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Adsorption of Polycyclic Aromatic Hydrocarbons using Low-Cost Activated Carbon Derived from Rice Husk

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Abstract. Polycyclic aromatic hydrocarbons (PAHs) have a great concern as a persistent organic pollutant in the aquatic environment due to their high toxicities, mutagenic and carcinogenic properties. Among various water treatment methods, adsorption could be a promising technique for removing organic pollutant from the aquatic environment. The present study proposes a low-cost activated carbon from rice husk and its potential as an adsorbent for removing PAHs (phenanthrene and fluoranthene) in the aquatic environment. Physical characterization of the activated carbon obtained was performed by Scanning Electron Microscope (SEM) and Fourier Transform Infrared (FT-IR). Effects of dose adsorbent, pH, and contact time on adsorption of PAHs have been investigated. SEM analysis showed that the adsorbent surface was irregular, rough, and highly porous structure. The FT-IR spectra indicated the presence of hydroxyl group at 3205 cm⁻¹ and carbonyl group at 1565 cm⁻¹. The result revealed that equilibrium time on phenanthrene and fluoranthene at pH 3 is found to be 60 and 30 minutes, respectively. The study shows that activated carbon from rice husk has a future perspective of low-cost adsorbents which effectively removes PAHs from the aquatic environment.

1. Introduction

PAHs are a class of hydrocarbon compounds with two or more benzene rings from the incomplete combustion of fossil fuels, coal, wood or petroleum from domestic, industrial, food processing activities such as burning and fumigation or derived from hydrocarbons and volcanic eruptions. PAHs are widely distributed in the air, water, soil, food, plants and other biotas. This class of compounds has become a class of organic pollutants that have received serious attention because of its toxic, persistent, accumulative, mutagenic and carcinogenic nature. The Environmental Protection Agency (US EPA) has listed PAHs as one of the most dangerous primary pollutants [1]. A recent study reported that PAHs also have the ability to affect the endocrine system of humans and animals [2] and increase lung cancer risk from the inhalation system exposure to PAHs [3-4]. Due to its negative nature, it is necessary to try removing PAHs compound promptly and efficiently.

A lot of efforts have been devoted to developing a method to remove PAHs from the environment, including physical, chemical, thermal, biological and phytoremediation [5-7]. However, most of these methods have certain disadvantages such as high investment and maintenance costs as well as complicated operating procedures. In addition, the secondary product release process is carcinogenic and mutagenic, for example, trihalomethanes and halo acetic acid, a compound that may add negative



effects on human health [8-9]. On the other hand, the adsorption method has been proven to be highly efficient, low initial cost, simple operating design and green method for removing pollutants [10].

Adsorption is an absorption process that occurs on a surface. Adsorption is generally defined as the accumulation of a number of molecules, ions, or atoms that occur at the boundary between two phases provided by the solid material referred to an adsorbent. Activated carbon was most widely used as adsorbent offering the most efficient methods available for removing organic pollutant. However, commercially activated carbon is still quite expensive material for a large number of developing countries. Hence, it is necessary to discover new adsorbent materials, preferably more natural, abundant, and cheaper materials to prepare activated carbon.

Several studies have demonstrated the use of various environmental wastes for alternative adsorbent materials [10-12]. Owabor et al. [13] show citrus zests as a naphthalene adsorbent in aqueous solution. In addition, Gupta [14] has also reported active carbon adsorbents from banana peels as adsorbents of PAH compounds having three benzene rings. The abundant agricultural waste in Indonesia, including Lampung, are rice hulls. As one of the major rice producing countries, Indonesia has produced 70.85 million tonnes of rice annually. If the rice husk is about 20%, there is 12.6 million/year. Rice husk is commonly disposed of open-air burning cause adverse effect to the environment. Meanwhile, it is known that rice husk contains high carbon, highly soluble material and one of the most economical and easiest sources of activated carbon materials. The potential of the big rice husk is still not used optimally. Activated carbon from rice husk has been applied as an adsorbent for removing of pollutants in wastewater nearly 100% effectiveness for removing heavy metal as reported Sountharajah [15]. However, the potential of activated carbon derived from rice husk as an alternative adsorbent for the removal of organic pollutant such as PAH is still limited and challenging research interest. The use of abundant tropical natural materials such as rice husks will reduce dependence on imports and increase the economic value of agricultural waste.

