CHARACTERIZATION AND KINETIC ADSORPTION OF THE DIFFERENT SOURCES ACTIVATED CARBON FOR LIQUID-PHASE ADSORPTION

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ABSTRACT

The activated carbon from oil-palm stones of agricultural by-products from palm-oil mills, a coconut shells and a solid waste exploring coals mining (ex-coal mining) were studied in this paper. The different chemical activators such as H₃PO₄, KOH, H₂SO₄ in the different ratio and also different activated temperature from 550 to 850°C was done. The adsorptive properties are including the textural properties of the activated carbons are investigated. For chemical characterization a Fourier transform infrared (FTIR) spectroscopy was used to identify the surface organic functional groups of the activated carbons. The adsorptive capacity of the activated carbons, adsorption of phenol was carried out using spectrophotometric analyses. It was found that the temperature and hold time had significantly influences on the surface area and pore size in the distribution of the activated carbon. The optimum conditions for preparing these activated carbons from chars, pyrolyzed at 600°C to derive the highest specific surface areas were found to be an activation temperature of 750°C for phenol adsorption of KOH for carbon from coconut shells, H₃PO₄ for oil palm stone and ex-coal mining activator in 850°C. Experimental results showed that phenol could be adsorbed effectively by the three different activated carbons. The adsorptive capacity of these activated carbons was comparable with those of some commercial activated carbons by using Juan et al. model's 23.

Keywords: activated carbon: oil palm stone, coconut shell, ex-coal mining, phenol reduction, adsorptive capacity

1. INTRODUCTION

Activated carbon is widely used as an adsorbent in many applications, such as purification and filtration of water, solvent recovery and catalyst support, due to its high specific surface area, adequate pore size distribution and relatively high mechanical strength 1, 8. There are three sources of activated carbon, which are activated carbon from oil-palm stones of agricultural by-products from palm-oil mills in several tropical countries, a coconut shells and a solid waste exploring coals mining (ex-coal mining) were studied in this paper. The activated and characterized three different sources of carbon are carried out both chemical and adsorptive properties. The raw material, oil-palm stone, coconut shell and carbon from ex-exploring mining are available due to industrial expansion in Jambi province 9.

In the properties of carbon was found a functional group already characterized well by Brennan 10 with chemical structure is well known. Identification and activation processes in carbon are very useful to understand of mechanism, reactivity and adsorptivety of the carbon. The characteristic of carbon porosity was well understood by Day 11, Jerez 12, about porosity of carbon, metal adsorption in multi component model by Girgis 13 and Tseng 5,7. In term of application, activated carbon from coconut shells, ex-mining coal and oil palm stone was used as adsorbent of local textile industries, gambut water and grounded water by Sutrisno et al. 14, 20 and Asyar et al. 21. But, there was no consideration of activation processes both chemical and adsorptive properties.

The purpose of the present study was to characterize both chemical and adsorptive properties of carbon by activated with KOH, H₂SO₄ and H₃PO₄ activators in the different activated temperature (550, 650, 750 and 850°C). The adsorptive phenol in the solution is done in a batch system and phenol adsorption was investigated with respect to initial pH, initial phenol concentration, and time variation. The adsorption equilibrium was model by using the Langmuir and Freundlich isotherm models to find out capacity of adsorption (k).

2. MATERIALS AND METHODS

2.1. Sample preparation

Three samples of carbon, oil-palm stones from a palm-oil mill in Jambi province, Indonesia, coconut shells, ex-coal mining were first dried at 110°C for 24 h to reduce the moisture content. The dried sample were then crushed and sieved to 2.8 – 4.0 mm. Both carbonization and activation were carried out in stainless-steel reactor (length, 550 mm; internal diameter, 38 mm), placed in

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vertical tube furnace (818-P, Lenton). The dried sample was mixed with KOH in a range of KOH/carbon weight ratio 0.5:1. The mixture was dehydrated in a furnace tube at 450°C under N\textsubscript{2} (13 cm\textsuperscript{3}/min) for 2 h and then subjected to thermal treatment up to 550 ± 20°C (550, 650, 750 and 850°C) were also examined for selected samples, and held at temperature for 2 h. The reaction product was washed thoroughly with demineralized water to pH 6-7, and finally dried in an oven at 120°C for 2 h. By using the same ratio and the same treatment with activator H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{3}PO\textsubscript{4} and carbon without chemical activator are also carried out.

