

## Acid – treated activated carbon for phenolic compound removal in acid pre-treatment of lignocellulosic biomass for biogas production

Sofiah Hamzah<sup>1,\*</sup> , Siti Zulaikha Ramli<sup>1</sup>, Nurul Aqilah Mohammad<sup>1</sup>, Nazaitulshila Rasit<sup>1</sup>, Alyza Azzura Abd Rahman Azmi<sup>2</sup>, Nur Hanis Hayati Hairom<sup>3</sup> and Abdul Wahab Mohamad<sup>4</sup>

<sup>1</sup>Faculty of Ocean Engineering, Technology and Informatics, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu Malaysia

<sup>2</sup>Faculty of Science and Marine Environment, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu Malaysia

<sup>3</sup>Faculty Of Engineering Technology, Universiti Tun Hussein Onn Malaysia, Hab Pendidikan Tinggi Pagoh, KM 1, Jalan Panchor, 84600, Muar, Johor, Malaysia

<sup>4</sup>Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia 43600 UKM Bangi, Selangor, Malaysia

\*corresponding author e-mail address: [sofiah@umt.edu.my](mailto:sofiah@umt.edu.my) | Scopus ID [54954085300](https://orcid.org/0000-0002-5495-4085)

### ABSTRACT

Phenolic compound can be an inhibitor during acid pre-treatment process in the conversion of biomass into bioenergy and consequently reduces the production yield. Thus, this study aimed to investigate the potential use of activated carbon from coconut shell for phenolic compound removal and gallic acid was used as model phenolic. Granular activated carbon was treated by using 20% concentration of phosphoric acid to its properties and function. Acid treated and untreated activated carbon were characterized in term of morphology, surface functionalities and material phase by means of SEM, FT-IR and XRD. Few parameters that influenced the removal of gallic acid were studied which included the effect of adsorbent dosage, initial concentration, contact time, and pH. It is observed that the acid treated activated carbon was successfully remove the gallic acid for about 97% using of 0.5g/L adsorbent dosage, with initial concentration of 100 mg/L, at pH value of 4 and 150 minutes contact time. The adsorption behavior was fixed with Langmuir isotherm fixed the experiment data which indicates homogenous adsorption. These experimental results also revealed that coconut shell based activated carbon is viable cheaper adsorbent for phenolic compound removal.

**Keywords:** *activated carbon; phenolic compound; lignocellulosic; biomass, adsorption.*

### 1. INTRODUCTION

Coal, crude oil and natural gas are examples of important resources in fossil fuel refinery that is very essential in sustaining the life of the modern world in this era of technology. Using this non – renewable energy can increase the level of pollutions and also reduce the sources from which it originates. Nowadays, coal and also fossil fuels promote air pollution problems if emits into the air. Emission of greenhouse gases (GHG) such as carbon dioxide, methane and nitrous oxide are one of the examples of many more problems arising from fossil fuel refinery or combustion.

As known, these sources can be depleted and might went someday. So we need to recognize renewable energy such as energy from biomass or agricultural wastes to replace the non – renewable energy in order to promote a healthy environment.

Biorefineries are one of the technologies that can be used to reduce the problem associated with wastes in the environment.

The continuous process should be run efficiently in order to ensure the product yield is optimum [1]. Acid pretreatment has been recognized as one of the crucial process step for the biochemical conversion of lignocellulosic biomass into biogas or biofuel [2]. However, one of the major problems in this stage is the presence of inhibitor mainly the phenolic compound such as gallic acid.

This compound will slow down the process of biogas production and should be removed at early stage of process. Therefore, great effort is required to search for efficient adsorbent which can remove the phenolic compound efficiently.

There are some methods to remove and degrade these substrates in order to make the biogas or any other bio-production becomes more efficient. Some common techniques that are used in removing phenolic compound are biological treatment, solvent extraction, electro coagulation, chemical oxidation, reverse osmosis, membrane filtration, ion exchange, precipitation, distillation and also adsorption [5]. Among these techniques, adsorption has shown the most efficient method to remove organic compound in aqueous solution.

