed in Table 4.





(a)



(b)

Figure 7 EDX test (a) Fresh. (b) Spent CSAC adsorbent.

**Table 4:** The components of activated carbon derived from coconut shell fresh and spent adsorbent.

Element	Component of fresh adsorbent (Weight %)	Components of spent adsorbent (Weight % )
Carbon (C)	76.575	73.24
Oxygen (O)	17.9	25.6
Potassium (K)	5.511	0.38
Sulfur (S)	0	0.724

#### 4.0 CONCLUSIONS

In this study the variables for preparations of CSAC for H<sub>2</sub>S removal from wastewater was investigated. The optimum preparation variables conditions are examined. SEM and EDX



characterizations are conducted. The result shows that the optimum conditions of factors are temperature of 857 °C, chemical impregnation ratio of 3.4 wt% and activation time of 66 min with removal efficiency of 88.8 %.

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## Chapter 5

# CARBON GEL-BASED ADSORBENTS FOR ANIONIC DYES REMOVAL

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### ABSTRACT

Resorcinol-formaldehyde (RF) carbon gel is a new type of porous material that is gaining popularity because of its flexible nanostructure and exceptional characteristics. Its physical properties are unique and can be customized by modifying the synthesis and processing conditions in order to accommodate varying applications. Carbon gels have been used as adsorbent for the removal of water pollutants, catalyst supports, ion exchange resin and electrodes in the electro-catalysis process. This chapter is aimed to provide a concise summary on the different types of RF carbon gels, the preparation techniques and activation strategies, and also the unique physical properties (porosity, surface area and morphology) of the synthesized materials for water pollutants removal. Besides, a case study to evaluate the adsorptive performance and kinetics of the laboratory synthesized RF carbon gel-based adsorbents on the removal reactive orange 16 and congo red from water are discussed to shed some light on the promising use in the treatment of wastewater containing anionic dyes.

*Keywords:* Adsorbent, Adsorption, Anionic dye, Carbon gel

## 1.0 Introduction

Over the past decade, a considerable attention has been devoted to resorcinol-formaldehyde (RF) carbon-gel for various applications. Carbon gel was first synthesized by Pekala (1989). In general, the preparation process involved sol-gel polymerization and polycondensation reactions of resorcinol and formaldehyde. Carbon gel is formed by an aggregate of nanoparticles, and the pores are developed through the formation of voids between the nanoparticles. The hierarchical pore system of macropores and mesopores is influenced by the synthesis and drying process, while the development of micropores takes place during the subsequent carbonization and activation steps (Lufrano et al., 2011). Carbon gels are porous in nature, and normally exhibit a high surface area and pore volume, and a controllable pore structure and pore size distribution (Lee and Zaini, 2017a).

Depending on the drying methods in the synthesis, different types of carbon gels can be produced. Simple evaporative drying is suitable for dense carbons or when the only target criterion is the pore size. The carbon gel produced via this method is known as carbon xerogel. On the other hand, carbon aerogel is produced via supercritical drying, and it normally has high pore volume and wide texture range. However, the residual surface tensions and shrinkage are compromised in the resultant material with low density or when the pore size is too small. As compared to the evaporative and supercritical drying, monoliths are more difficult to be developed by freeze drying. Moreover, the appearance of huge channels due to ice crystal growth at high dilution ratio hinders the fabrication of low density materials. The carbon gel prepared by freeze drying is also known as carbon cryogel (Job et al., 2005).

The preparation of carbon gel includes mixing, gelation, aging, solvent exchange, drying, carbonization and activation (Al-Muhtaseb and Ritter, 2003). The first preparation step is a mixing of resorcinol (R) and formaldehyde (F) in a solvent at an appropriate molar ratio in the presence of a basic catalyst (C) such as sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). Sometimes, an acidic catalyst is used. The most common stoichiometric R/F molar ratio is 0.5. The solvent can be either water (W) or organic solvent such as acetone or methanol. The major reaction between R and F is a sol-gel polymerization which occurs at the gelation step. During the reaction, the polymer structure is formed, which is referred as hydrogel and alcogel, i.e., when water and alcohol is used as the solvent, respectively. The aging step is carried out with an intention to increase the crosslinking density by promoting the progress of the condensation reaction. It increases the mechanical strength of the gel. However, a huge difference between the surface

tension of the co-existing vapor and liquid phase of water within the voids could result in a dramatic mechanical stress that leads to the collapse (or shrinkage) of the pore structure. To minimize the variation of surface tensions, a new solvent is introduced to replace the water within the voids through a repetitive washing procedure. The choice of solvents depends on the evaporative properties and/or mutual solubility with water or CO<sub>2</sub>. The dried organic gel is produced at the drying step after the solvent is removed. Conventional evaporation, which is a simple oven drying produces dried dense polymers called xerogels. Aerogels are produced when the liquid solvent is removed by supercritical drying with CO<sub>2</sub> or organic solvent. The aerogel is dried without going through a vapour-liquid interface of CO<sub>2</sub> or organic solvent, and this could minimized the shrinkage of pores. The cryogels are dried under freeze condition, in which the solvent within the voids is frozen and removed by sublimation to avoid the formation of a vapour-liquid interface.

Carbonization step transforms the organic gel into carbon gel by thermal heating to remove any remaining oxides and hydrogen groups at an elevated temperature. This step enhances the specific surface area of gel by increasing the number of mesopores and micropores. The activation process by means of either chemical or physical method is introduced to functionalize the carbon gel with oxygenated surface groups. Physical activation with air creates phenolic and carbonyl groups, while chemical activation with nitric acid introduces carboxylic groups on the carbon surface. The physical activation is usually held at higher temperature than the chemical activation, but the former is not requiring a washing post-treatment (Elkhata and Al-Muhtaseb, 2011).

## 2.0 Carbon gel-based adsorbent

Carbon gel is a potential adsorbent for water pollutants removal because of its unique textural characteristics that can be tailored by controlling the synthesis process (Mreno-Pirajan and Giraldo, 2013). Moreover, it can be synthesized in the form of monoliths, powder, microspheres and thin film so as to accommodate the desired application requirements (Esther et al., 2011). Tables 1, 2 and 3 summarize the processing conditions and adsorptive performance of xerogels, aerogels and cryogels, respectively.

