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# Adsorption of toluene and xylene from aqueous solution on SBA-15 from rice husk

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# Adsorption of toluene and xylene from aqueous solution on SBA-15 from rice husk

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**Abstract.** Synthesis of Santa Barbara Amorphous-15 (SBA-15) from rice husk ash (Oryza Sativa L.) as toluene and xylene adsorbents has been performed. SBA-15 was synthesised by the modified surfactant template method. SBA-15 from rice husk ash has a surface area of 680 m2/g, a pore diameter of 1.49 nm and a pore volume of 12.5 cm3/g. SAXS pattern of the SBA-15 showed the presence of three distinctive peaks of SBA-15 at 0.99°, 1.54° and 1.74° 2 theta with miller indices [100], [110] and [200]. SEM pictures showed that SBA-15 from rice husk ash has an irregular shape and the particles are in aggregate form. The maximum adsorption capacities of SBA-15 from rice husk ash to toluene and xylene based on the Langmuir isotherm were 175.44 mg/g and 142.86 mg/g, respectively with RL (equilibrium parameter) value within the range 0-1.

## 1. Introduction

Indonesia is an agricultural country with a large portion of its population living in the agricultural sector. As a result, the by-products produced in the rice milling process in the form of rice husk are very abundant, which is about 20% of grain weight [1]. Rice husk ash derived from the combustion products may contain up to 94-96% silica ($SiO_2$), so it can be used in various chemical processes [1], such as synthesis of mesoporous silica materials (e.g. SBA-15).

Santa Barbara Amorphous-15 (SBA-15) is a silica-based mesoporous material that has cylindrical pores with a hexagonal structure [2]. SBA-15 has a high hydrothermal stability and large surface area. In addition, SBA-15 has a big pore size, and a large pore volume [3] so that this material can be used as an adsorbent [4].

Hazardous chemicals that can be reduced by adsorption are aromatic compounds such as toluene and xylene[5]. Toluene and xylene can be found in waste from the clothing, paint, gasoline, color and solvent industries. If the waste is not handled properly it will cause environmental pollution [6]. Handling this condition can be done chemically, using adsorbents [7]. Hydrocarbon compounds such as toluene can be adsorbed using mesoporous silica material [8]. This study reports synthesis, characterisation and the use of SBA-15 from rice husk ash as adsorbent for toluene and xylene from aqueous solution.

## 2. Materials and methods

*2.1 Chemicals*
Non-ionic block copolymer surfactant Pluronic P123 (Merck) and hydrochloric acid (37%) (Merck) were used for synthesis of SBA-15. Toluene (Univar) and xylene (Kanto Chemical) were used for adsorption studies.

*2.2 Sample preparation*
The samples used in this study were rice husks from Lempake, North Samarinda Regency, Samarinda City. Rice husk samples were washed using distilled water, dried and soaked in 1 M HCl solution for 1 hour. Then, the samples were put into a furnace and heated for 5 hours at a temperature of 600 °C to give white powder.

*2.3 Silica Extraction*
In the process of extracting silica from rice husk ash, the rice husk ash was first reacted with 1 M NaOH solution to form sodium silicate ($Na_2SiO_3$). Then the mixture was refluxed at 75 °C for 3 hours. The mixture were filtered using a vacuum pump to obtain a clear yellowish solution of sodium silicate ($Na_2SiO_3$) and brownish white rice husk ash residue. Then sodium silicate solution ($Na_2SiO_3$) was stored to be used as a source of silica.