Activated carbon is the most used and highly efficient for adsorption method. It is expensive but has shown to be effective for the removal of trace organic compounds. Therefore new options are being developed including chemical modification of the activated carbon, impregnation with nanoparticles, different sources of carbon, different activation methods as well as substitution with low cost bio adsorbents such as lignocellulosic biomass and chitin or chitosan, which these are the promising alternatives to remove phenolic compounds. A study by Liu et al.[6], used a composite of activated carbon and chitosan of 1:1 ratio to remove the phenolic compound and Chromium (VI) and achieved 95% removal of both and reaching equilibrium time in 40 minutes [6]. Research by Bernal et al. [7] have developed a chemical modified activated carbon which includes granular and pelletized.

This activated carbon was impregnated with phosphoric acid or potassium hydroxide. Both of the impregnations have modified the surface area, micro pore volume and the volumes of meso pore due to the reaction with superficial oxygen groups. The

result from this study showed that phosphoric acid has shown better adsorption of 2, 4 – dinitrophenol compared to the potassium hydroxide. Other research by Atieh [8] stated that activated carbon has the highest removal efficiency with 65% followed by carbon nanotubes 47%, carbon fly ash 43% and lastly carbon nanofibers 31% .

Activated carbon from coconut shell has been chosen in this study due to its availability and high adsorption efficiency. The activated carbon relatively has high fixed carbon content & presence of inherent porous structure. It is inexpensive and has shown to be effective for the removal of organic compounds or phenolic compounds.

Several studies had been conducted by researchers on the use of activated carbon from coconut shell in term of characterization and their uses. For example, Hidayu & Muda [9], stated that coconut shell based activated carbon contains high surface area which is about 1011 m<sup>2</sup>/g by physical activation.

Karri et al. [5], investigated the use of activated carbon form coconut shell in phenol removal, which is 96% removal of phenol that can be achieved with lower the loads of activated carbon and shorter residence time. Other reported uses of coconut shells activated carbon to include the increase of percentage saturation with an increase in initial concentration and flow rate

while the percentage saturation will decrease when the particle size increase [10]. Lima et al.[11], also stated that the modified coconut powder bagasse was efficiently removed anions from aqueous solution. Another study conducted by Din et al. [12] proved that activated carbon produced from coconut shell was found to be effective to remove phenol from aqueous solution. Fang [13] and Teli [14] were also found a good findings on the utilization of activated carbon for pollutant or impurities removal.

The present study deals with the comparison of treated and untreated activated carbon for phenolic compound removal from black liquor of lignocellulosic treatment for biogas production. The commercial activated carbon was treated with sulphuric acid to improve its properties and performance. The prepared adsorbent was characterized using scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR). Batch adsorptions were performed to study the effects of different experimental parameters such as pH, contact time, adsorbent dosage and initial phosphate concentration on the adsorption performance.

This study has also revealed the mechanism of phenolic compound (gallic acid) adsorption onto the modified adsorbent by fitting the experimental data to isotherm model.

## 2. MATERIALS AND METHODS

### 2.1. Materials.

The coconut shell based activated carbon was obtained from Amgo Sdn. Bhd. Gallic acid monohydrate (ACS Reagent), Iron (III) chloride 6-hydrate (HmbG Chemicals), Potassium ferricyanide (III) powder (99%,10um, Sigma-Aldrich), Ortho-Phosphoric Acid (Mw=98.00 g/mol, Bendosen), and Gum Arabic from acacia tree (Sigma) used for the Blue Prussian Assay, while 3,5- Dinitrosalicylic acid (Sigma), used in colorimetric determination of reducing sugar (Sigma).

### 2.2. Pre-treatment of of Activated Carbon.

Activated carbon was immersed in 20 % phosphoric acid overnight to ensure a complete reaction. The materials then washed with distilled water several times until it reaches neutral pH value and dried in oven for 24 hours at 100° C. Phosphoric, activated carbon ratio of 1.5 proportion was used in this method.