**Table 1:** Processing conditions and adsorption performance of xerogels

Reactant	R/F	W	R/W	C	R/C	pH	Carbonization			Activation			$S_{BET}$	$R_{Meso}$ (%)	$d_p$	Adsorbate	$Q_m$	Reference				
							$T$	$t$	Yield	Agent	$T$	$t$										
R: Furfural, Hexa- methylene- tetramine	2, 33.3	-		KOH	-	7.0	900	3	-				887	28.8	30.9	Methylene blue	240	Zhou et al., 2011				
																Acid blue 40	222					
																Reactive black 5	35					
						8.1											944		39.7	26.3	Methylene blue	249
																Acid blue 40	246					
																Reactive black 5	25					
						8.8											898		29.9	23.0	Methylene blue	238
																Acid blue 40	223					
																Reactive black 5	20					
						9.9											600		5.96	12.7	Methylene blue	199
																Acid blue 40	115					
																Reactive black 5	10					
R:F	-	-	-	-	6.5	800	6	-	-	-	617	100	31.3	Ciprofloxacin	112	Carabineiro et al., 2011						
R:F	0.5	Water	35	Na <sub>2</sub> CO <sub>3</sub>	1000	-	900	2	-	-			630	78.5	28-40	Methylene blue	212.2	Páez et al., 2012				
										CO <sub>2</sub>	900	4	1015	75.3	29-40		438.2					
												6	1365	71.5	28-43		531.8					
												8	2180	65.0	29-41		714.3					
R:F	0.5	Water	0.2	Na <sub>2</sub> CO <sub>3</sub>	500	-	750	2	-	-	78	-	-	-	-	Cotet et al., 2013						

R:F	0.5	Water	0.1	Na <sub>2</sub> CO <sub>3</sub>	100	-	-	-	-	-	-	489	79.8	2.84	-	Oyedoh et al., 2013			
					200							522	94.0	4.32					
					500							310	96.6	15.7					
					600							217	96.3	25.6					
					700							175	98.3	29.9					
					800							127	98.4	31.3					
			0.05		200							376	95.7	3.94					
			0.1									454	96.6	5.20					
			0.15									465	95.7	7.92					
R:F	0.5	Water	-	malonic acid	1	-	850	3	-	-	1201	26.3	1.91	Cu <sup>2+</sup>	260.4	Xiao et al., 2013			
										HNO <sub>3</sub>	50	10	1150		39.7		1.98	299.4	
R:F	0.5	Water	0.5	Na <sub>2</sub> CO <sub>3</sub>	-	-	1000	4	-	-	-	-	190	35.5	2.40	-	Tsuchiya et al., 2014		
												CO <sub>2</sub>	1000	0.6	460			34.6	2.40
														1.05	230			37.5	2.40
												-	640	64.3	3.80				
												CO <sub>2</sub>	1000	0.65	1400			47.5	3.30
														1.2	1900			44.0	2.40
												-	700	84.7	9.30				
												CO <sub>2</sub>	1000	0.85	1900			76.5	9.30
														2	2421			76.12	7.10
												-	630	83.3	44.0				
CO <sub>2</sub>	1000	0.75	1700	76.2	69.0														
		2	2965	85.0	44.0														



R:F	0.5	Water	0.3	KOH	150	-	600	-	-	-	684	73.9	-	Ni <sup>2+</sup>	0.415	Luzny et al., 2014	
										-	-	-	-	Cu <sup>2+</sup>	0.585		
										-	-	-	-	Zn <sup>2+</sup>	0.428		
										steam	850	-	1870	66.9	Ni <sup>2+</sup>		0.508
										-	-	-	-	Cu <sup>2+</sup>	0.352		
										-	-	-	-	Zn <sup>2+</sup>	0.232		
					KOH	600	-	276	23.1	Ni <sup>2+</sup>	0.453						
					-	-	-	-	Cu <sup>2+</sup>	0.574							
					-	-	-	-	Zn <sup>2+</sup>	0.578							
					-	-	-	741	86.1	Ni <sup>2+</sup>	0.044						
					-	-	-	-	Cu <sup>2+</sup>	0.209							
					-	-	-	-	Zn <sup>2+</sup>	0.084							
R:F	0.5	Water	0.25	Na <sub>2</sub> CO <sub>3</sub>	100	4	-	-	-	-	189	0	3.80	-		Ratchahat et al., 2015	
					150	5					248	0	3.10				
					200	6					277	0	2.50				
					250	7					202	0	2.80				
R:F	0.5	-	Na <sub>2</sub> CO <sub>3</sub>	-	-	800	12	-	-	606	83.8	9.79	Pb <sup>2+</sup>	64.2	Yang et al., 2015		
R:F, Melamine	0.5, 5.2			100						531	64.4	3.41		74.5			
				150						573	82.6	8.02		83.8			
				200						530	58.0	3.75		71.7			

	0.5, 10.4				150						560	71.9	4.21		69.9			
	0.5, 6.9										609	78.5	6.38		73.2			
R:F	0.5	Water	0.53	NaOH	-	6.1	800	4	-	-	367	64.0	-	Caffeine	79.1	Alvarez et al., 2014		
														Diclofenac	58.5			
										H <sub>2</sub> SO <sub>4</sub>	200	3		288	60.5		Caffeine	52.6
																	Diclofenac	78.8
										HNO <sub>3</sub>	boiled	3		347	62.5		Caffeine	50.9
																	Diclofenac	54
										HNO <sub>3</sub> , urea	boiled, 200	3, 2		435	71.4		Caffeine	185.4
					Diclofenac	140.2												
R:F	0.5	Water	0.3	NaOH, HNO <sub>3</sub>	-	3	750	2	46.6	-	484	8.80	9.0	Methylene blue	102	Girgis et al., 2017		
						5			49.6		498	52.7	8.0		108			
						6			51.8		513	19.8	9.0		123			
						6.5			66		622	42.7	5.9		128			
						7.2			54.2		412	15.7	6.4		91			
						6.5			600		2	72	308		94.9		8.0	90
						6.5			700		2	68.6	449		86.2		9.7	93
						6.5			800		2	60	433		6.40		9.0	113
						6.5			750		2	56	541		12.0		6.2	-
R:F	0.5	Water	0.3	Na <sub>2</sub> CO <sub>3</sub>	1000	6	750	3	-	-	444	-	3.61	Pb <sup>2+</sup>	16.95	Osinska, 2017		
														Cu <sup>2+</sup>	6.64			
														Co <sup>2+</sup>	5.46			
														Ni <sup>2+</sup>	4.16			