*2.4 SBA-15 Material Synthesis*
The synthesis of SBA-15 was carried out using a modified method by Zhao *et al.* [9]. In a typical preparation, 15 grams Pluronic 123 was dissolved in 600 mL 2 M HCl and stirred at 37-40 °C until Pluronic 123 was completely dissolved. Then, sodium silicate solution ($Na_2SiO_3$) was added to the mixture and the mixture was mixed using a magnetic stirer at 37-40 °C for 20 hours. After 20 hours the solution mixture were subjected to aging for 24 hours at 100 °C under static conditions in an autoclave. After the aging process, the solution was cooled at room temperature and then filtered to isolate the product in the form of white solids. Then the solids were neutralized with distilled water until the pH is equal to the pH of distilled water and then filtered and dried. Then, the solids were calcined at a temperature of 500 °C for 8 hours and solid white powder was obtained. The product was characterized using Small Angle X-Ray Scattering (SAXS), Fourier Transform Infra Red (FTIR), $N_2$ Adsorption Desorption Analysis and Scanning Electron Microscopy (SEM).

*2.5 Adsorption*
Different mass of toluene or xylene was dissolved in water to make 25-200 mg/L solutions. Then 0.1 grams of SBA-15 was added to the aqueous solution and was stirred at room temperature for 30 – 180 minutes. Then, the mixture was filtered using filter paper and the resulting filtrate was taken. Furthermore, the filtrates were measured by using a UV spectrophotometer at 203 nm for xylene and 205 nm for toluene. The concentrations of toluene and xylene which were not adsorbed by SBA-15 were calculated using the calibration curve.

*2.6 Data Processing*
The percent adsorption value was calculated using the formula

$$\%\ \text{Adsorption} = \frac{\text{initial concentration(mg/L) - final concentration(mg/L)}}{\text{initial concentration(mg/L)}} \text{ x } 100\% \quad (1)$$

Then the adsorption capacity (Qe) was calculated using the formula:

$$\text{Qe} = \frac{\text{initial concentration(mg/L) - final concentration(mg/L)}}{\text{adsorbent weight(g)}} \text{ x volume of solution(L)} \quad (2)$$

Subsequently made% adsorption curve and adsorption capacity versus concentration / time.

*2.7 Maximum Adsorption Capacity*

Determination of the maximum adsorption capacity was carried out using the Langmuir isotherm equation [10] as follows:

$$\frac{C_e}{q_e} = \left[\frac{Ce}{q_{maks}}\right] + \frac{1}{q_{maks}} \cdot \frac{1}{K_L} \quad (3)$$

The graph Ce/$q_e$ vs $C_e$ was made and then the maximum adsorption capacity can be determined. Determination of RL values (equilibrium parameters) was conducted using the following formula:

$$RL = \frac{1}{1+KL.Co} \quad (4)$$

The RL value indicates the type of isotherm and the nature of the adsorption process. The feasibility of the reaction is explained by using the RL value as follows:

RL > 1 : Adsorption nature is unfavourable
RL = 1 : Adsorption nature is linear
RL 0-1 : Adsorption nature is favourable
RL 0 : Adsorption nature is irreversible

## 3. Result dan discussion

*3.1 Characterization of SBA-15 Materials*

*3.1.1 $N_2$ Adsorption / desorption.*

SBA-15 from rice husk ash produced in this study has a surface area of 680 $m^2$/g, pore volume of 1.49 $cm^3$/ g and an average pore diameter of 12.5 nm. Based on the porosity of the material produced, SBA-15 produced from rice husk ash can be classified as mesoporous material because it has a pore diameter between 2-50 nm [11].