### 2.3. Characterization of Adsorbents.

Both adsorbents; treated and untreated activated carbon were characterized in term of morphology, functional group and their crystalline structure as described by Hamzah et al [15].

### 2.4. Adsorption experiments.

To evaluate the performance of adsorbents, the Folin Ciocalteu reagent was prepared. In a 100 ml volumetric flask, 0.5g of dry powdered Gallic acid was inserted in 10 ml of ethanol and then diluted to volume with water. The Folin reagent was mixed with the gallic acid stock solution and then a gallic acid standard curve was plotted.

The samples were analysed on the effect of contact time (30- 180 min) and different dosages of adsorbent (200-600 mg/L). Other parameters such as initial concentration with a range 25-125 mg/L and pH 2-12 were also analysed. All of the parameters were carried out to determine the optimum condition to obtain the highest efficiency of phenolic compound removal.

The amount of adsorbed gallic acid by activated carbon was calculated as shown in equation (1):

$$\text{Percentage removal} = \frac{C_i - C_0}{C_i} \times 100\% \quad \dots 1$$

Where,  $C_i$  is initial concentration (mg/l),  $C_0$  is the concentration after using adsorbent (mg/l)

### 2.5. Adsorption Isotherm study.

Adsorption isotherm was used to represent the equilibrium states of an adsorption system and gain understanding on the mechanism of adsorption process [16]. This is to describe how the solute interacts with the adsorbents at optimize condition. Several adsorption isotherms have been studied such as Langmuir and the Freundlich Isotherms which used to determine the adsorbates layer formation on the surface of adsorbent [17]. The analysis of the equilibrium data by fitting them into different isotherms models is a very important step to find a suitable model that can be used for design purposes [15].

Langmuir isotherm assumes monolayer and homogenous adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir Isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad 2$$

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) and  $Q_0$  and  $b$  are Langmuir constant related to the adsorption capacity and rate of adsorption respectively.

Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. The logarithmic form of Freundlich isotherms is given below:

$$\log Q_e = \log K_F + (1/n) \log C_e \quad 3$$

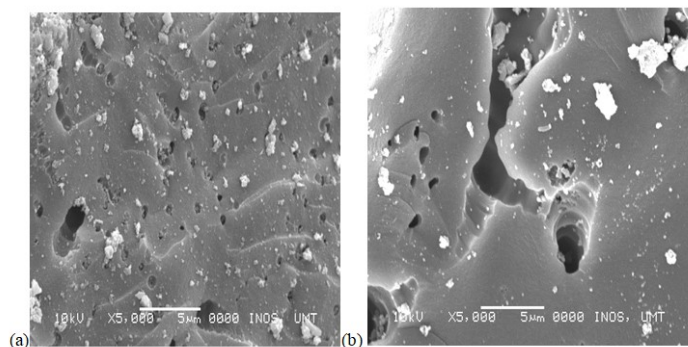
Where,  $C_e$  is the equilibrium concentration of the adsorbate (mg/l),  $Q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g) and both  $K_F$  and  $n$  are Freundlich constants with  $n$  giving

an indication of how favorable the adsorption process,  $K_F$  (mg/g (1/mg)<sup>1/n</sup>) is the adsorption capacity of the adsorbent.

### 3. RESULTS

#### 3.1. Characterization of adsorbents.

Scanning electron microscope (SEM) is used to view the surface morphology of acid-treated and untreated coconut shell activated carbon as depicted in Figure 1.