R:F	0.5	Water	0.5	Na <sub>2</sub> CO <sub>3</sub>	100	-	600	3	42.8	-			476	23.7	1.86	Reactive orange 16	Lee and Zaini, 2017	0
									HNO <sub>3</sub>	60	5	301	0	1.33	0			
									49.6	-			608	46.3	2.36			2.73
									HNO <sub>3</sub>	60	5	567	44.9	2.33	0			
									42.6	-			639	69.8	6.89			6.80
									HNO <sub>3</sub>	60	5	712	75.1	7.68	6.52			
R:F	0.5	Water	0.5	Na <sub>2</sub> CO <sub>3</sub>	1000	-	600	3	53.7	-			631	59.2	3.56	Congo red	Tang and Zaini, 2017	2.25
									HNO <sub>3</sub>	60	5	586	59.3	3.57	5.84			
									42.6	-			639	69.8	6.89			10.6
									HNO <sub>3</sub>	60	5	712	75.1	7.68	2.51			
									53.7	-			631	59.2	3.56			4.36
									HNO <sub>3</sub>	60	5	586	59.3	3.57				

R: resorcinol, F: formaldehyde, W: solvent, C: catalyst, R/F & R/C in molar ratio, R/W in g/cm<sup>3</sup>, T: Temperature in °C, t: time in h, Yield in %, S<sub>BET</sub>: BET surface area in m<sup>2</sup>/g, R<sub>Meso</sub>: mesopore content, d<sub>p</sub>: average pore diameter in nm; Q<sub>m</sub>: maximum adsorption capacity in mg/g

**Table 2:** Processing conditions and adsorption performance of aerogels

Reactant	R/F	W	R/W	C	R/C	pH	Carbonization			Activation			S <sub>BET</sub>	R <sub>Meso</sub> (%)	d <sub>p</sub>	Adsorbate	Q <sub>m</sub>	Reference
							T	t	Yield	Agent	T	t						
R:F	0.5	Water	1.5	Na <sub>2</sub> CO <sub>3</sub>	500	-	1000	1	-	-	-	-	420	-	6	-		Feng et al., 2011
			0.068										630		139			
			0.016										717		563			

	0.5		0.061		50								618		14					
					300								616		51					
					800								710		193					
R: Furfural, Hexa- methylene- tetramine	0.5, 30	Ethanol	339	acetic acid	-	5.1	900	6	-	CO <sub>2</sub>	1000	1	803	71.3	0.65	Benzene	242.3	Moreno-Pirajan & Giraldo, 2013		
																Hydroquinone	32.44			
																Catechol	27.54			
																Resorcinol	21.45			
R:F	0.5	Water	0.2	Na <sub>2</sub> CO <sub>3</sub>	500	-	750	2	-	-	-	570	-	-	Cd <sup>2+</sup>	11.5	Cotet et al., 2013			
															Cu <sup>2+</sup>	8				
R:F	0.5	Water	0.5	Na <sub>2</sub> CO <sub>3</sub>	5	6	900	1	-	-	-	-	846	19.0	-	-	Czakkel et al., 2013			
R:F, TTIP	0.5, 1																	223	27.7	
R:F	0.5																	38	1990	17.1
R:F, TTIP	0.5, 1																	50	718	32.5
R:F	0.5																	38	TTIP	r.t
R:F	0.5	Water	0.3	KOH	50	-	600	-	-	-	-	-	623	72.3	-	Ni <sup>2+</sup>	0.048	Luzny et al., 2014		
																Cu <sup>2+</sup>	0.494			
																Zn <sup>2+</sup>	0.332			
																Ni <sup>2+</sup>	0.256			
																Cu <sup>2+</sup>	0.427			
																Zn <sup>2+</sup>	0.25			

R: resorcinol, F: formaldehyde, TTIP: Titanium tetraisopropoxide, W: solvent, C: catalyst, R/F & R/C in molar ratio, R/W in g/cm<sup>3</sup>, T: Temperature in °C, t: time in h, Yield in %,  $S_{BET}$ : BET surface area in m<sup>2</sup>/g,  $R_{Meso}$ : mesopore content,  $d_p$ : average pore diameter in nm,  $Q_m$ : maximum adsorption capacity in mg/g

**Table 3:** Processing conditions and adsorption performance of cryogels

Reactant	R/F	W	R/W	C	R/C	pH	Carbonization			Activation			$S_{BET}$	$R_{Meso}$ (%)	$d_p$	Adsorbate	$Q_m$	Reference
							$T$	$t$	Yield	Agent	$T$	$t$						
R:F	0.5	Water	0.2	Na <sub>2</sub> CO <sub>3</sub>	100	-	1000	4	-	-			500	-	-	-	Mukai et al., 2005	
R:F	0.5	Water	20	Na <sub>2</sub> CO <sub>3</sub>	100	-	800	-	-	CeO <sub>2</sub>	r.t	0.25	614	-	14	As <sup>3+</sup>	4.34	Arsic et al., 2016

R: resorcinol, F: formaldehyde, W: solvent, C: catalyst, R/F & R/C in molar ratio, R/W in g/cm<sup>3</sup>, r.t: room temperature,  $T$ : Temperature in °C,  $t$ : time in h, Yield in %,  $S_{BET}$ : BET surface area in m<sup>2</sup>/g,  $R_{Meso}$ : mesopore content,  $d_p$ : average pore diameter in nm,  $Q_m$ : maximum adsorption capacity in mg/g

From Table 1,  $\text{Na}_2\text{CO}_3$  is noted as the most commonly used catalyst in the preparation of xerogels. The R/C molar ratio is ranging between 50 and 2000. Simple evaporation of solvent – water, acetone or tert-butanol (TBA) – is employed to produce dried xerogels. Without carbonization, the specific surface area of xerogels can reach ca.  $500 \text{ m}^2/\text{g}$  (Oyedoh et al., 2013). After carbonization at  $850^\circ\text{C}$  for 3 h, the specific surface area of carbon xerogels can increase up to  $1200 \text{ m}^2/\text{g}$  (Xiao et al., 2013). Similarly, the activation process with  $\text{CO}_2$  at high temperature produces carbon xerogels with specific surface area greater than  $2000 \text{ m}^2/\text{g}$  (Carlos et al., 2012, Tsuchiya et al., 2014).

