The Performance of Activated Carbon from Used Coffee Grounds Combined with Iron(III) Oxide under UV Light and Ultrasound for Phenol Degradation

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ABSTRACT

Coffee consumption over the past four years has continued to increase the amount of used coffee grounds. Usually, the used coffee grounds are simply thrown away. In fact, it can still be used as other materials that are more efficient and environmentally friendly, such as activated carbon. Activated carbon can be utilized as an adsorbent to adsorb compounds that are carcinogenic and potentially last a long time in the environment, such as phenols. Phenol decomposition through chemical can be carried out by Advanced Oxidation Process (AOP) which utilize hydroxyl radicals. This method used a catalyst such as iron(III) oxide under ultraviolet light. Phenol decomposition can also be carried out using ultrasound. This study presents the performance of the combination of activated carbon-catalyst with ultrasound in phenol decomposition. The results showed that the mass of the composite influenced the 0.1 M phenol degradation by the activated carbon – iron(III) oxide assisted with ultraviolet light, ultrasound, and 0.01 M hydrogen peroxide, for 45 minutes. The best degradation of phenol was obtained when 0.5 g adsorbent was applied with the adsorption capacity of phenol was 704.37 mg/g. The concentration of hydrogen peroxide also affects the decomposition of phenol in solution. From the variation of the hydrogen peroxide solution used (0.01; 0.02; and 0.03 M), the optimal concentration in degrading phenol was 0.01 M with the adsorption capacity of phenol was 393.70 mg/g.

Keywords: Activated carbon, used coffee grounds, Fe2O3, UV light, ultrasound, H2O2

INTRODUCTION

Drinking coffee has become a part of life for all Indonesians. Indonesian people enjoy coffee by drinking it alone or in groups. Drinking coffee is an activity to fill spare time or build intimacy with friends, relations, and clients. Coffee providers also vary from the level of stalls, cafes, to coffee shops. Coffee consumption has continued to increase over the past four years. However, the amount of coffee grounds as waste is also increase. Almost 6 million tonnes of dry SCG are produced worldwide each year [1].

Used coffee grounds are defined as the residue obtained after brewing coffee with hot water. The main components of used coffee grounds are polysaccharides in the form of cellulose and hemicellulose and lignin [2]. Usually used coffee grounds are taken by collectors and then sold to be used as compost, bioenergy production materials, and mushroom growing media [3]. However, the application of used coffee grounds directly for these purposes still creates problems because they contain substances that are toxic to the...
environment [4]. Therefore, it is not only need to be processed into something more efficient, but also expected to be a safe and environmentally friendly.

Phenol is a compound that is widely used by various industrial fields. Phenols in water will bind with other compounds to form phenol derivatives, namely chlorophenol, methyl phenol, alkylphenol, and bisphenol. These phenolic compounds are more toxic than phenols. The high concentration of phenol in the human body results in heart failure, leading to death. The results also showed that high concentrations of bisphenol in mice could cause infertility [5].

Phenol decomposition has been carried out in several ways, such as degradation using hydrogen peroxide [6], microorganisms [7], degradation using catalysts [8], and degradation using microwaves and ultrasound [9]. Studies that combine catalysts with microwaves and ultrasound have also been conducted [10,11]. Each method has its own limitations. However, the published study about activated carbon’s performance combined with a catalyst and microwave or ultrasound in phenol decomposition remains limited.

In this research, activated carbon combined with catalyst under UV light assisted by ultrasound is proposed as a new alternative for phenol decomposition. Coffee grounds containing cellulose, hemicellulose, and lignin, rich in carbon elements, will be converted into activated carbon, which acts as an adsorbent. Iron(III) oxide is used as the catalyst. Iron oxide reacted with hydrogen peroxide in combination with the heat obtained from a radiation source, will be more efficient to decompose phenol [8]. Ultrasound is used because it produce a higher yield than that of microwaves [9]. The presence of adsorbents and catalysts in the system is expected to create synergy to enhance the phenol decomposition rather than using ultrasound or catalysts alone.