**Figure 1.** SEM images of (a) treated activated carbon (b) untreated activated carbon at magnification 5,000X.

It can be seen that there was a change on the surface of treated activated carbon compared to the surface of untreated activated carbon after acid impregnation process. Different size of pores was observed for both treated and untreated activated carbon samples. The image indicated that the treated activated carbon contained more open and homogenous pores on the external surfaces and irregular, also highly porous surface if compared to the untreated sample which has less pores on the external surface. This result postulated that acid modification causes the removal of volatiles and producing a fixed carbon mass with widening of pore networks that are present in activated carbon samples. According to Oginni et al., [18], phosphoric acid can act as cleaning and dehydrating agent, which promotes bond cleavage reaction in biomass precursor and facilitate crosslinking process. These exterior pores can act as the main conduit to the micropores on the inner surface of the activated carbon [19]. The morphology result did not proof the influence of acid treatment on pore geometry of this activated carbon, but the opening of few cavities mouth and pores improvement are evident [20].

The surface chemistry of both adsorbents was investigated by FT-IR. It was a well-known method and most useful in providing information about the presence or absence of specific functional groups. The spectra display a number of absorption peaks, which indicating a complex nature of the material examined. The FTIR spectrum of untreated and treated activated carbon samples are shown in Table 1 and 2 respectively.

**Table 1.** Functional groups and the classification of compounds detected in the untreated activated carbon.

Number	Frequency range (cm <sup>-1</sup> )	Functional groups	Classification of compounds
1	3200 - 3550	O-H	alcohols & phenols
2	2500 - 3300	O-H	carboxylic acid & derivatives
3	2100 - 2250	C=C	Alkynes
4	1210-1320	O-C	carboxylic acid & derivatives

**Table 2.** Functional groups and the classification of compounds detected in the untreated activated carbon.

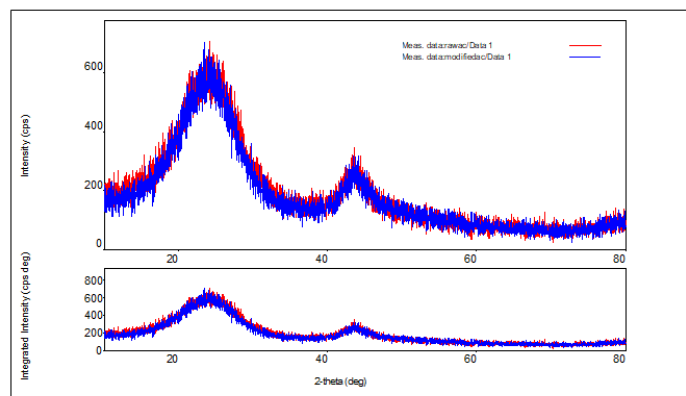
Number	Frequency range (cm <sup>-1</sup> )	Functional groups	Classification of compounds
1	3200 - 3550	O-H	Alcohols & phenols
2	2850 - 3000	CH <sub>3</sub> , CH <sub>2</sub> , CH	Alkanes
3	2100 - 2250	C=C	Alkynes
4	1900 - 2000	C=C	Alkenes

At range of 3200 – 3550 cm<sup>-1</sup>, a broad represented to O-H stretching in alcohols and phenols. The adsorption peak at 2500–3300 cm<sup>-1</sup> and 1210–1320 cm<sup>-1</sup> shows the presence of carboxylic acid and its derivatives can be attributed to O-H stretching vibrations of cellulose, absorbed water, hemicellulose and lignin. The weak peak observed at 2100– 2250 cm<sup>-1</sup> can be attributed to the C=C stretching.

At range of 2850 - 3000 cm<sup>-1</sup>, 2100 - 2250 cm<sup>-1</sup> and 1900 - 2500 cm<sup>-1</sup>, the functional groups of aliphatic hydrocarbon (C=C) stretching were present in the sample of the treated activated carbon [20]. At range 3200 - 3550 cm<sup>-1</sup>, O-H bond is present indicates there is alcohols and phenols functional groups [21].

The X-Ray Diffraction profile of the treated and untreated activated carbon from coconut shell is shown in Figure 2. For the treated activated carbon samples, XRD pattern exhibit only one diffuse peak which is at 2θ = 24.18° while the untreated activated carbon samples exhibit seven diffuse peak which located at 2θ = 18.99°, 30.33°, 30.55°, 30.74°, 31.03°, 43.39° and 53.28°. This revealed the presence of amorphous structure which is disorderly stacked up by carbon rings and helpful for producing well, defined adsorbent.