Supercritical drying with  $\text{CO}_2$  is a common step in the preparation of aerogels. Without carbonization, an aerogel can possess a specific surface area as high as  $850 \text{ m}^2/\text{g}$ , and a mesoporosity as low as 18% (Czakkel et al., 2013). The carbonization process at temperatures between  $600$  and  $1000^\circ\text{C}$  gives a specific surface area of carbon aerogel in the range of  $600$  to  $700 \text{ m}^2/\text{g}$  (Feng et al., 2011, Luzny et al., 2014). In general, the textual properties of carbon gels are influenced by the ratio of reactant and catalyst. To date, the studies on cryogel as adsorbent are still limited in much of published literature. Freeze drying with TBA has been reported in cryogel production. Cryogel is often characterized as megaloporous material, which is associated with its larger pores compared to that of xerogel and aerogel (Muhtaseb and Ritter, 2003). Therefore, presumably it may not be suitable to be used as adsorbent to remove water pollutants.

From Table 1, xerogel is widely tested as adsorbents for wastewater treatment. It is efficient to remove dyes (Zhou et al., 2011, Carlos et al., 2012, Girgis et al., 2017, Lee and Zaini, 2017, Tang and Zaini, 2017) and heavy metals (Xiao et al., 2013, Luzny et al., 2014, Yang et al., 2015, Osinska, 2017). Adsorption of organic pollutants and heavy metals onto aerogels were also reported in literature as summarized in Table 2. For example, high benzene capacity of  $242.33 \text{ mg/g}$  by carbon aerogel was reported by Moreno-Pirajan & Giraldo (2013). The removal of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ , etc. by carbon aerogels are in the range of  $0.25$  to  $11.5 \text{ mg/g}$  (Cotet et al., 2013, Luzny et al., 2014). Carbon cryogel had an  $\text{As}^{3+}$  adsorption capacity of  $4.34 \text{ mg/g}$  (Arsic et al., 2016).

## 2. Case Study: Carbon gels for the adsorption of anionic dyes

## 2.1 Rationale

About 1.3 million tons of dyes are produced and used in the textile industries annually. Of these, 10 to 25% of the textile dyes is lost during the dyeing process, and 2 to 20% is discharged as effluent. In other words, up to 0.26 million tons of dyes are lost to the effluent every year due to the inefficiency of the dyeing process. The most commonly used textile dyes are categorized under basic, acid and reactive dyes. The effusion of dye containing wastewater into downstream can bring about adverse effect to the aquatic living organisms and public health (Lee and Zaini, 2017b; Tang and Zaini, 2017).

Reactive dyes are mainly used in ink-jet printing of textiles, while direct dyes exhibit a high affinity to cellulosic fibres such as cotton and rayon. These dyes are water soluble anionic dyes, which contain functional groups such as azo, phthalocyanine, stilbene and oxazin. These functional groups give dyes a high stability to chemical, photochemical and biological degradation, hence it is likely that they may still remain in the aquatic environment for an extended period of time (See et al., 2015).

Anionic dyes can cause carcinogenic action, allergies, dermatitis, tissular changes and skin irritation when in contact with human. Azo groups can cause benign (not cancerous) and malignant (cancerous) tumours – the potential cancer initiators – especially in the bladders. Some anionic dyes combine with human serum albumin, and releasing immunoglobulin E that can cause respiratory and skin sensitization risks including dermatitis, allergic conjunctivitis, rhinitis, occupational asthma and other allergic reactions (See et al., 2015). It is therefore imperative to remove anionic dyes in the effluent before it enters the water bodies. A number of excellent adsorbents has been synthesized and tested for dyes removal. However, a treatment process is always required to enhance the adsorption of anionic dyes (Lee, 2016). The present case study reports the evaluation of carbon gel (xerogel) as potential adsorbents for anionic dyes removal from water.

## 2.2 Research Strategies

**Materials.** Formaldehyde (HCHO,  $m_w = 30.03$  g/mol, 37wt% in water), resorcinol (C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>,  $m_w = 110.11$  g/mol, assay 99%), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>,  $m_w = 105.99$  g/mol, assay 99.5%), tert-butyl alcohol ((CH<sub>3</sub>)<sub>3</sub>COH,  $m_w = 74.12$  g/mol, assay 99%), nitric acid (HNO<sub>3</sub>,  $m_w = 63.01$ ,

65%), reactive orange 16 (RO16,  $mw = 617.54$  g/mol) and congo red (CR,  $C_{32}H_{22}N_6Na_2O_6S_2$ ;  $mw = 696.7$  g/mol) were used in the synthesis of RF carbon gels and adsorption studies. The chemicals for carbon gel preparation and dyes for adsorption studies were obtained from Wako Pure Chemical Industries Ltd and R&M Chemicals, respectively and all are of analytical reagents grade.