The purpose of this study is to prepare of activated carbon rice husk as an adsorbent to remove PAH from waters or waste. The two PAHs namely phenanthrene and fluoranthene was selected for this study to represent the PAHs compound which has high availability in wastewater or aqueous environment. The optimum condition that may affect adsorption processes such as adsorbent level, adsorbate concentration and contact time was investigated.

2. Materials and Methods

Phenanthrene and fluoranthene were purchased from Sigma-Aldrich. Distillate water was used throughout the analysis. Stock solutions of PAHs were made by dissolving a definite amount of PAHs in methanol. The other solution such as 25% NaOH, HCl 1 N, ZnCl₂ 10% were obtained from Merck in analytical grade level. The precursor for synthesized activated carbon materials used in this study is rice husk collected from a local farmer, Lampung Province, Indonesia. The adsorbent was characterized using SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-Ray) and FTIR (Fourier Transform Infra Red) while the adsorption test was determined by UV-VIS (Ultra Violet-Visible) spectrophotometer.

Activated carbon was prepared from rice husk by going through the following steps. Firstly, rice husk was sorted to remove stones, shaft, and debris and washed with hot water. After soaking in hot water, rice husk was washed using distilled water for a night to remove all contaminant. Rice husk was dried and dissolved by using 1N HCl solution into 1000 ml beaker glass for 1 hour while heated using a heating mantle with temperature 75°C. The solution was filtered and the solid residue washed repeatedly with distilled water to remove the metal ions that was still attached to the rice husk. After washing process finished, rice husk was dried overnight in an oven at 90°C to constant weight. The dried rice husk was then stored in a dry container prior to the carbonization process.

Carbonization is essentially used to convert the material to char and open the pores of the char for adsorption process. In the present study we used two sample, one sample of rice husk was removed from silica, and another go directly to the carbonization process. For removing silica, the dried rice husk was weighted 40 grams and dissolved with 600 ml of 25% NaOH into a 1000 ml beaker glass and heated for 1 hour by using hot plate with magnetic stirrer at 90°C. Then, the rice husk residue was washed with distilled water repeatedly and dried to constant weigh using an oven at 105°C for 4

hours. The rice husk residue is now free from silica, was weighed and then carbonized in the furnace at a temperature of 350°C. The carbonized rice husk was removed from the furnace and activated by soaking them using 10% zinc chloride (ZnCl_2) for 2 hours and subjected for drying in an oven at 105°C for 3 hours to evaporate the entire water content and then cool the carbon in the desiccator. Then the impregnated carbon is heated by using a furnace at the temperature of 400°C for 1 hour. The activated carbon was removed from the furnace, allowed to cool, and then washed with distilled water several times until the pH reached a neutral point. The activated product was grounded and sieved using Siever with a size of 100 micrometers to obtain a homogeneous sample. Finally, the washed activated carbon sample was dried in oven at 105°C for 24 hours and stored in a desiccator in order to prevent from moisture.

For the adsorption experiment, 20 ml aliquots of 10 ppm PAHs (phenanthrene and fluoranthene) with adsorbent using variations of dose (7, 9, 11, 13, 15, 17, 19, 21, 23, 25 mg) were mixed and shaken on a shaker for 1 hour at 150 rpm. Then the solution was centrifuged at 2000 rpm for 10 minutes. Each mixture was filtered and the residual concentration was determined by a UV-Vis spectrophotometer at a wavelength of 250 nm.