EXPERIMENT
Chemicals and instrumentation
Chemicals used for this research were coffee grounds, phosphoric acid 85% (Merck), hydrochloric acid 37% (Merck), iron(III) oxide powder (<5 µm, Sigma-Aldrich), polystyrene powder (1 µm, Sigma-Aldrich), isopropanol 99.5% (Smart Lab), phenol solids (Smart Lab), hydrogen peroxide 3% (Merck), water, and distilled water.

Instrumentation applied in this research were oven (Memmert UN 260), furnace (Daihan Scientific), portable pH meter (Digital ATC), a closed container containing a UV lamp (220 V, 50 Hz) and an ultrasound generator machine (JP-020S, Skymen, frequency 40 kHz), Scanning Electron Microscopy-EDX (Hitachi TM 3000), FTIR spectrophotometer (Shimadzu IR Prestige 21, sample was analyzed using NaCl plate), and UV-Visible spectrophotometer (Shimadzu UV-1800).

Procedure
Preparation of used coffee grounds
Commercial coffee grounds made from mixed of Arabica and Robusta coffee beans (2.16 kg) were brewed to become used coffee grounds. The used coffee grounds were washed with distilled water, dried at a temperature of 105°C for 24 hours, and sieved using a 100-mesh sieve.

Preparation of activated carbon from used coffee grounds
Dry used coffee grounds (101.75 g) were impregnated with 1 M phosphoric acid solution (1:2) for 24 hours at room temperature. The mixture was filtered off, and the solid residue then dried in an oven at 105°C for 12 hours. The impregnated used coffee grounds
were then carbonized using a furnace at 700°C for 30 minutes. The activated carbon was washed with a 0.1 M solution of HCl and distilled water until the pH of the filtrate reached 7. The wet activated carbon then dried in an oven at 105°C for 24 hours.

**Preparation of activated carbon and iron(III) oxide composite**

The mixture of iron(III) oxide powder, activated carbon, and polytetrafluoroethylene (PTFE) powder (50: 45: 5 mass ratio) was dissolved in a 1: 1 solution of isopropanol and distilled water. The dough then heated for 45 minutes at 80°C in an oven to evaporate the isopropanol. The dry dough was characterized by SEM-EDX and FTIR spectrophotometer.

**Influence of the amount of the composite on phenol decomposition**

Activated carbon – iron(III) oxide material (1.5 g), hydrogen peroxide solution (0.01 M, 5 mL), and phenol solution (0.1 M, 50 mL) were added to the ultrasound generator machine. The machine and the UV lamp were placed in a closed container. The two instruments were turned on together for 45 minutes. The phenol concentration after the decomposition process was analyzed using a UV-Visible spectrophotometer. These steps were repeated for a solid amount of activated carbon – iron(III) oxide 0; 0.5; and 1 g. These steps were also repeated for activated carbon and iron(III) oxide 1 g each for comparison purposes. Figure 1 showed the schematic figure of the reaction chamber.

**Effect of hydrogen peroxide concentration on phenol decomposition**

Phenol solution (0.1 M, 50 mL), 1 g of activated carbon - iron(III) oxide, and hydrogen peroxide solution (0.01 M, 5 mL) were added to the ultrasound generator machine. The machine and UV lamp were placed in a closed container. The two instruments were turned on together for 45 minutes. The phenol concentration after the decomposition process was analyzed using a UV-Visible spectrophotometer. These steps were repeated for the concentration of hydrogen peroxide of 0.00; 0.02; and 0.03 M.