2.2. Chemical Characterization

The surface organic functional groups were studied by Fourier transform infrared spectroscopy (FTIR-2000, Perkin-Elmer). The spectra were recorded from 4000 to 400 cm\textsuperscript{-1}.

2.3. Experimental

The adsorption experiment was conducted in 150 ml Erlenmeyer flasks. 0.6 gram of activated carbon was contacted with a known concentration of phenol solution, 10 ppm of phenol in Erlenmeyer flasks with working volume of 100 ml at desired temperature and pH. The flasks were shaken at 150 rev min\textsuperscript{-1} on a rotary shaker for 2 h, allowing sample time for adsorption equilibrium. After 90 minutes, the pH of solution was measured and recorded as the final pH. Phenol was separated from the medium using whatman #1 filter paper and the concentration of phenol measured using UV-Visible Spectrophotometer. Each experiment was repeated three time and results are given as averages.

The adsorption capacity of powdered activated carbon was evaluated by amount of carbon adsorbed: \( q_e = \frac{(C_o - C_t)}{m} V/m \) and by percent of phenol removal: \( R \% = \frac{(C_o - C_t)}{C_o} \times 100 \% \) where \( C_o \) and \( C_t \) are initial and the equilibrium concentration of phenol in solution (mg/L), \( m \) is amount of adsorbent (g) and \( V \) is volume of solution (mL). The adsorption equilibrium data were fitted to the Freundlich equation.

3. RESULTS AND DISCUSSION

3.1. Activation processes and characteristic of Carbon

The varied temperature was carried out in this experiment i.e. between 550-850°C. From the activation processes found that the maximum weight of activated carbon was 60% for coconut shells with H\textsubscript{2}SO\textsubscript{4} and KOH as activators, ex-mining coal 37.7% (H\textsubscript{3}PO\textsubscript{4}), 49.6% oil palm stone (H\textsubscript{3}PO\textsubscript{4}) and activated carbon without chemical was 45.5. The surface area and micropore surface area were investigated for three different activated carbon in the optimum temperature. The results are in Table 1.

The Fourier transform infrared (FTIR) spectra of the three different activated carbon with optimum temperature and chemical activator were recorded and they were shown in Figure 1. The char spectrum displayed the following bands. 1747 cm\textsuperscript{-1} C=O stretching vibration in ketones, 1648 cm\textsuperscript{-1} stretching vibration in quinones. There was found NH\textsubscript{2} and OH in activated carbon and, of course, this is different result compared with Breenan et al.\textsuperscript{10}. It is predicted that functional groups was evaporated during the activation processes. 1507 cm\textsuperscript{-1}, C=C stretching vibration in aromatic ring. The main surface functional groups present in the char were carbonyl groups (e.g. ketone and quinone) and aromatic ring. These results are in agreement with the surface properties of the char from the other agricultural by-products, such as peach stone and rockrose. By increasing temperature such as 850°C only aromatic rings were remained. In brief, the surface organic functional groups of the activated carbon were markedly affected by the activation conditions. However, these surface organic functional groups were generally neutral, which should not have much influence on the adsorptive capacity of the activated carbon. The FTIR spectra is in Figure 1.

![Figure 1. The Fourier transform infrared (FTIR) spectra of the three different activated carbon](image1)

![Figure 2. Effect of temperature for adsorptive phenol by using activated carbon from coconut shells](image2)
Table 1. The surface and micro pore of three activated carbons in optimum condition

| No  | Activated carbon     | Optimum temperature (°C) | Activator   | Surface area m²g⁻¹ | Micropore surface area m²g⁻¹ |
|-----|----------------------|---------------------------|-------------|---------------------|-----------------------------|
| 1   | Coconout shells      | 750                       | KOH         | 918                 | 342                         |
| 2   | Ex-mining coal       | 850                       | H₃PO₄       | 950                 | 518                         |
| 3   | Oil palm stone       | 850                       | H₂SO₄       | 1366                | 950                         |

The optimum temperature for adsorptive phenol was 750°C with an activator KOH, H₂SO₄ and H₃PO₄ at 850°C. The overall result showed the percentage of adsorptive phenol is higher compared to Miura[24] was 45% with KOH (1:1) as an activator.

An activated carbon from ex-mining coal: By using the same condition in the range of temperature 550-850°C and activators KOH, H₂SO₄ and H₃PO₄ are carried out in this experiments. By increasing temperature in activation processes was effected to adsorptive phenol, that was 96.3% with H₃PO₄ and 92.8% at 850°C respectively. All activators showed that effected to activated carbon for absorbing phenol, Figure 3.

