

COFFEE GROUND ACTIVATED CHARCOAL AND ITS POTENTIAL AS AN ADSORBENT OF Ca^{2+} AND Mg^{2+} IONS IN REDUCING WATER HARDNESS

Achmad Khaerul Mustaqim^{a)}, Sutanto^{a)}, Yulian Syahputri^{a*)}

^{a)} Department of Chemistry, Universitas Pakuan, Bogor, 16143, Indonesia

^{*)} Corresponding Author: syahputri.yulian@unpak.ac.id

Article history: received 05 September 2021; revised 19 October 2021; accepted 25 November 2021; published 31 December 2021

Abstract

Residents of Ciaruteun Udik Village experienced complaints about the well water they use, namely the presence of scale on cooking utensils, soap is difficult to foam, and indigestion due to consuming hard water. One way to reduce water hardness is by adsorption. Coffee grounds can be used as activated charcoal and function as an adsorbent for calcium and magnesium metal ions. The purpose of this study was to determine the optimum contact time, pH, and weight of coffee grounds in the maximum adsorption of hardness in water. This study begins with the preparation of samples in hard water and coffee grounds, namely by activation with HCl, then the FTIR test of coffee grounds before and after activation. Activated coffee grounds charcoal was tested for adsorption capacity against hardness in water with variations in contact time, pH, and weight of the adsorbent. The results showed that coffee grounds activated charcoal can be used as an adsorbent in reducing water hardness. The optimum pH and contact time of coffee grounds activated charcoal in adsorption of hardness in water was at a contact time of 75 minutes and pH 7 with a hardness level in water of 565.17 mg CaCO_3/L decreasing to 56 mg CaCO_3/L . The optimum weight of coffee grounds activated charcoal in adsorption of hardness in water was 10 grams with hardness levels in water from 565.17 mg CaCO_3/L decreasing to 12 mg CaCO_3/L .

Keywords: Adsorption; Hard water; Coffee grounds; Complexometry

1. INTRODUCTION

Indonesia was the world's fourth largest coffee producer in 2015-2016. Indonesia's coffee production reaches 739 thousand tons (ICO [1]). The type of coffee that is mostly produced by farmers and consumed more is robusta (Najiyati and Danarti [2]). The number of coffee production and people who are consumptive of coffee is directly proportional to the coffee grounds waste produced and is not balanced with the utilization of the coffee grounds waste. Coffee grounds waste reaches 324 tons (Khusna and Joko [3]). Coffee grounds are organic materials that can be used as activated charcoal as an adsorbent or absorbent material (Aman et al [4]). According to Ristiana et al [5] activated charcoal can reduce water hardness up to 31.43 mg/L.

Water hardness is caused by the presence of Ca^{2+} and Mg^{2+} ions (Marsidi [6]). According to Sulistyani et al [7] and Budiman et al [8] water hardness can cause scale around the pan when boiling and soap is difficult to foam. High water hardness causes health problems, among others, can cause cardiovascular disease (blockage of the arteries of the heart) and urolithiasis (kidney stones). Residents of Ciaruteun Udik Village experienced complaints about the well water they use, namely the presence of scale on cooking utensils, soap is difficult to foam, and digestive disorders due to consuming the water. According to the Regulation of the Minister of Health of the Republic of Indonesia No. 492/MENKES/PER/IV/2010 concerning drinking water quality requirements, the maximum allowed hardness level is 500 mg/L. One way to reduce water hardness is by adsorption. Based on the description above, a

research was conducted on the use of coffee grounds as activated charcoal to reduce water hardness with variations in contact time, pH, and weight of the adsorbent.

2. RESEARCH METHODS

The tools used include erlenmeyer, volumetric pipette, volumetric flask, stirring rod, burette, test tube, measuring cup, watch dish, filter paper, spatula, porcelain dish, desiccator, oven, furnace, and the instrument used is FTIR. The materials used include coffee grounds, hard water sample solution, $\text{Na}_2\text{S}_2\text{O}_2$ (Merck), iodine solution (Merck), NaOH (Merck), HNO_3 (Merck), starch (Merck), Na_2EDTA (Merck), EBT indicator, pH buffer solution 10 and aquades.