**Synthesis and characterization.** The sol mixture was initially prepared using resorcinol, formaldehyde, water (solvent) and sodium carbonate (alkaline catalyst) at the desired resorcinol/catalyst (R/C), resorcinol/water (R/W) and resorcinol/formaldehyde (R/F) ratios. The R/C ratios of 1,000 and 2,000 mol/mol were used, and the resultant materials were denoted as RC3 and RC4, respectively (Tang and Zaini, 2017; Lee and Zaini, 2017). The R/W and R/F ratios were fixed at 0.5 g/mL and 0.5 mol/mol, correspondingly. Briefly, 25 g of resorcinol, 0.241 g of  $Na_2CO_3$  and 29.7 g of water were mixed in a disposable cup, followed by an addition of 36.85 g of formaldehyde. The sol mixture was stirred and poured into a mould to allow gelation of RF sol solution at 35°C for 48 h (Al-Muhtaseb and Ritter, 2003). Next, the aging step was held by heating the cured gel at 60°C for 72 h. After that, the RF hydrogel was placed into a capped bottle filled with tert-butyl alcohol (TBA) and retained at 50°C for 72 h to eliminate the surplus water by solvent exchange process. The TBA was exchanged with a fresh one twice a day. The RF organic gel was then dried at 110°C for 48 h and crushed to obtain uniform particle size of 1 mm. Lastly, the organic gel was carbonised at 600°C for 3 h to produce RF carbon gel and labelled as RC3 (R/C, 1,000 mol/mol) and RC4 (R/C, 2,000 mol/mol). The additional oxidation step was performed by soaking the carbon gel in  $HNO_3$  (65 - 66 %) at room temperature for 3 h, followed by heating at 60 °C for 5 h. The oxidized RC3 and RC4 were denoted as RC7 and RC8. The resultant materials were washed with distilled water to a constant pH. The single point specific surface area of carbon gel samples were determined by  $N_2$  adsorption and desorption isotherms at 77 K using a surface area analyzer (Micrometrics PulseChemiSorb 2705, USA). The surface morphology of the samples were obtained using a scanning electron microscope (Philips SEM-50, Holland).

**Adsorption kinetics.** Kinetics study is crucial to an adsorption process as it illustrates the uptake rate of adsorbate and controls the retention time of the entire adsorption process. The batch method (or also known as bottle-point-technique) was performed to determine the relationship between the contact time and the adsorbate concentration for adsorption process (Tang, 2016). The adsorption kinetics of anionic dyes was studied based on two initial concentrations, i.e., 5



mg/L and 10 mg/L at various time intervals. Briefly, 0.05 g of carbon gel was added into different batches of conical flasks containing 50 mL of anionic dye solution of desired concentration. The mixtures were agitated in a shaker at room temperature and 120 rpm for 72 h. At different time intervals, the supernatant of the identified flask was taken for concentration measurement to analyze the uptake of anionic dye uptake. The concentration measurements were performed using visible spectrophotometer (Halo-Vis 10) at wavelengths of 510 nm and 523 nm and for congo red and reactive orange 16, respectively. The experiments were done in triplicate to elicit accurate mean value. The kinetics data were fitted into kinetics models to evaluate the rate of adsorption. The pseudo-first-order, pseudo-second-order, Boyd and intraparticle diffusion models are among the most widely used kinetics models in interpreting the kinetics data. The mathematical expressions of these models are summarized in Table 4.

**Table 4:** Kinetics models Calvete *et al.*, 2009)

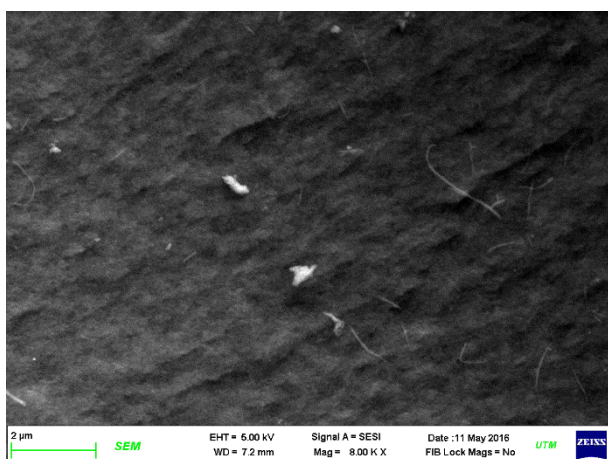
Kinetic Model	Non-linear equation	Linear equation	Linear Plot
Boyd	$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 Bt)$	$Bt = -0.4977 - \ln(1 - F);$ $F = \frac{q_t}{q_o}$	$Bt \text{ Vs } t$
Pseudo first order	$q_t = q_e [1 - \exp(-k_1 t)]$	$\ln(q_e - q_t) = \ln(q_e) - k_1 t$	$\ln(q_e - q_t) \text{ Vs } t$
Pseudo second order	$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t} \text{ Vs } t$
Intra-particle diffusion	$q_t = k_{diff} t^{0.5} + C$	$q_t = k_{diff} t^{0.5} + C$	$q_t \text{ Vs } t^{0.5}$

## 2.2 Findings and Discussion

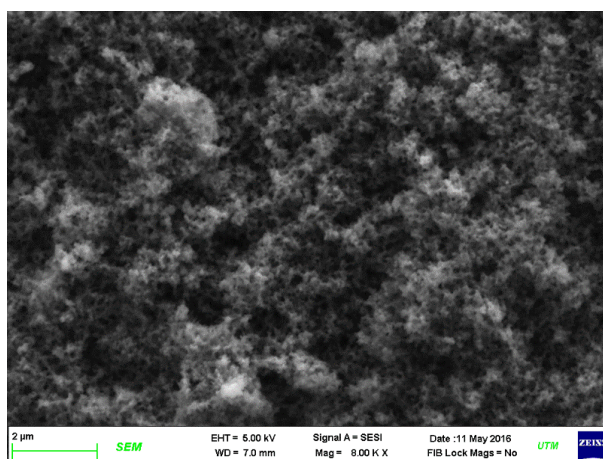
**Carbon gels.** Resorcinol-formaldehyde (RF) carbon gels can be used in different applications such as adsorbents for the removal of wide range of environmental pollutants, catalysis supports for reaction processes and gas filters in gas treatments, all in all due to their unique and highly flexible textural properties, and exceptional surface morphology, porosity and surface area. To maximize the capacity of RF carbon gels, the morphology of the material

should be closely monitored. Honeycomb, thin film, powder, granule, fiber and microsphere are examples of different types of morphology of these porous materials (Mukai et al., 2005).