![Figure 3](image-url)

Figure 3. Effect of temperature for adsorptive phenol by using activated carbon from ex-mining coal

Activated carbon from Oil palm stone: contrast with two activated carbon, H₃PO₄ and H₂SO₄ are better results in absorption of phenol compared to KOH as an activator 88.9% at 650°C adsorptive phenol without activated and the different temperature of activated carbon from oil palm stone showed in Figure 4.

![Figure 4](image-url)

Figure 4. Effect of temperature for adsorptive phenol by using activated carbon from oil palm stone.

93.8% phenol was adsorbed with H₃PO₄ as activator at 850°C. Surprisingly, the adsorptive phenol was found 92.6% with H₂SO₄ at 650°C. The effect of activator in

3.3. Adsorption Isotherm Studies

Adsorption equilibrium data were fitted to the Freundlich equation. The varied concentration of phenol between 5 - 25 ppm mixed with 0.6 gram activated carbon from coconut shells (KOH and 850°C) for 2 h in 100 ml showed in table 1. Plot between adsorptive phenol against adsorptive phenol divided to mass of carbon is equal to Y = 0.9106x + 2.2797 and R² = 0.9739. The intercept of this equation represent to absorptive capacity (k). The calculations of adsorptive phenol in the different concentrations by using coconut shells activated carbon were in Table 2.

![Figure 5](image-url)

Figure 5. Plot phenol (log x) versus (log x/m)
Table 2. The varied concentration of phenol with coconut shells carbon

| Initial (phenol) in (ppm) | (Adsorbed phenol) as (x) in ppm | log(x)   | x/m    | Log(x/m) |
|---------------------------|---------------------------------|----------|--------|----------|
| 5                         | 3.9                             | 0.5910646| 650    | 2.812913 |
| 10                        | 8.4                             | 0.9242799| 1400   | 3.146128 |
| 15                        | 13.3                            | 1.1222159| 2208   | 3.344065 |
| 20                        | 14.9                            | 1.1743506| 2490   | 3.396199 |
| 25                        | 19.8                            | 1.2966651| 3300   | 3.518514 |

Table 3. The varied concentration of phenol with activated carbon from ex-mining coal

| Initial (phenol) in (ppm) | (adsorbed phenol) as (x) in ppm | Log (x)   | (x/m)   | log(x/m) |
|---------------------------|---------------------------------|----------|--------|----------|
| 5                         | 4.75                            | 0.67669361| 792    | 2.898542 |
| 10                        | 9.96                            | 0.99825934| 1660   | 3.220108 |
| 15                        | 14.8                            | 1.17026171| 2467   | 3.39211  |
| 20                        | 19.7                            | 1.29446622| 3283   | 3.516315 |
| 25                        | 23.7                            | 1.37474835| 3950   | 3.596597 |

Table 4. The varied concentration of phenol with activated carbon from oil palm stone.

| Initial (phenol) in (ppm) | (adsorbed phenol) as (x) in ppm | Log(x)   | (x/m)   | log(x/m) |
|---------------------------|---------------------------------|----------|--------|----------|
| 5                         | 3.3                             | 0.51851394| 550    | 2.740363 |
| 10                        | 9.7                             | 0.98677173| 1617   | 3.20862  |
| 15                        | 13.5                            | 1.13033377| 2250   | 3.352183 |
| 20                        | 18.9                            | 1.27646180| 3150   | 3.498311 |
| 25                        | 20.6                            | 1.31386722| 3433   | 3.535716 |

Table 5. Effect of contact time for absorbing phenol by using activated carbon from coconut shells

| Varied time (minute) | without activator at 650°C | KOH (activator) at 850°C | H₂SO₄ (activator) at 850°C | H₃PO₄ (activator) at 750°C |
|----------------------|-----------------------------|---------------------------|-----------------------------|-----------------------------|
| 30                   | 30                          | 54.9                      | 45                          | 53                          |
| 60                   | 35                          | 72.8                      | 52                          | 67                          |
| 90                   | 45                          | 87.8                      | 65                          | 69                          |
| 120                  | 48                          | 84.1                      | 62                          | 83                          |

The same analytical processes was carried out for activated carbon from ex-mining coal, and the linear equation to be \( Y = 1.0063x + 2.2165 \) with \( R^2 = 0.9999 \). The results showed in Table 3.

By using the same method, the linear regression for activated carbon from oil palm stone was \( Y = 1.0613x + 2.1825 \), with \( R^2 = 0.9974 \) and the result showed in Table 4.