2.1. Determination of Hard Water

The hard water used was obtained from Ciaruteun Udik Village. Hard water was taken from wells with a depth of 10 meters which was carried out on May 04, 2020 and May 11, 2020.

2.2. Coffee Ground Activation

The coffee grounds were dried at 105°C for 5 hours, then put in a 450°C furnace for 45 minutes. The coffee grounds were sifted to obtain a homogeneous size of 100 mesh. Activation of coffee grounds was carried out by immersing 150 grams of coffee grounds using 500 mL HCl 0.1 M for 48 hours. The activated coffee grounds were then filtered, and washed again using distilled water until the pH of the filtrate was neutral. Activated coffee grounds were

dried in an oven at 100°C for 4 hours (Aman et al [4] and Samosir et al [9]).

2.3. Characteristics of Coffee Ground Activated Charcoal

Characterization of coffee grounds activated charcoal using FTIR to determine functional groups. The chemical characteristics of activated charcoal include analysis of moisture content, ash content, volatile matter content, carbon content, and iodine absorption. The activated charcoal analysis procedure refers to the Indonesian National Standard 06-3730-1995 regarding technical activated charcoal.

2.4. Optimization of Contact Time, pH and Adsorbent Weight

Determination of contact time in the optimum adsorption process was carried out by making a solution of 100 mL of water hardness sample with a concentration of 565.17 mg/L. 2 grams of coffee grounds activated charcoal was added to the sample solution. Stirred with a stirrer with variations in contact time of 30, 45, 60, 75, and 90 minutes and variations in pH 4, 5, 6, and 7. Adjusting the pH of the solution using HNO₃ 0.01 M and NaOH 0.01 M. The test sample solution then filtered and determined the concentration of Ca and Mg by complexometric titration (Imawati and Adhitiyawarman [10]). Determination of the mass of activated charcoal in the optimum adsorption process was carried out by making a solution of 1 L of water hardness sample with a concentration of 565.17 mg/L. The sample solution was contacted with coffee grounds activated charcoal with a mass variation of 5 g/L; 6 g/L; 8 g/L; and 10 g/L. Then stirred with optimum contact time and pH conditions.

2.5. Determination of Total Hardness by Complexometric Titration

The sample of water hardness that has been in contact with the adsorbent of activated charcoal coffee grounds is taken 25 mL then put into a 250 mL Erlenmeyer and added 25 mL of distilled water. The sample solution was added with 1-2 mL of pH 10 buffer solution and 30 mg of EBT (Eriochrome Black-T) indicator. The sample solution was then titrated with Na₂EDTA 0.01 M slowly until a purplish red color changes to blue (Astuti et al [11]).

3. RESULTS AND DISCUSSION

3.1. Characteristics of Coffee Ground Activated Charcoal

Activated charcoal or often called activated carbon is a carbon that has large pores and a large surface area (Prabarini [12]). The characterization of coffee grounds activated charcoal is presented in Table 1.

Table 1. Characteristics of Coffee Ground Activated Charcoal

Test Parameters	Rate	SNI 06-3730-1995
Water content	7%	Max. 15%
Ash Level	4%	Max. 10%
Substance Level Easy Fly	9%	Max. 25%
Carbon Content	80%	Min. 65%
Iodine Number or Adsorption Capacity	749.86 mg/g	Min. 750 mg/g

The less water content contained in activated charcoal so that it can produce larger pores. The larger the pores, the surface area of the activated carbon will increase, resulting in an increase in the adsorption ability of activated carbon (Sulaiman et al [13]). The characteristics of the coffee grounds activated charcoal listed in Table 1 has a water content according to SNI, which is below 15% with a water content of 7%.

In activated charcoal, the ash content is tried to be as small as possible because it will reduce its adsorption capacity in both gas and solution form (Sulaiman et al [13]). The characteristics of the coffee grounds activated charcoal listed in Table 1 has an ash content according to SNI, which is below 10% with an ash content of 4%.