**Data analysis**

Phenol degradation efficiency was calculated based on equation 1. The phenol concentration before degradation is expressed as \( C_0 \), and the phenol concentration after degradation is stated as \( C_1 \).

\[
\text{Phenol degradation efficiency} = \frac{C_0-C_1}{C_0} \times 100\% \quad (1)
\]
Equation 2 was used to find out the amount of phenol adsorbed per mass of the adsorbent, in which $Q_e$ is the adsorption capacity (mg/g), $C_0$ is the phenol concentration before degradation, $C_1$ is the phenol concentration after degradation, $V$ is the volume of phenol (L), and $m$ is the mass of the adsorbent (g).

$$Q_e = \frac{[(C_0-C_1)V]}{m} \quad (2)$$

RESULT AND DISCUSSION
Preparation of used coffee grounds

Six-packs of coffee powder were purchased on the market with a net weight of 360 g so that a total of 2.16 kg of ground coffee was obtained. Used coffee grounds were made from the coffee powder. As much as 101 g used coffee grounds were obtained, while the rest was in the form of coffee drinks and volatile compounds. Used coffee grounds' appearance and component analysis were done using Scanning Electron Microscopy (SEM) - EDX. Figure 2 shows the appearance of used coffee grounds at 1000x and 5000x magnifications. The used coffee grounds were in the form of chunks. The pore size was in the macroporous range. The most dominant atoms were carbon (56.13 - 60.03%) and oxygen (35.67 - 38.89%). The used coffee grounds also contain minerals such as phosphorus (3.65 - 4.31%), potassium (0.30 - 0.59%), sulfur 0.2%, and aluminum 0.12 - 0.15%. This profile is different from the used coffee grounds studied before [2]. The conditions during the preparation of used coffee grounds and the type of coffee powder can cause this difference.

**Figure 2.** The magnifications of used coffee grounds (a) 1000x; (b) 5000x

Preparation of activated carbon from used coffee grounds

Activated carbon has been made from used coffee grounds. Carbonization at high temperatures is intended to remove water vapor and volatile compounds at temperatures of 100 - 150°C and break the bonds of hemicellulose compounds at 200 - 250°C, cellulose at 280 - 320°C, and lignin at 400°C [12]. The activated carbon was washed with hydrochloric acid solution and distilled water to remove impurities. The carbonization process resulted in a 48.11% yield of activated carbon. This data is similar to the data obtained before [13].

The morphology and content of activated carbon from coffee grounds were observed using Scanning Electron Microscopy (SEM) - EDX. Figure 3 shows the results of the analysis. Compared to Figure 2, at the same magnification of 1000x and 5000x, the chunk shown in Figure 2 turn into smaller sizes. Figure 3 shows that the activated carbon made by chemical activation has succeeded in opening the carbon's pores from the used coffee grounds.
The carbon atom increases about 5 - 7% compared to the used coffee grounds before carbonization. The oxygen atoms were removed from the materials, approximately 10-12%. The decrease in oxygen atoms occurs due to the decomposition of organic compounds and the dehydration reaction with phosphoric acid [14]. Before activation, coffee grounds only contain phosphorus, potassium, sulfur, and aluminum. After activation, the number of phosphorus increased about 3-5%. The increasing number of phosphorus comes from the impregnation solution. The amount of potassium and aluminum has also increased. The EDX found silicon, calcium, and magnesium instead of sulfur. The presence of unwanted minerals might be because of impurities dissolved in the washing solution [15].

Temperature influences the carbon’s pore size. Carbonization at 700°C results in the formation of micropores. Increasing the activation temperature (800–900°C) produce mesopores and macropores. Along with temperature, time also affects the pore size. Longer time makes micropores changes to mesopores. This is caused by the release of volatile compounds, which causes the space formerly filled by the substance becomes more open hence causing the pore size to become wider [16].

**Preparation of activated carbon and iron(III) oxide composite**

The preparation of composite made from used coffee grounds activated carbon mixed with iron(III) oxide and PTFE was then carried out. Material morphology was observed by SEM-EDX. FTIR spectrophotometer is used for functional group identification. Figure 4 shows three photos of the material by SEM.
According to IUPAC [17], there are three major pore sizes: macropores (>50 nm), mesopores (2 - 50 nm), and micropores (<2 nm). Figure 4 shows the material's pores are in the microporous and mesoporous range with the size of 1.49 - 4.35 µm obtained from Scanning Electron Microscopy (SEM) - EDX analysis. The figure is similar to the result obtained by the previous one [18], which shows that the pore size is different, and the pore distribution is uneven. After mixing activated carbon with solid iron (III) oxide and PTFE, almost all the activated carbon’s surface in Figure 3(a) is covered with smaller solids. At 5000x magnification, the carbon pores are filled with small sprinkle solids. This indicates that the size of iron(III) oxide aggregates is smaller than the pore size of activated carbon.