For kinetic experiment 20 mL of 10 ppm PAH solution was added to the optimum adsorbent dose. The mixture was stirred using a Shaker with variations of time (10, 30, 60, 90 and 120 minutes) at 150 rpm. The solution then was centrifuged at 2000 rpm for 10 minutes. The resulting filtrate was analyzed by a UV-Vis spectrophotometer at a wavelength of 250 nm to determine the adsorbed phenanthrene and fluoranthene content.

For optimum PAHs concentration, adsorbent was mixed with 20 mL of PAH varying concentration 5, 10, 15, 20, and 25 ppm respectively and shaken on a shaker for 1 hour at 150 rpm. Then the solution was centrifuged at 2000 rpm for 10 minutes. Each mixture was filtered and the residual concentration was determined by a UV-Vis spectrophotometer at a wavelength of 250 nm.

3. Results and Discussion

3.1 Activated Carbon Characterization

Preparation of activated carbon of rice husk has been done through the carbonization process which then continued with chemical activation. Figure 1 (a) presents rice husk sample that was washed and dried before carbonization, figure 1 (b) shows a rice husk which was carbonized using furnace at 300°C for 2 hours. Carbonization is enriching carbon content and generating an initial porosity. The carbonization yield was subsequently purified and activated using chemical activation. The activated process further develop the porosity and create structure a highly porous solid with accessible active sites for adsorption interaction. Chemical activation is achieved by impregnation of carbon materials in 10% ZnCl_2 solution for 24 hours. ZnCl_2 is one of the most commonly used for activation lignocellulosic materials. ZnCl_2 is a strong dehydrating agent which alter the structure of carbon material to give a porous surface with higher reaction sites [16,17]. The activated carbon of rice husk after being activated can be seen in figure 1 (c).

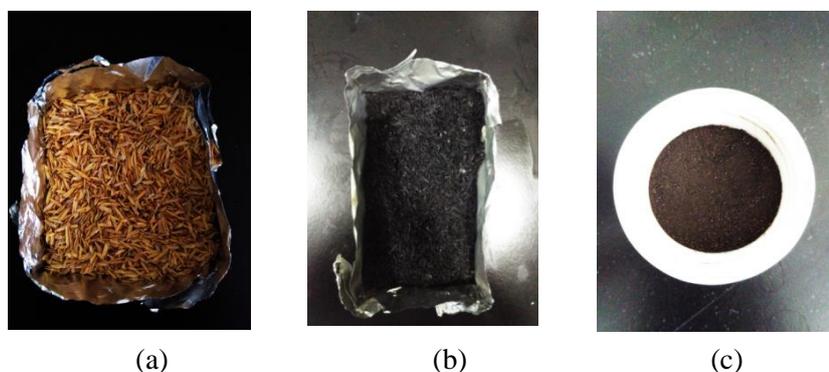


Figure 1. Preparation of activated carbon from rice husk (a) Rice husk, (b) carbonized rice husk, (c) activated carbon

Analysis of surface morphology and adsorbent composition was performed using SEM-EDX. figure 2 shows that there is the difference of surface structure between activated carbon in the absence of silica and activated carbon still containing silica element. The morphological analysis on the surface of the activated carbon shows that the active carbon without the silica element is irregular, rough, and highly porous as presented in figure 2 (b), indicating its good adsorption properties, whereas in the activated carbon with silica elements there were no pores as illustrated in figure 2 (a), due to the silica content that may cover the pores on the surface. The silica removal process can improve the surface properties of a material and improves the quality of the activated carbon produced. Pores found on activated carbon can increase the ability of activated carbon to adsorb adsorbate. The elemental composition on the activated conducted by SEM-EDX as shown in Table 1.