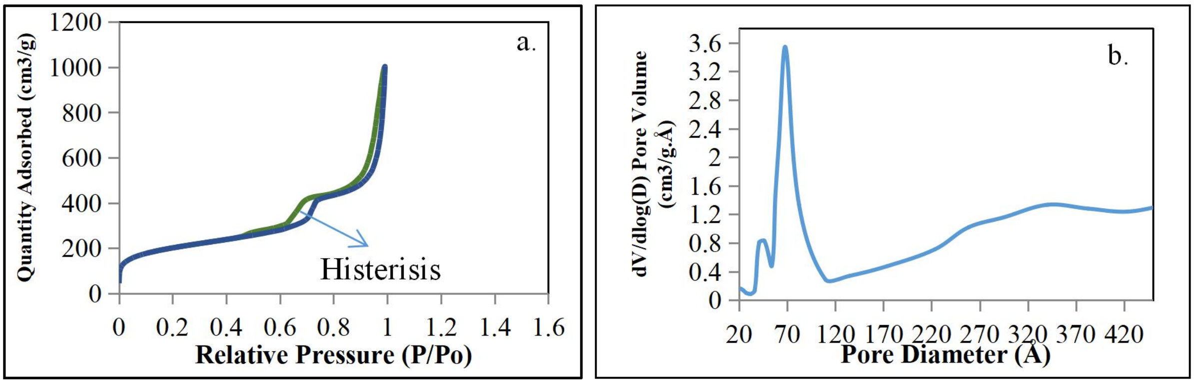


**Figure 1.** a. $N_2$ adsorption / desorption isotherm, b. Pore distribution of SBA-15 material from rice husk ash

Figure 1a shows that the SBA-15 sample has a type IV isotherm indicating that the material produced was mesoporous. The hysteresis loop in the isotherm was caused by the difference in the amount of nitrogen gas during adsorption and desorption [12]. In the condensation process the hysteresis loop was formed due to the presence of pores on the surface of the material so that there is a limitation on the number of layers in nitrogen gas (adsorbate). The size of the hysterysis depends on the amount of adsorbate left in the pore material during the desorption process [13]. According to Zhao *et al*. the hysteresis in the isotherm is the characteristic of mesoporous material [9]. The pore distribution of SBA-15 material from rice husk ash (Figure 1b) shows that SBA-15 from rice husk ash has relatively homogeneous pores. The high level of homogeneity in the SBA-15 material may indicate that the material has a regular pore shape.

*3.1.2 Small Angle X-ray Scattering (SAXS)*

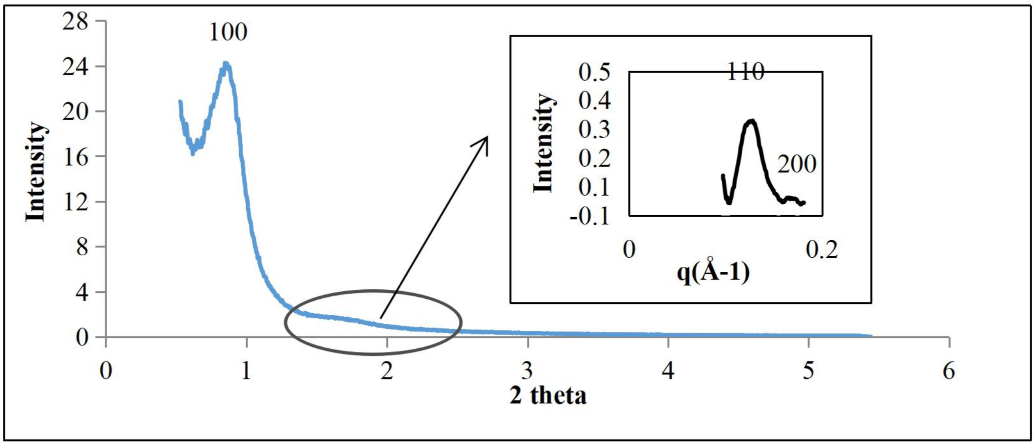


**Figure 2**. SAXS Pattern of SBA-15 Rice Husk Ash

The SAXS pattern of SBA-15 rice husk ash shows 3 peaks in the area of 0-5 ° 2 theta angle (Figure 2). The three miller index values are [100], [110] and [200], respectively, which are group structures of p6mm two-dimensional hexagonal shapes [9]. The [200] peak has a very weak intensity when compared to the same peak of the SBA-15 material from TEOS [14]. This may imply that the SBA-15 rice husk ash produced was not as well ordered as the SBA-15 material from TEOS. To see the [200] peak, the transformation method must be done with the decoupling approach with parameter q (vector scattering) [15]. The angle of 2 theta is proportional to q (scattering vector).