Based on EDX analysis, the atoms detected in the materials were iron (39.30%), carbon (27.17%), oxygen (26.47%), phosphorus (2.976%), and potassium (0.385%). There are no significant differences between the material and the activated carbon. The only difference is the number of iron atom increases, which causes a decrease in carbon number. The silicon, calcium, and magnesium that were originally present on the activated carbon were no longer found in these materials. This is probably due to the washing process after dissolving the materials with a 1: 1 solution of isopropanol and distilled water.

**Figure 5.** Infrared spectrum of the materials made from activated carbon, iron(III) oxide, and PTFE

Figure 5 shows that the infrared spectrum’s main regions were at wavelengths 3000 - 3500 cm⁻¹, 1500 - 1750 cm⁻¹, 1100 - 1250 cm⁻¹, and in areas below 700 cm⁻¹. The absorption in the 3000 - 3500 cm⁻¹ region shows a typical -OH group peak. The peaks in the area of 1500-1750 cm⁻¹ indicate the presence of a carboxyl group. The bands around 1250 cm⁻¹ might be the results of C-OH stretching from the remaining polysaccharide in the composite [19,20]. The peak in areas below 700 cm⁻¹ indicates a Fe-O bond [21]. The broad peak at 575 cm⁻¹ is the absorption characteristics of Fe₃O₄ [22].

**The influence of the amount of the material on phenol decomposition**

The decomposition of 0.1 M phenol using materials consist of activated carbon and iron(III) oxide assisted by 0.01 M hydrogen peroxide, ultrasound with a frequency of 40 kHz, and ultraviolet light for 45 minutes in a closed container was conducted. Phenol degradation by ultraviolet light alone is insufficient because phenol is a very stable compound. Phenol can
only be degraded by a radical species attack. Therefore, to achieve high efficiency, a combination of ultrasonic and an oxidizer such as hydrogen peroxide must be added. The bubbles formed during the sonication process produce hydrogen and hydroxyl radicals due to the fragmentation of water molecules. The presence of hydroxyl radicals will react with phenol. Phenol will be converted into hydroquinone, catechol, and \( p\)-benzoquinone, which will be then converted into acetylene, maleic acid, carbon monoxide, and carbon dioxide\[11,23]\.

Phenol degradation efficiency obtained in this study is in the range of 72 - 76%. This efficiency is similar to the results achieved previously. The phenol degradation efficiency increased when more materials were applied to the system. The optimum degradation efficiency was shown by the mass of 1.5 g (75.78%). The relationship between the amount of material and degradation efficiency is presented in Figure 5.

![Figure 6. The relationship between the amount of material and efficiency of phenol degradation](image)

The degradation efficiency reaches the lowest point when 1 g of the material was used (72.43%). This is probably caused by the free site were less than another and unable to be filled by phenol due to the repulsion between the phenol molecules [24]. Activated carbon with the same amount of mass gave a slightly better efficiency (73.39%). The degradation efficiency given by iron(III) oxide was worse than that of the activated carbon (66.56%). This implied that the material acts more predominantly as an adsorbent than as a catalyst.