The XRD pattern of treated and untreated activated carbon samples are approximately the same where it can be observed that activated carbon before and after the impregnation process did not exhibit well defined peaks in any regions. This indicated that no discrete mineral phase was detected. Thus, the activated carbon has a completely amorphous structure, which is expected for organic materials [22]. The hump in the 2θ range 20 – 30° implies the high degree of disorder expected for the produced carbonaceous material.



**Figure 2.** XRD of treated and untreated activated carbon.

### 3.2. Evaluation performance of adsorbent on the removal of phenolic compound (Gallic acid).

#### 3.2.1. Contact time for effective absorption.

To understand the performance of Gallic acid adsorption on activated carbon against the contact time, different experiments using treated and untreated activated carbon were conducted. Both of these experiments were conducted at a fixed adsorbent dosage of 100 mg/L. The initial Gallic acid concentration used was 100 mg/l and pH of 4 for each sample. The result of the removal efficiency is shown in Figure 3. The most effective contact time between Gallic acid and the adsorbent was determined from this experiment.

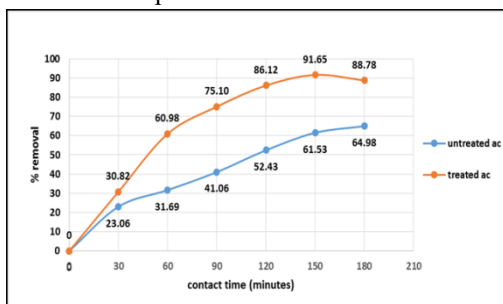


Figure 3. Effect of contact time on Gallic acid removal.

It is observed that increase the contact time was increased the gallic acid removal and optimum removal achieved at contact time of 150 minutes (91.65 % gallic acid removal) and this is agreeable with the study conducted by Hamzah et al. [23]. Increase the adsorption would not give a significant increase of removal efficiency since the adsorbent has reached its saturation state beyond that time. The results indicated that the sorption process can be considered fast because of the large amount of Gallic acid can be absorbed by the treated activated carbon within the first 90 min of adsorption.

In comparison, the result for the Gallic acid removal efficiency using untreated activated carbon only yield 61.537% at the same contact time of 150 minutes. However, the removal efficiency continues to increase gradually within the contact time of 180 minutes but after this period, the removal efficiency is considered to be slower as longer contact time will affect the acid pretreatment process.

#### 3.2.2. Effect of adsorbent dosage.

Figure 4. shows the effect of adsorbent dosage on gallic acid removal using acid treated and untreated activated carbon.

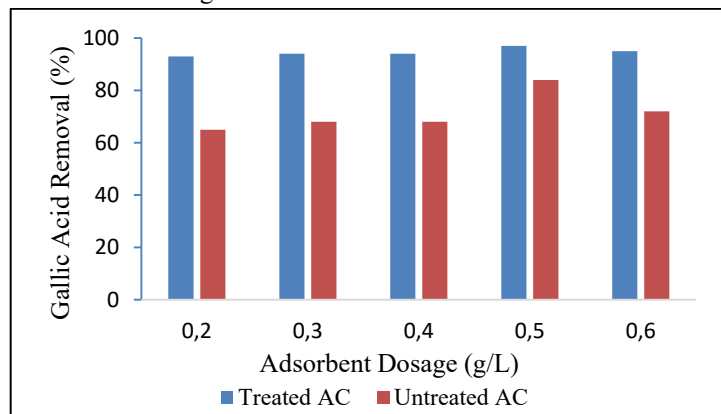


Figure 4. The effect of adsorbent dosage on Gallic acid removal.