*3.1.3 Fourier Transform Infra Red (FTIR)*

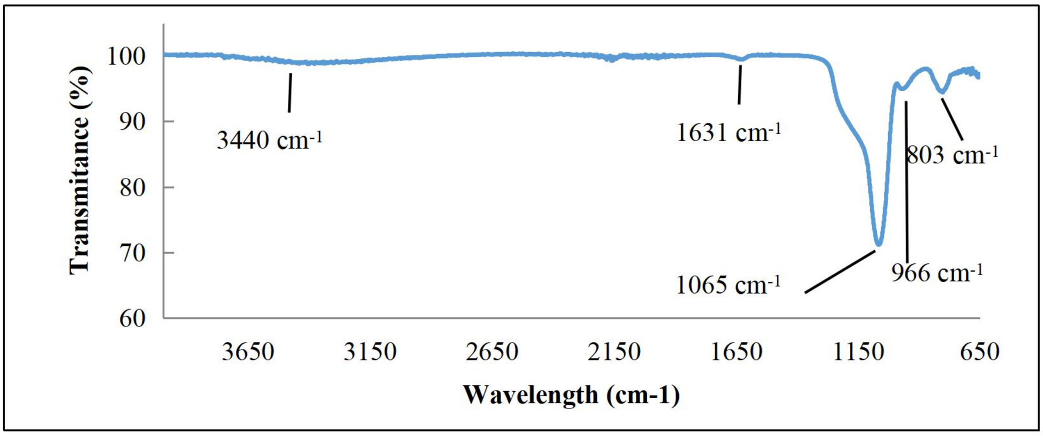


**Figure 3**. FTIR spectrum of SBA-15 material from rice husk ash

The SBA-15 from rice husk ash spectrum shows peaks at at 803 $cm^{-1}$ and 1065 $cm^{-1}$ indicating the anti-symmetrical functional groups of Si-O-Si and symmetrical Si-O-Si groups (Figure 3). A peak at 966 $cm^{-1}$ wave number indicates that silica material has a symmetrical Si-OH silanol functional group. In the spectrum, a weak peak observed at 1631 $cm^{-1}$ is due to the presence of –OH group from water adsorption on SBA-15 material. Furthermore, the peak observed at 3440 $cm^{-1}$ indicates the physical vibration between the silanol -OH group and the water molecule [16].

*3.1.4 Scanning Electron Microscopy (SEM)*

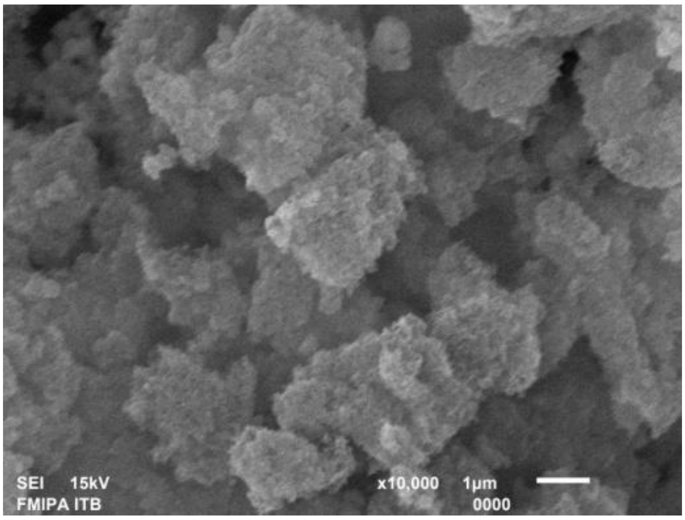


**Figure 4.** SEM picture of SBA-15 material from rice husk ash

Figure 4 shows that the SBA-15 material from rice husk ash has an irregular shape with a particle size of about 1 μm. The SBA-15 material appears to have a large bulky shape or aggregate. Irregular morphology of SBA-15 may be due to high HCl concentration and excess amount of silica used in the synthesis of SBA-15 [17]