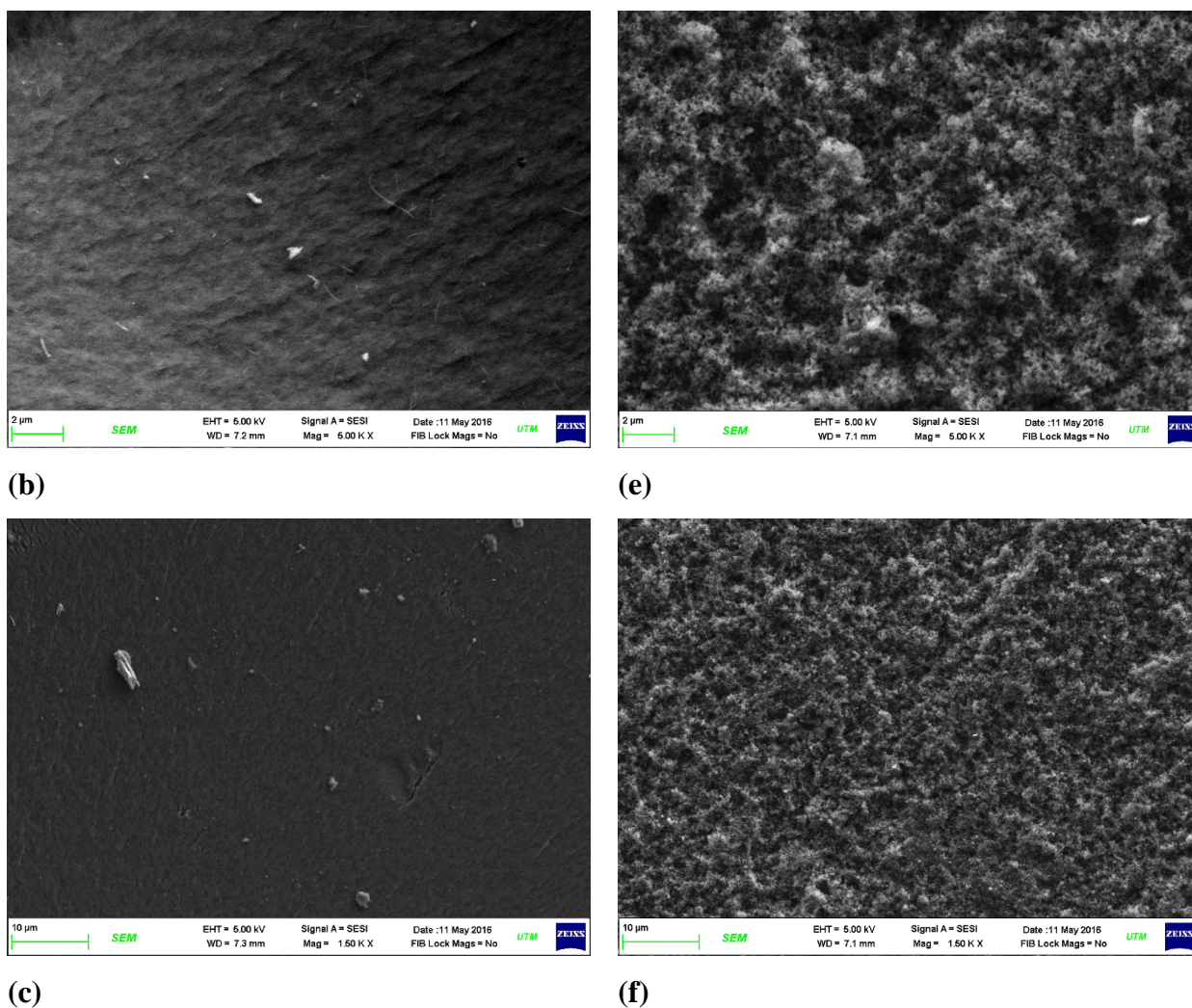
Figure 1 shows the SEM images of RF carbon gels, RC3 and RC4 in three magnifications. It can be seen that RC4 (Figure 1(d), (e), (f)) has a honeycomb-like surface that is highly porous with the presence of voids of small micropores and mesopores. On the other hand, RC3 (Figure 1(a), (b), (c)) exhibits a smooth and uneven surface with almost no apparent pore formation. In this study, the R/W and R/F ratios were fixed at 0.5 g/mL and 0.5 mol/mol respectively, while R/C ratios were 1000 (RC3) and 2000 (RC4). A decrease in reactant (resorcinol) concentration and an increase in catalyst amount caused the resulting carbon gel to possess smaller particles and pore sizes, and denser gel structure with less voids (Al-Muhtaseb and Ritter, 2003). In other words, low R/C, R/W or R/F ratios produces less porous carbon gels with less compaction during aggregation of nanoparticles. During pyrolysis, the organic gel is carbonized into carbon gel, whereby the burnout of the organic matters triggers the formation of new micropores and mesopores, hence enhancing the surface area of carbon gel (Tang and Zaini, 2017). The yield and textural properties of RF carbon gels, as shown in Table 5 was reported by Lee and Zaini (2017a). The yield after carbonization is about 50%, while the BET surface area and mesoporosity increased with increasing R/C ratio, and somewhat decreased upon oxidation.



(a)



(d)