According to the results obtained, there are only a slight increment of gallic acid removal when the dosage increase from

0.2-0.6 g/L. The maximum removal obtained at 0.5 g/L dosage with 97% removal. A higher dose of adsorbent promotes an increase of surface area, thus more adsorption sites are available causing higher removal of Gallic acid. Additional dosage would not improve the removal due to the saturation of adsorbate. Furthermore, increase in dosage after their optimum level induces the accumulation of the adsorbent itself and would overlapped the active site, thus decreased the removal efficiency [24]. A lower performance observed for native activated carbon which removed the gallic acid in the range of 65 to 84%. This result might due to the lower surface area and internal pores present with the absence of phosphoric acid treatment.

#### 3.2.3. Effect of initial concentration.

Initial solute adsorbate concentration provides an important driving force to overcome all mass transfer resistance of adsorbate between aqueous and solid phase. Figure 5 shows the effect of initial concentration on gallic acid removal. It can be seen that the percentage of Gallic acid removal using acid treated activated carbon only varies from 96 to 97%. In other words, within the range of concentration used in this study, there are no significant improvement of gallic acid removal when its initial concentration increased. A lower performance with the untreated one was due to its properties and characteristics.

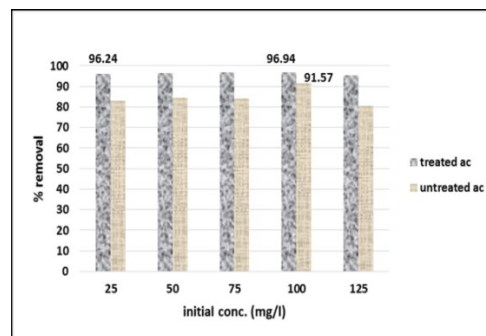


Figure 5. Effect of initial concentration on Gallic acid removal.

#### 3.2.4. Effect of pH.

The pH of aqueous solution is a very critical parameter that affects the adsorption process due to functional group of both adsorbed molecules and adsorbent particles being affected by the concentration of hydrogen ions ( $H^+$ ) in the solution. The  $H^+$  ions in solution are involved in the adsorption process at the active sites of the activated carbon. According to Figure 6, gallic acid removal increase slightly with increasing the pH value from 2 to 4 for the treated adsorbent, but then, decreases at pH 6 until 12.

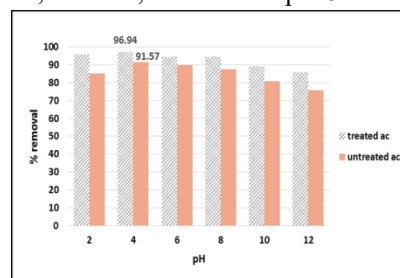


Figure 6. Effect of pH values on Gallic acid removal.

The most effective pH for Gallic acid removal occurred at pH 4. The peak has high removal efficiency which achieved removal around 97% and 92% for treated and untreated activated carbon, respectively. At low pH value,  $H^+$  ions suppressing the ionization hence improve the adsorption and removal efficiency.

Increase the pH from 6 to 12 would gradually reduce the removal efficiency due to the competition of  $H^+$  and  $OH^+$  ions for the active site in the adsorbent surface. It was also observed that when pH increased, the colour of the solution becomes darker due to the increase of ( $OH^+$ ) ions and high  $OH^+$  ions accumulated on the adsorbent surface would retard the adsorption to take place.

### 3.3. Adsorption Isotherms.

Adsorption isotherm is useful to describe how solutes interact with adsorbents and very important to evaluate feasibility of the adsorbent- adsorbate system. The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [15]. The adsorption equilibrium data obtained for the untreated and treated activated carbon were fitted into two different isotherms models to determine the most suitable model to represent the adsorption process. The adsorption capacities on Gallic acid for the two activated carbon were then compared.

#### 3.3.1. Langmuir Isotherm.

Langmuir Isotherm is based on an assumption that the adsorption occurs at specific homogenous sites within the adsorbent and the monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. Langmuir isotherm of this study is shown in Figure 7.