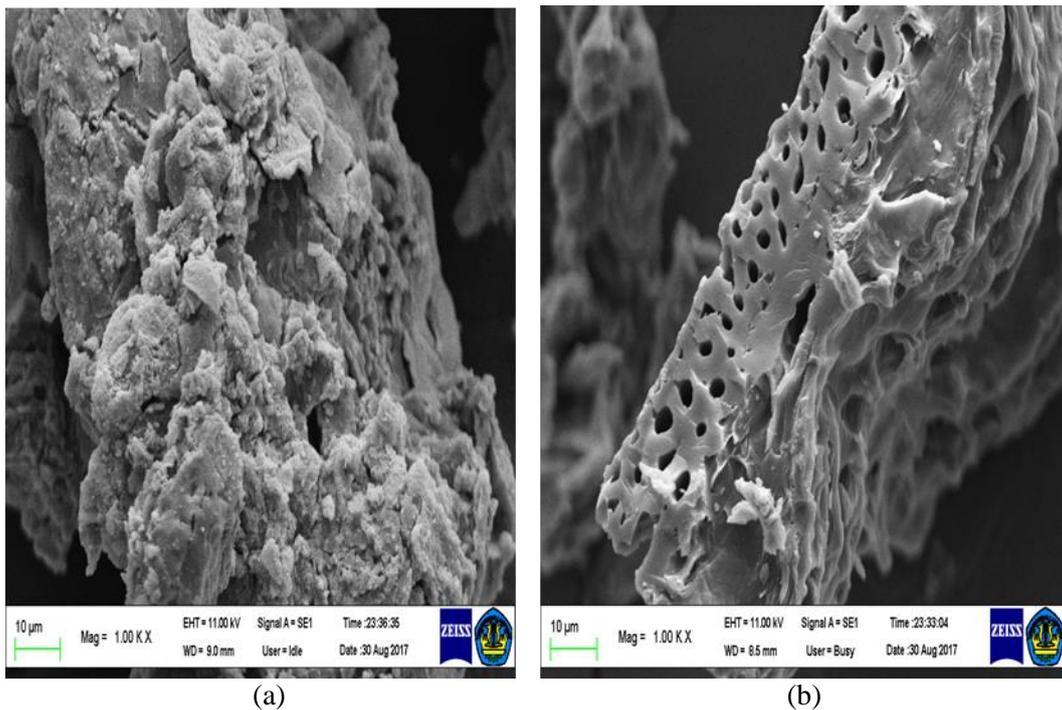


Figure 2. SEM results with 1,000x magnification on the surface of the adsorbent in the form of (a) activated carbon with silica elements and (b) activated carbon without silica elements

Table 1. Composition activated carbon derived from rice husk

Element	Percentage (%)
Carbon	87,47
Silica	-
Oxygen	11,06
Sodium	0,73
Calcium	0,74

The results showed that the activated carbon without element of silica contained a high enough amount (87.47%) of carbon (C) with indicating the success of the process of making activated carbon from rice husks. The high composition of carbon elements makes activated carbon can be used as a potential adsorbent in the adsorption process. This is because activated carbon is a porous solid which consists mostly of free carbon elements and each binds covalently so that the surface of activated carbon tends to be non-polar. The high amount of carbon makes the surface properties of activated carbon more non-polar, thus active carbon is able to adsorb PAH compounds which are also non-polar. Analysis of activated carbon functional groups was performed using FT-IR as can be seen in figure 3.