*3.2 Adsorption study*

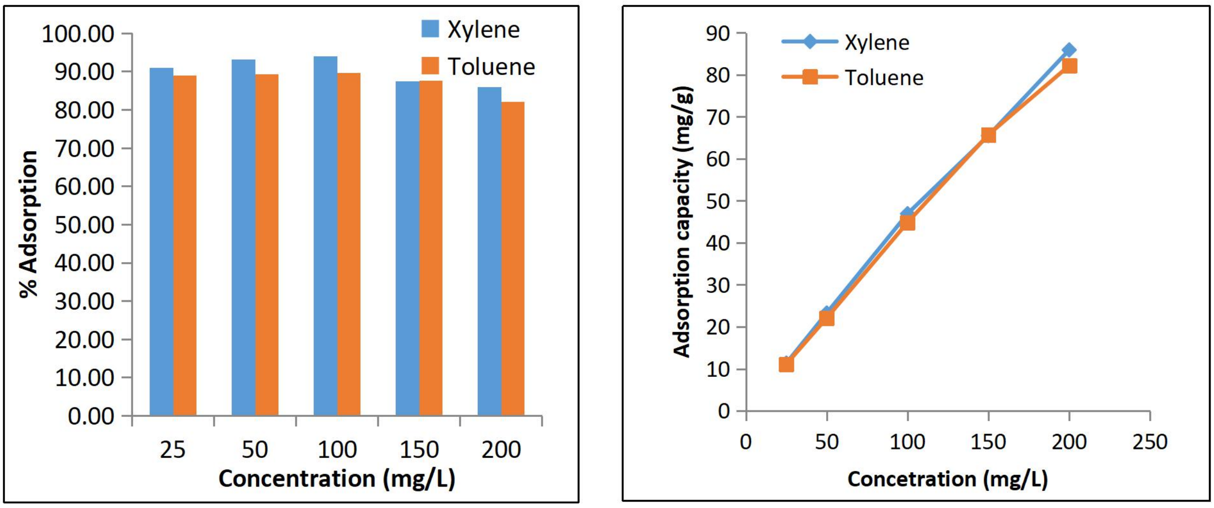


**Figure 5.** % Adsorption and Adsorption Capacity of toluene and xylene with SBA-15 from rice husk ash (SBA-15 mass = 0.1 grams, adsorption time = 60 minutes)

The increase in toluene or xylene concentration resulted in the rise of the percent adsorption up to a concentration of 100 mg/L (Figure 5). The adsorption capacity increases to a concentration of 200 mg/L because SBA-15 materials still have available active sites and pores that can absorb toluene and xylene.