Because the material acts more as an adsorbent than as a catalyst, Equation 2 was used as an approach. The calculated data reveals that the least amount of material (0.5 g), gives the greatest adsorption capacity (704.37 mg/g). Figure 7 shows that the greater the amount of material applied to the system, the lower the adsorption capacity obtained. Theoretically, the addition of the adsorbent mass increases the adsorption active site so that it can adsorb more adsorbate. However, this decrease may be due to the use of exceeding amount of the material so that when the ultrasound generator machine was running, the solids became coagulated. This coagulation leads to not all active sites being exposed to the adsorbate.
Effect of hydrogen peroxide concentration on phenol decomposition

The decomposition of 0.1 M phenol by activated carbon - iron(III) oxide and a variation of hydrogen peroxide solutions assisted by ultraviolet light and ultrasound in a closed container was carried out. The highest efficiency achieved by 0.01 M hydrogen peroxide solution (83.67%). The 0.02 M hydrogen peroxide gave the lowest phenol degradation (66.52%) as shown in figure 8. Theoretically, the addition of hydrogen peroxide can reduce phenol degradation because hydrogen peroxide reacted with hydroxyl radicals derived from water. The hydrogen peroxide became oxygen and water instead of giving another hydroxyl radical to the system [25]. The presence of iron in the system also may lead to a competition between iron and ultrasound in terms of hydrogen peroxide utilization. Iron will use hydrogen peroxide as a catalyst while ultrasound utilizes hydrogen peroxide in the thermal decomposition of phenol [26].

Figure 7. Relation of the amount of material to phenol adsorption capacity

Figure 8. The relationship of hydrogen peroxide concentration to the percentage of phenol degradation efficiency
Figure 9. The relationship of hydrogen peroxide concentration to the phenol adsorption capacity

The determination of phenol adsorption capacity at each hydrogen peroxide concentration was calculated according to equation 2. The average adsorption capacity of phenol ranges from 313 - 394 mg/g. A 0.01 M hydrogen peroxide solution gave the highest adsorption capacity. The lowest adsorption capacity was obtained at 0.02 M. Figure 9 display the relationship between hydrogen peroxide concentration and phenol adsorption capacity. There is no significance difference in the profile between hydrogen peroxide concentration relationship to the phenol percentage efficiency and to the adsorption capacity. This is because the amount of material used in this study for each hydrogen peroxide solution variation was exactly the same (1 g). The effect of time and initial concentration on phenol degradation is offered for future research.

CONCLUSION

All stages of the study consisting of used coffee grounds preparation, activated carbon production from used coffee grounds, preparation of material made from used coffee grounds activated carbon iron(III) oxide, and phenol decomposition have been completed. The appearance of used coffee grounds based on SEM analysis at magnifications of 1000x and 5000x were still chunks. Used coffee grounds contain about 56.13 - 60.03% carbon atoms and oxygen ranging from 35.67 - 38.89%. The carbonization process resulted in a 48.11% yield of activated carbon. At the same magnification, the chunks were already converted into smaller pieces. Compared with used coffee grounds before carbonization, the carbon content increases by 5 - 7%. The oxygen atom was removed around 10-12%. The material made from activated carbon and iron(III) oxide had pores of 1.49 - 4.35 µm. The three largest atomic compositions in the composite are iron (39.30%), carbon (27.17%), and oxygen (26.47%).

The results showed that the amount of material had an effect on the 0.1 M phenol degradation by a solid mixture of activated carbon - iron(III) oxide assisted by 0.01 M hydrogen peroxide, ultraviolet light, and ultrasound for 45 minutes. When more amount of the composite was used, the adsorption capacity decreases. The optimum amount of the material degrades phenol at 0.5 g with an adsorption capacity of 704.37 mg/g. The hydrogen peroxide concentration also affects the decomposition of phenol in solution. There is an increase in adsorption capacity after adding a hydrogen peroxide solution for phenol degradation. From various hydrogen peroxide concentrations, the optimal concentration in phenol degradation was 0.01 M (393.70 mg/g).
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REFERENCES