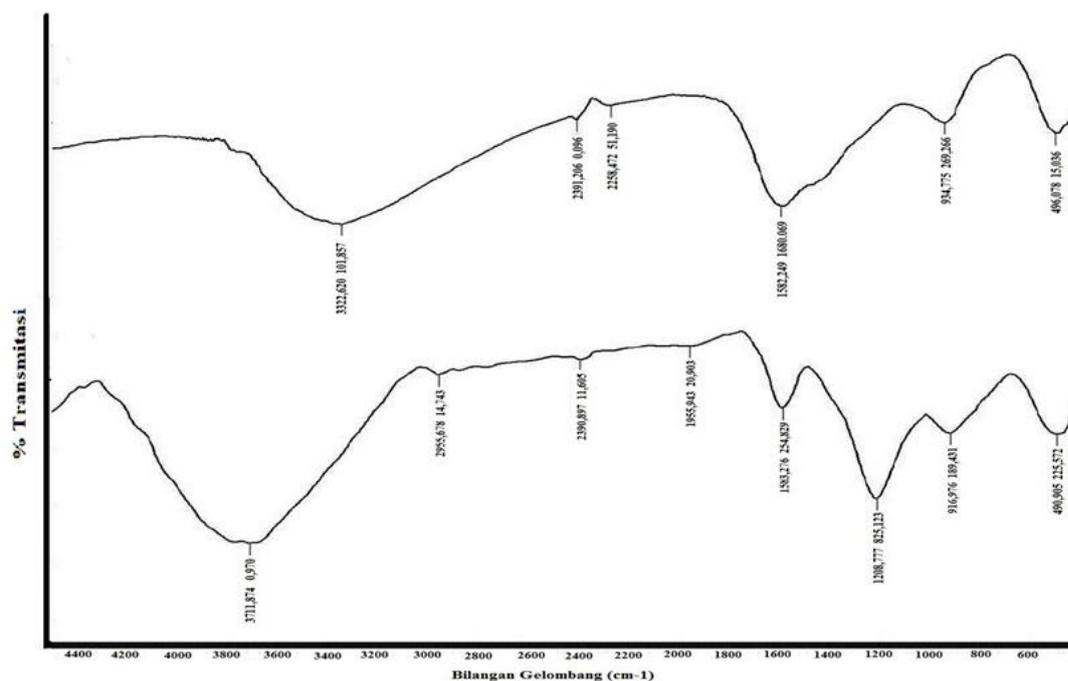


Figure 3. FTIR spectrum of activated carbon from rice husk

The qualitative characterization of surface functional group of activated carbon was performed by the FTIR instrument. The results illustrated in figure 3 shows the broad peak at 3322.87 cm^{-1} at FTIR spectrum, that can be assigned to O-H stretching of hydroxyl groups or adsorbed water. The peak at 2955 is attributed to C-H stretching of aliphatic carbon or due to CH_2 or CH_3 deformation. The peaks appearing at 1582.16 cm^{-1} corresponds to the C = O vibration of lactonic, carboxyl or anhydride group. The spectrum FTIR of activated carbon with silica as illustrated in figure 3b show similar peak of hydroxyl and carbonyl group at 3711.87 and 1583.25 cm^{-1} . In addition, the peak at 1208.77 cm^{-1} may indicate Si-O group which was not detected in figure 3 (a). The results of the activated carbon characterization obtained in this study are similar to those of other research [15,16].

3.2 Adsorption Investigation

Determination of optimum adsorbent dose was conducted by interaction of phenanthrene and fluoranthene solution with activated carbon using variation of adsorbent dose ranging from 10 mg to 30 mg. Figure 4 shows the effect of adsorbent dose on percent adsorption of phenanthrene and fluoranthene. The percent adsorption of PAHs compound increases with increasing of adsorbent dose from 10 to around 23-25 mg and then becomes decreasing after $> 25\text{ mg}$. As shown in figure 4, initially the adsorption process increased rapidly over the initial stage of adsorption and then remained constant or decreased. Yakout, et al [18] also found the same adsorption behavior indicating that there were many readily accessible sites available on the surface of activated carbon from rice husk.