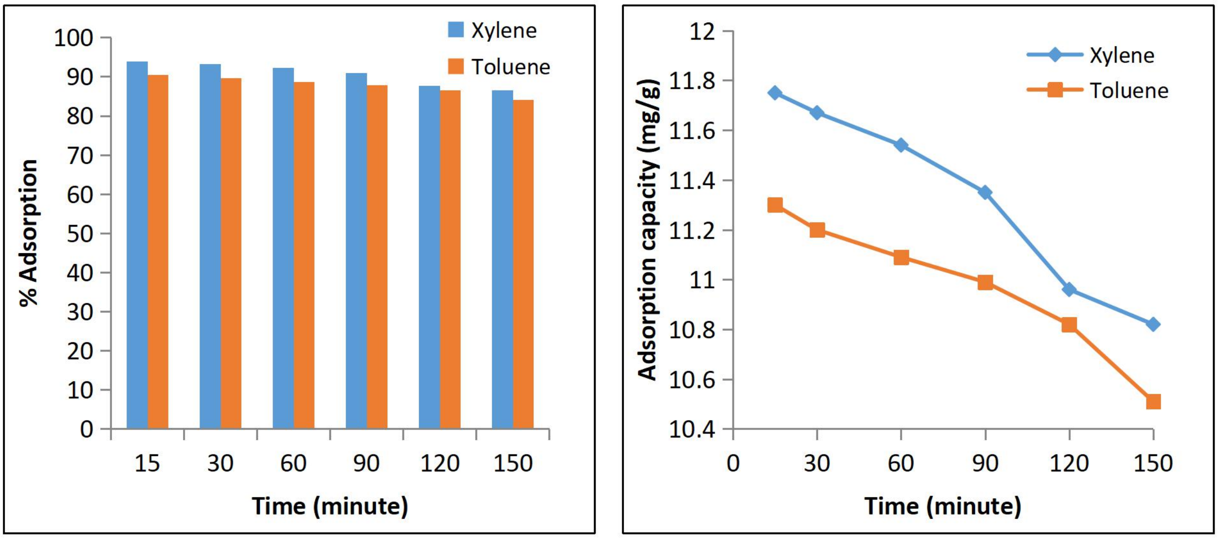


**Figure 6.** % Adsorption and Adsorption Capacity (SBA-15 mass = 0.1 grams, concentration of toluene and xylene = 25 mg/L)

Figure 6 showed that the longer the adsorption time, the lower % adsorption and adsorption capacity. According to Jodeh [10] the increase in adsorption time may cause part of the toluene and xylene absorbed outside the pores to be relased, because the long adsorption time increases the impact between materials resulting in weaker interaction between toluene or xylene with the porous adsorbent. The results showed that the optimum adsorption time with maximum absorption value was 15 minutes.

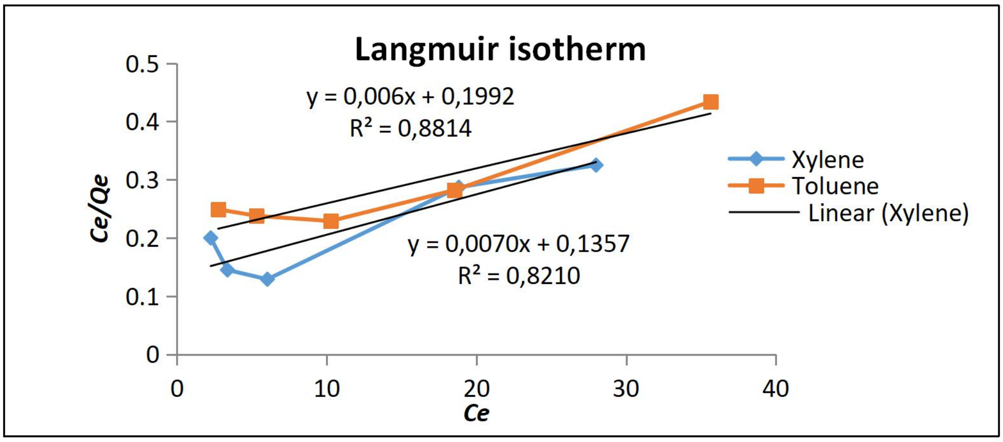


**Figure 7.** Langmuir Isotherm Graph

The maximum adsorption capacity of toluene and xylene obtained was 175.44 mg/g and 142.86 mg/g. Based on the RL value (0-1) , the Langmuir isotherm can be used for the toluene and xylene adsorption. The result implies that toluene and xylene adsorptions take places at specific homogeneous sites within the SBA-15 material and form monolayer and there is no significant interaction among adsorbed species [8].

## 4. Conclusions

The SBA-15 material from rice husk ash was successfully synthesized. The maximum adsorption capacities of toluene and xylene were 175.44 mg / g and 142.86 mg /g, respectively.

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