[1] Hardgrove, S. J., Livesley, S. J. *Urban Forestry & Urban Greening*. 2016, 18, 1–8.
[2] Ballesteros, L. F., Teixeira, J. A., Mussatto, S. I. *Food Bioprocess Technol.*, 2014, 7 (12), 3493–3503.
[3] Campos-Vega, R., Loarca-Piña, G., Vergara-Castañeda, H. A., Oomah, B. D. *Trends in Food Science & Technology* 2015, 45 (1), 24–36.
[4] Cruz, R., Cardoso, M. M., Fernandes, L., Oliveira, M., Mendes, E., Baptista, P., Morais, S., Casal, S. J. *Agric. Food Chem*. 2012, 60 (32), 7777–7784.
[5] Gami, A. A., Shukor, M. Y., Khalil, K. A., Dahalan, F. A., Khalid, A., Ahmad, S. A. *JEMAT* 2014, 2 (1), 11–24.
[6] Prasannakumar, B. R., Regupathi, I., Murugesan, T. *J. Chem. Technol. Biotechnol*. 2009, 84 (1), 83–91.
[7] Liu, Z., Xie, W., Li, D., Peng, Y., Li, Z., Liu, S. *IJERP* 2016, 13 (3), 300.
[8] Yu, L., Chen, J., Liang, Z., Xu, W., Chen, L., Ye, D. *Separation and Purification Technology*. 2016, 171, 80–87.
[9] Wu, Z.-L., Ondruschka, B., Cravotto, G. *Environ. Sci. Technol*. 2008, 42 (21), 8083–8087.
[10] Parida, K. M., Parija, S. *Solar Energy* 2006, 80 (8), 1048–1054.
[11] Yehia, F. Z., Eshaq, Gh., Rabie, A. M., Mady, A. H., ElMetwally, A. E. *Egyptian Journal of Petroleum*. 2015, 24 (1), 13–18.
[12] Yuliusman, Nasruddin, Afadh, M. K., Haris, F., Amilian, R. A., Hanafi, A., Ramadhah, I. T. *Adv Sci Lett*. 2017, 23 (6), 5751–5755.
[13] Aznar, J. S. Characterization of activated carbon produced from coffee residues by chemical and physical activation. Master Thesis, KTH Vetenskap Och Konst, Stockholm, 2011.
[14] Alves, A. C. F., Antero, R. V. P., de Oliveira, S. B., Ojala, S. A., Scalize, P. S. *Environ Sci Pollut Res*. 2019, 26 (24), 24850–24862.
[15] Kante, K., Nieto-Delgado, C., Rangel-Mendez, J. R., Bandosz, T. J. *Journal of Hazardous Materials*. 2012, 201–202, 141–147.
[16] Zhou, J., Luo, A., Zhao, Y. *Journal of the Air & Waste Management Association*. 2018, 68 (12), 1269–12777.
[17] Zdravkov, B., Čermák, J., Šefara, M., Janků, J. *Open Chemistry*. 2007, 5 (2), 385–395.
[18] Gao, Y., Zou, D., Liu, Y., Guan, H., Sun, W. *Clean – Soil, Air, Water*. 2019, 47 (10), 1900095.
[19] Taleb, F., Ammar, M., Mosbah, M. ben, Salem, R. ben, Moussaoui, Y. *Sci Rep*. 2020, 10 (1), 11048.
[20] Kim, M.-S., Kim, J.-G. *Environments*. 2020, 7 (4), 24.
[21] Farahmandjou, M., Soflaee, F. *PCR*. 2015, 3 (3).
[22] Togashi, T., Naka, T., Asahina, S., Sato, K., Takami, S., Adschiri, T. *Dalton Trans*. 2011, 40 (5), 1073–1078.
[23] Kidak, R., Ince, N. H. *Ultrasonics Sonochemistry*. 2006, 13 (3), 195–199.
[24] Patrulea, V., Negrulescu, A., Mincea, M. M., Pitulice, L. D., Spiridon, O. B., Ostaffe, V. *BioResources*. 2013, 8 (1), 1147–1165.
[25] Xu, P., Zeng, G., Huang, D., Liu, L., Lai, C., Chen, M., Zhang, C., He, X., Lai, M., He, Y. *RSC Adv.* **2014**, *4* (77), 40828–40836.

[26] Papadaki, M. *Separation and Purification Technology* **2004**, *34* (1–3), 35–42.