The Langmuir model yielded the best fit at all initial concentration, as the  $R^2$  values were relatively high (close to unity) compared to the other isotherm model. The  $R^2$  value for the treated activated carbon was 0.97 while for the untreated activated carbon, the Langmuir isotherm also gave the best fit for the adsorption of Gallic acid with  $R^2$  value of 0.96. The  $1/n$  values obtained for the activated carbon at all optimum conditions studied were below one. This indicated that the adsorption process followed a normal Langmuir isotherm where each of Gallic acid molecule/carbon adsorption had equal adsorption activation energy. This confirmed that the Langmuir isotherm was favorable

for adsorption of Gallic acid on both activated carbon under the conditions used in this study.

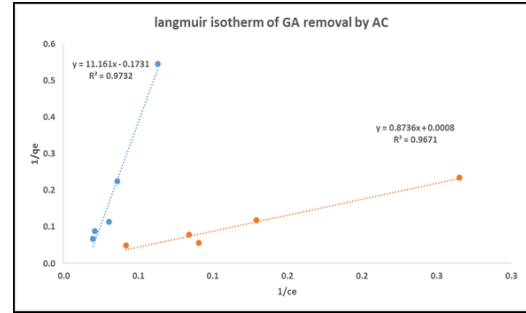


Figure 7. Langmuir Isotherm for Gallic acid adsorption on treated  $\bullet$  and untreated  $\bullet$  activated carbon

#### 3.3.2. Freundlich Isotherm.

Freundlich isotherm in the other hand assumes heterogeneous surface energies, in which the energy term in Langmuir isotherm varies as a function of the surface coverage. From this isotherm model (as shown in figure 8), it can be observed that the plot of  $\log q_E$  versus  $\log C_e$  gave a straight line with  $R^2$  values of treated and untreated activated carbon were 0.96 and 0.88 respectively. The high correlation coefficient values for treated activated carbon which was found greater than 0.9 show the applicability of this isotherm model. However, the  $R^2$  value for the untreated activated carbon is less than 0.9 which makes this isotherm did unfavorable for this adsorbent – adsorbate system.

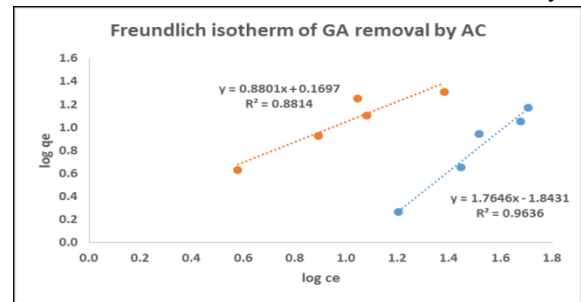


Figure 8. Freundlich Isotherm Gallic acid adsorption on  $\bullet$  treated and untreated  $\bullet$  activated carbon

## 4. CONCLUSIONS

Shell based activated carbon can be a good precursors for producing highly porous activated carbon by simple preparation methods. The conclusion of current research is that we are able to produce coconut shell based activated carbon treated with phosphoric acid to remove phenolic compound (Gallic acid). For the first objective, the modification and characterization of activated carbon from coconut shell for phenolic compound removal have been well achieved. The characterization of SEM shows variation of different circular shapes were obtained from the treated and untreated activated carbon. XRD pattern of both activated carbon samples is approximately the same where it can

be observed that activated carbon has a completely amorphous structure. FTIR analysis showed the functional groups of carboxylic acid & derivatives has dominated the untreated AC while the treated AC was dominated by aliphatic hydrocarbon functional groups. For the second objective, The optimum condition that contributes to the highest percentage removal of phenolic compound using treated coconut shell based activated carbon is contact time of 150 minutes, adsorbent dosage of 500 mg, initial concentration of 100 mg/l and pH of 4. For the last objective, the Langmuir isotherm had shown the best favourable isotherm model to represent the adsorbent- adsorbate system.

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