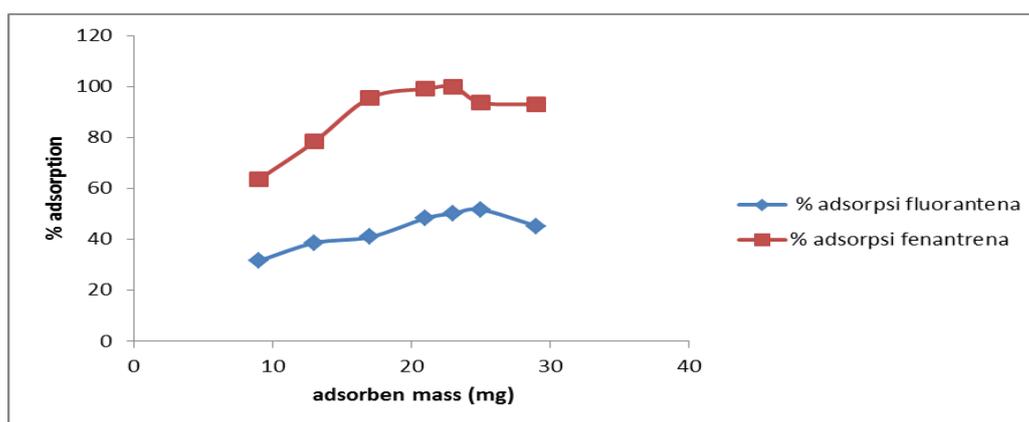


Figure 4. Effect of adsorbent dose

The effect of contact time on percent adsorption of PAHs compound was studied over a contact time of 10-120 minutes. Figure 5 presents the result of effect contact time on percent adsorption of phenanthrene and fluoranthene. The percent adsorption of fluoranthene increased with increasing time, and became decreased and constant after 30 minutes, while the percent adsorption of phenanthrene increased with increasing time, and became constant after 60 minutes. These result suggested that increasing time would enhance diffusion of PAHs compound into the surface of the adsorbent. For all the two studied PAHs, the prolonged contact time had no adverse effect on the adsorption.

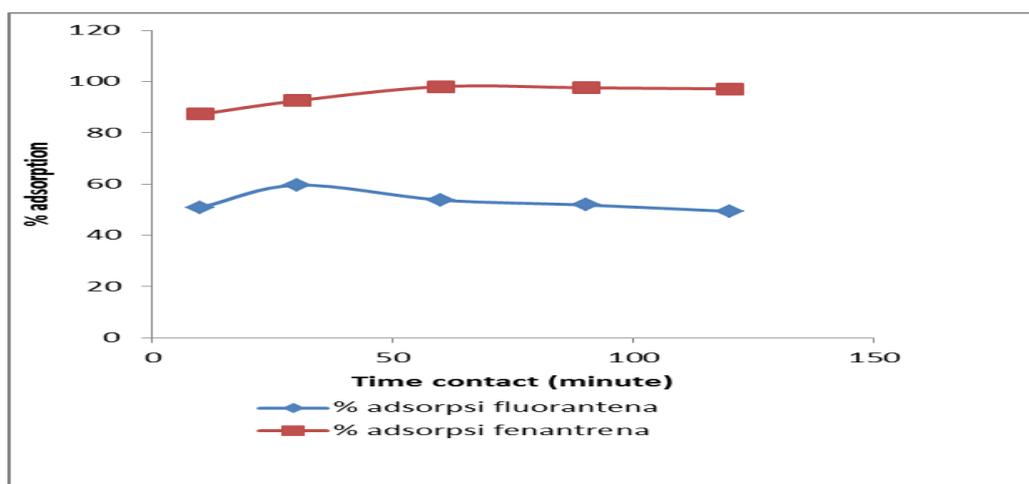


Figure 5. Effect of contact time

Figure 6 presents the effect of concentration of sorbate on percent adsorption of phenanthrene and fluoranthene. The result shows that the maximum concentration of adsorbate, phenanthrene and fluoranthene, revealed at 10 ppm and decreasing thereafter, indicating adsorption process into adsorbent was optimum at 10 ppm and may continue desorption process due to saturated pore in a surface of activated carbon. The more time required for the PAH system solution to reach equilibrium at high concentration. It was due to as more as sites filled, it is more difficult for the solute molecules to use a site for adsorption. Eventually, it is more difficult for the PAH compound to penetrate the layer of adsorbed PAH with covering the surface sites with PAH compounds [17]. This study also showed that adsorption of phenanthrene into activated carbon derived from rice husk have higher adsorption around at 98-99% than fluoranthene around at 50%. This result may be attributed to the smaller molecular weight and ring benzene of phenanthrene (178, 3-ring benzene) than fluoranthene. The three benzene ring of phenanthrene was adsorbed easier than four benzene ring of fluoranthene.