The intercept from linear regression denoted to the adsorption capacity of phenol (\( k \)). As a result, \( k \) of activated carbon from coconut shells was 164., mg/g, 152.4 mg/g for carbon from ex-mining coal and 190.1 mg/g for carbon from oil palm stone. These values is higher than Tseng's results those are 80 - 100 mg/g. It was consistent with effect of temperature and chemical activator for activated carbon to adsorptive phenol in solution.

3.4. Effect of contact time with adsorptive of phenol

The comparative of phenol adsorption in activated carbon with the best condition (temperature and each activator) was carried out. The varied time for absorbing phenol was done to find out the best condition of contact time. Results are in Table 5.
Table 6. Effect of contact time for absorbing phenol by using activated carbon from ex-mining coal

| Varied time in minute | Without activator at 850°C | KOH activator at 850°C | H₂SO₄ activator at 850°C | H₃PO₄ activator at 850°C |
|-----------------------|---------------------------|-----------------------|--------------------------|-------------------------|
| 30                    | 15                        | 82.5                  | 98.6                     | 90.1                    |
| 60                    | 18.9                      | 95.4                  | 79.1                     | 84.6                    |
| 90                    | 96.3                      | 96.5                  | 87.3                     | 97.9                    |
| 120                   | 93.8                      | 94.5                  | 99.5                     | 96.3                    |

Table 7. Effect of contact time for absorbing phenol by using activated carbon from oil palm stone

| Varied time in minute | Without activator at 850°C | KOH activator at 850°C | H₂SO₄ activator at 650°C | H₃PO₄ activator at 650°C |
|-----------------------|---------------------------|-----------------------|--------------------------|-------------------------|
| 30                    | 75.5                      | 86.7                  | 64                       | 85.7                    |
| 60                    | 79                        | 89.6                  | 86                       | 92.9                    |
| 90                    | 80                        | 94.9                  | 94                       | 96.5                    |
| 120                   | 84                        | 91                    | 92.6                     | 96.8                    |

Figure 6. Varied time for adsorptive phenol of an activated carbon from coconut shells (phenol; C=100 mg/l, T=25°C, t=120 min., W=0.6 g, V=50 ml, UV-vis at λ_max=270 nm)

Carbon from coconut shells without activated was adsorbed phenol longer than activated with KOH (850°C), H₂SO₄ (850°C) and H₃PO₄ (750°C). The optimum of the contact time was 90 minutes. The best chemical activator is KOH for coconut shell activated carbon. Figure 8, showed that the optimum condition for contact time was 90 minutes for phenol adsorption. Using the same condition the optimum contact time for adsorptive phenol in solution was carried out for activated carbon from ex-mining coal and oil palm stone and the results are presented in Table 6.

By increasing temperature in activation processes was influence of activated carbon products. The best activator is H₃PO₄ at 750°C for ex-mining coal with contact time 90 minutes.

Figure 7. Effect of contact time for activated carbon from ex-mining coal (Solution test: phenol; C=100 mg/l, T=25°C, t=120 min., W_sample=0.6 g, V=50 ml, analysis UV-vis λ_max=270 nm)

The H₃PO₄ at 750°C is the best activator for activated carbon of oil palm stone with contact time 90 minutes for absorbing phenol (Table 7). The characteristic of phenol depends on the pH. In acidic solution phenol will be ionized to be H⁺ ion and phenolate ion, meanwhile in higher pH phenol to form neutral molecule.
4. CONCLUSIONS

Based on the experiment investigations, the following conclusions can be drawn.

Three different sources of activated carbon were potential for absorbing phenol by activated with KOH for coconut shell, ex-mining coal with H₂PO₄ and oil palm stone with H₂PO₄ and H₂SO₄ as chemical activators. The best temperature for activation processes was 650 to 850°C and depend on chemical activator with contact time between 90 to 120 minutes. The fit of the adsorption data into the Langmuir isotherm confirmed monolayer adsorption. The adsorptive capacity of three different activated carbon are coconut shells with KOH as an activator (750°C) is 164.4 mg/g, ex-mining coal with H₂PO₄ (850°C) is 152.4 mg/g, and oil palm stone with H₂PO₄ as an activator (850°C) is 190.1 mg/g and consistent with a Ferderich equation. The adsorptive capacity of oil palm stone activated carbon was associated to the concentration of absorbents, the adsorption temperature and the particle size of the raw material. The adsorptive capacity of the oil palm stone was also found related to the surface area.

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