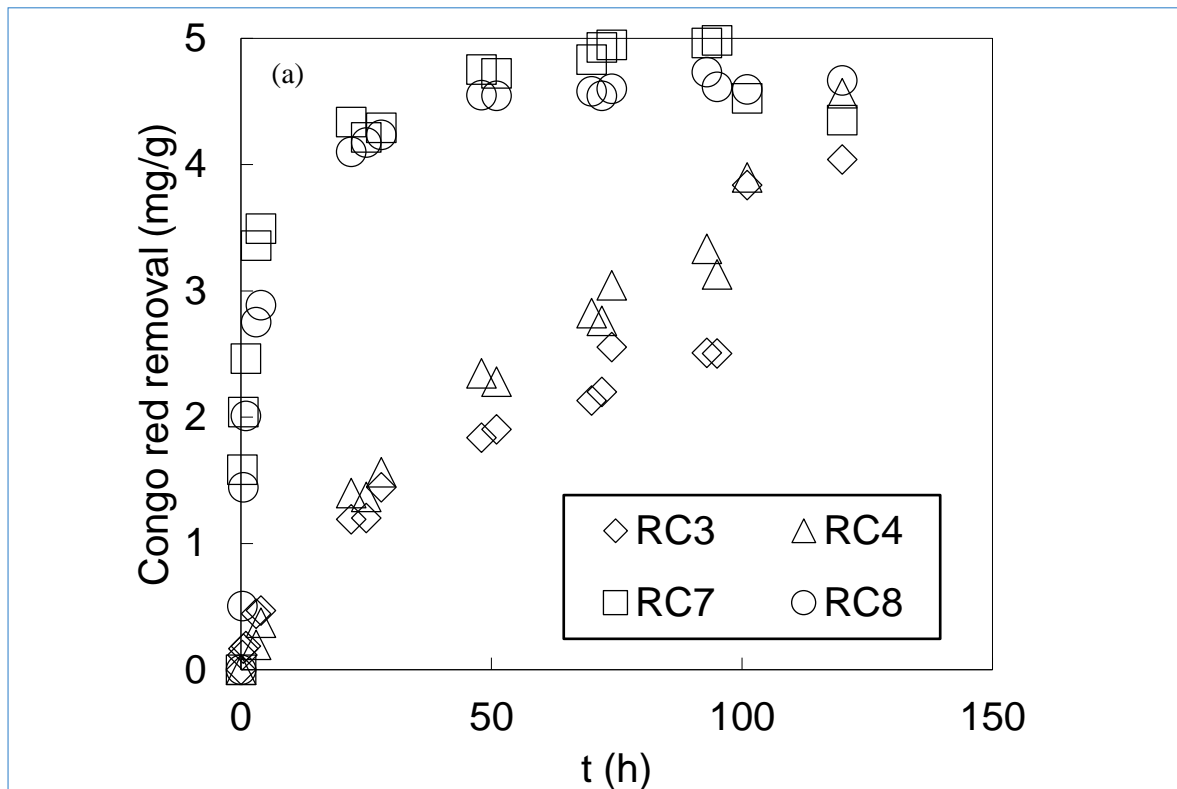


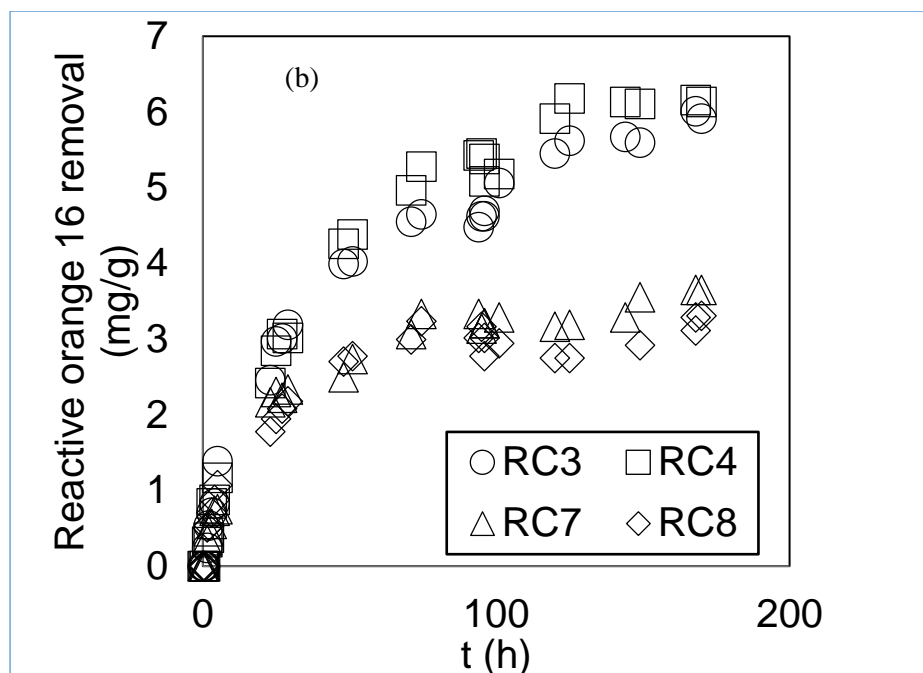
**Figure 1:** SEM images of carbon gels: RC3, magnification (a) 8 k, 2  $\mu\text{m}$ , (b) 5 k, 2  $\mu\text{m}$ , (c) 1.5 k, 10  $\mu\text{m}$ ; and RC4, magnification (d) 8 k, 2  $\mu\text{m}$ , (e) 5 k, 2  $\mu\text{m}$ , (f) 1.5 k, 10  $\mu\text{m}$

**Table 5:** Textural properties and yield of carbon gels (Lee and Zaini, 2017a)

Carbon gel	Oxidation	R/C ratio	BET surface area ( $\text{m}^2/\text{g}$ )	Mesoporosity (%)	Average pore diameter (nm)	Yield (%)
RC1	Non-oxidized	100	476.0	23.74	1.86	42.8
RC2		200	608.2	46.34	2.38	49.6
RC3		1000	638.9	69.80	6.89	42.6
RC4		2000	630.5	59.19	3.56	53.7
RC5	oxidized	100	301.2	0.00	1.33	42.8
RC6		200	566.7	44.89	2.33	49.6
RC7		1000	711.5	75.10	7.68	42.6
RC8		2000	586.2	59.34	3.57	53.7

**Evaluation of Adsorption kinetics.** The pseudo-first-order and pseudo-second-order models were employed to discuss the rate of anionic dyes adsorption by carbon gels. The intraparticle diffusion and Boyd models were used to evaluate the diffusion mechanisms. The kinetics plots (for  $C_o = 10$  mg/L) are shown in Figure 2, and the respective constants are tabulated in Table 6. For reactive orange 16 (RO16), the  $R^2$  values for the pseudo-first-order model are more closer to 1.0 than that of the pseudo-second-order, indicating the applicability of the pseudo-first-order model to describe the rate of adsorption that lies on the assumption that physisorption may be the rate-limiting step (Lee and Zaini, 2017). On the other hand, the pseudo-second-order has a higher  $R^2$  for congo red (CR) adsorption kinetics, suggesting that the overall adsorption rate is chemically controlled through sharing or exchange electron between congo red molecules and carbon gel surface (Tang and Zaini, 2017). This is in agreement with the patterns displayed in Figure 2, whereby the removal of congo red is dominated by the oxidized carbon gels, while unoxidized carbon gels exhibit a better performance for reactive orange 16 adsorption. For both cases, carbon gel with pore width of 3.6 nm (mesoporous) showed a slightly higher uptake compared to the macroporous carbon gel (pore width > 5 nm).