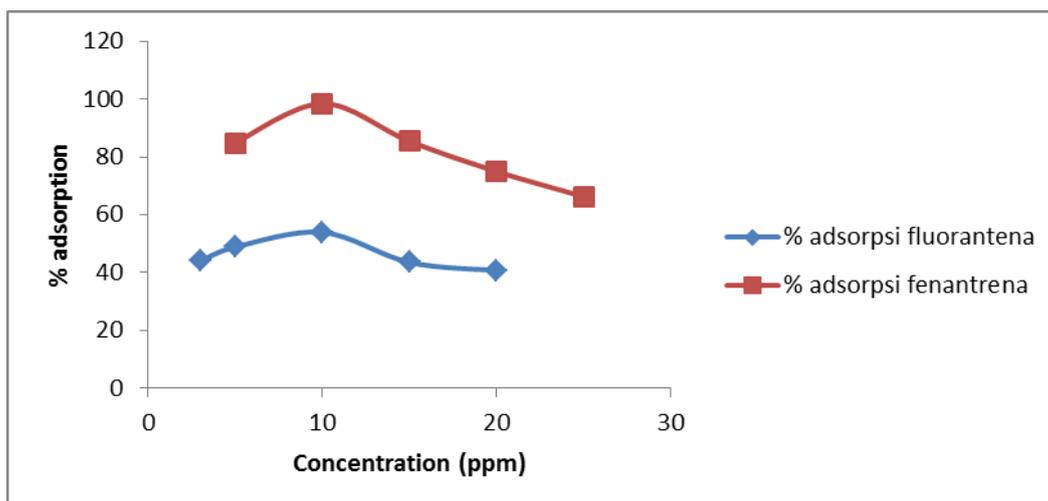


Figure 6. Effect of adsorbate concentration

3.3 Isotherm Modelling

The interaction between adsorbate and adsorbent can be evaluated by Langmuir and Freundlich isotherm. The Langmuir model is based on monolayer adsorption on active sites of adsorbent, while the Freundlich model is governed by heterogeneous adsorption. The experimental data were fitted to a linear equation of both model isotherm and further evaluated with a value of the correlation coefficients (R^2) obtained. The linearized correlation of Langmuir isotherm model equation is expressed as:

$$\frac{C_e}{Q_e} = \frac{1}{bK} + \frac{C_e}{b} \tag{1}$$

Where C_e (mg/L) is the equilibrium concentration of the adsorbates, Q_e (mg/L) is the amount of adsorbate adsorbed per unit mass of adsorbent, b and K are related rate of adsorption and adsorption capacity respectively and were determined by plotting C_e/Q_e against C_e . The linearized correlation of Freundlich isotherm model is expressed in a linear logarithmic equation as:

$$\log Q_e = \log K_f + n \log C_e \tag{2}$$

A plot of $\log Q_e$ against $\log C_e$ was used to determine the Freundlich constant, K_f and n . The experimental data for phenanthrene was plotted to Langmuir and Freundlich equation as shown in figure 6 and 7. In general, acceptable or good correlation coefficients were observed for both model, Freundlich and Langmuir isotherm. The value correlation coefficient of activated carbon obtained from Freundlich isotherm was higher than Langmuir isotherm, indicating that adsorption process tends to Freundlich isotherm. This result is good agreement with other research previously [19].

4. Conclusions

The activated carbon derived from rice husk is important to attempt providing the future perspective of low-cost adsorbent that effectively removes PAHs from aqueous systems. It has shown excellent adsorbent and eco-friendly to remove phenanthrene from the aquatic environment.

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