**Figure 2:** Adsorption kinetics of (a) congo red and (b) reactive orange 16 by carbon gels at dyes initial concentration of 10 mg/L

Adsorption is generally governed by four sequential steps: (1) bulk diffusion – diffusion of dye molecules from the bulk solution to the surface of adsorbent; (2) film diffusion – diffusion of dye molecules through the boundary layer; (3) pore diffusion or intraparticle diffusion – diffusion of dye molecules from the adsorbent surface into the pores; and (4) adsorption – binding of dye molecules to the active sites (Lee and Zaini, 2017b). The intercept  $c$  of the intraparticle diffusion model indicates that pore diffusion is not the sole rate-limiting step in the adsorption mechanisms of RO16 and CR. A larger  $c$  signifies a greater contribution of film diffusion in the rate-limiting step. In order to determine the rate-limiting step, the Boyd's model was used to analyze the kinetics data. The observance of an intercept in Boyd's model indicates pore diffusion is not the rate-limiting step, but it can be either film diffusion or chemical reaction (Lee and Zaini, 2017b). Effective diffusion coefficient is expressed as,  $B = \frac{\pi^2 D_i}{r^2}$ , where  $B$  is the straight line slope in Boyd's plot,  $D_i$  (cm<sup>2</sup>/s) is the effective diffusion coefficient and  $r$  (cm) is the radius of the adsorbent particle. By knowing that the average carbon particle size is 0.05 cm in radius, the effective diffusion coefficient was calculated to determine the rate-limiting step. The film diffusion could be the rate-limiting step if  $D_i$  is in range of 10<sup>-6</sup> to 10<sup>-8</sup> cm<sup>2</sup>/s (Karthikeyan & Sivakumar, 2012). Consequently, from the values shown in Table 6, it can be concluded that film diffusion is not the rate-limiting step in the adsorption of RO16 and CR onto carbon gels.

**Table 6: Kinetics constants.**

Adsorbate	Carbon gel	$C_o$ (mg/L)	$Q_{e, exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order				Intraparticle diffusion			Boyd		
				$k_1$ (h <sup>-1</sup> )	$Q_e$ (mg/g)	R <sup>2</sup>	$k_2$ (g/mg.h)	$Q_e$ (mg/g)	R <sup>2</sup>	$h$ (mg/g.h)	$k_{it}$ (mg/g.h <sup>0.5</sup> )	$c$ (mg/g)	R <sup>2</sup>	$c$	R <sup>2</sup>	$D_i$ (cm <sup>2</sup> /s)
Reactive orange 16	RC3	5	3.820	0.022	3.693	0.968	0.006	4.522	0.901	0.114	0.290	0.234	0.991	-0.071	0.930	9.15 x 10 <sup>-10</sup>
		10	5.912	0.026	5.572	0.978	0.004	6.884	0.953	0.191	0.483	0.073	0.972	-0.115	0.917	1.13 x 10 <sup>-9</sup>
	RC4	5	3.869	0.010	4.898	0.987	0.001	7.222	0.663	0.052	0.339	-0.411	0.990	-0.044	0.936	2.11 x 10 <sup>-10</sup>
		10	6.131	0.024	6.169	0.992	0.003	7.797	0.970	0.186	0.534	-0.029	0.970	-0.110	0.923	1.27 x 10 <sup>-9</sup>
	RC7	5	2.044	0.023	2.043	0.987	0.008	2.640	0.432	0.056	0.186	-0.117	0.960	-0.083	0.953	1.13 x 10 <sup>-9</sup>
		10	3.650	0.041	3.347	0.983	0.008	2.640	0.920	0.056	0.289	0.280	0.919	0.049	0.883	1.13 x 10 <sup>-9</sup>
	RC8	5	2.482	0.036	2.363	0.976	0.017	2.734	0.893	0.129	0.194	0.251	0.939	-0.002	0.837	1.34 x 10 <sup>-9</sup>
		10	3.309	0.048	3.029	0.969	0.021	3.391	0.948	0.238	0.244	0.442	0.872	0.153	0.665	1.13 x 10 <sup>-9</sup>
Congo red	RC3	5	3.263	0.017	3.314	0.659	0.015	2.937	0.837	0.132	0.260	-0.063	0.946	-1.103	0.860	1.90 x 10 <sup>-9</sup>
		10	4.040	0.015	4.133	0.655	0.010	3.580	0.801	0.131	0.315	-0.169	0.925	-1.166	0.870	1.78 x 10 <sup>-9</sup>
	RC4	5	2.990	0.026	2.533	0.941	0.035	2.982	0.975	0.315	0.264	0.279	0.979	-0.674	0.905	2.21 x 10 <sup>-9</sup>
		10	4.566	0.015	4.678	0.947	0.014	3.926	0.690	0.219	0.403	-0.447	0.977	-1.211	0.963	1.83 x 10 <sup>-9</sup>
	RC7	5	3.222	0.031	1.366	0.821	0.180	3.191	0.999	1.836	0.233	1.131	0.800	0.233	0.774	2.32 x 10 <sup>-9</sup>
		10	4.985	0.030	1.779	0.539	0.379	4.728	0.993	8.467	0.318	2.039	0.719	0.457	0.520	2.17 x 10 <sup>-9</sup>
	RC8	5	3.374	0.022	2.303	0.528	0.067	3.010	0.966	0.607	0.215	0.925	0.826	-0.238	0.580	1.79 x 10 <sup>-9</sup>
		10	4.732	0.034	2.141	0.871	0.104	0.212	0.999	0.005	0.366	1.483	0.792	0.116	0.810	2.53 x 10 <sup>-9</sup>

### 3.0 Conclusion

Carbon gel-based adsorbents are micropore-rich carbons produced via carbonization of aggregated nanometer-sized particles or organic resorcinol-formaldehyde (RF) gels. This chapter highlights the promising role of RF carbon gel as adsorbents in the removal of water pollutant, and the relationship between the adsorption performance and the unique textural properties of carbon gels. In the case study, both oxidized and unoxidized carbon gels exhibit high surface area to facilitate the adhesion of anionic dyes onto the surface of carbon gel. The analysis of adsorption kinetics showed that the film diffusion is not the rate-limiting step in the adsorption of reactive orange 16 (RO16) and congo red (CR) onto carbon gels. To conclude, carbon gel is a potential adsorbent for anionic dyes removal due to its adjustable textural properties.

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