The volatile matter content is the result of the decomposition of charcoal constituents due to the heating process during cooking and is not a component of charcoal (Kusdarini et al [14]). The characteristics of the coffee grounds activated charcoal listed in Table 1 has a volatile substance content according to SNI, which is below 25% with a volatile substance content of 9%.

The high and low levels of carbon are influenced by the amount of water content, ash content, and levels of volatile substances in the material (Permatasari et al [15]). The characteristics of the coffee grounds activated charcoal listed in Table 1 has a carbon content according to SNI, which is above 65% with a carbon content of 80%.

According to Imawati and Adhitiyawarman [10] the iodine number indicates the amount of iodine (mg) that can be absorbed by one gram of activated charcoal. Coffee grounds activated charcoal has an iodine adsorption capacity according to SNI, which is below 750 mg/g with an iodine adsorption of 749.86 mg/g.

3.2. Spectra FTIR Coffee Ground Charcoal Before and After Activation

The frequency data of the activated charcoal functional group of coffee grounds can be seen in Table 2.

Table 2. IR Interpretation of Coffee Ground Charcoal Before and After Activation (Source: Fessenden [16])

No	Frequency (cm ⁻¹)	Frequency Range (cm ⁻¹)	Bond Type	Functional group
Before Activation				
1	3694.00	3600-3000	OH	Alcohol
2	2922.59	2800-3000	CH	Alkene
3	1565.49	1450-1600	CC	Aril
4	1059,19	1000-1300	CO	Esther
After Activation				
1	3365.93	3600-3000	OH	Alcohol
2	2924.99	2800-3000	CH	Alkene
3	1744.99	1705-1750	C=O	Ketones
4	1458.05	1450-1600	CC	Aril
5	1060.48	1000-1300	CO	Esther

Based on the analysis of the interpretation of the FTIR spectrum on coffee grounds charcoal before and after activation, it showed the presence of O-H (Alcohol), =C-H (Alkene), C=C (Aryl), C=O (Ester) groups, and the appearance of C=O (Ketone) groups on coffee grounds activated charcoal. The presence of an alcohol group in the activated charcoal of coffee grounds can increase the adsorption capacity (Alya et al [17]).

3.3. Optimization Results of Contact Time, pH, and Mass of Activated Charcoal Coffee Grounds Against Hardness in Water

The adsorption capacity of coffee grounds activated charcoal with variations in contact time and pH to water hardness is shown in Figure 1.

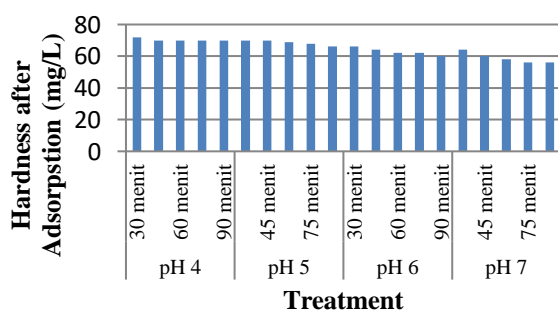


Figure 1. Water Hardness Levels After Adsorption by Activated Charcoal of Coffee Grounds with Variations in Contact Time and pH

Figure 1 shows that there was a decrease in the level of water hardness after the adsorption process by activated charcoal with variations in time and pH. The longer the contact time and the higher the pH used, the greater the adsorption, which is indicated by the decrease in the level of hardness in hard water. The optimum contact time and pH that can reduce the level of hardness in water is the best at a contact time of 75 minutes and pH 7 with a hardness level in water of 56 mg/L and % Recovery is 96. The

optimum time for adsorption of hardness in water by activated charcoal of coffee grounds is 75 minutes. The optimum time is reached when the increase in adsorbate levels reaches its maximum point so that the addition of contact time will not have a significant effect on reducing the adsorbate levels in the sample (Lestari [18]). The longer the contact time, the greater the interaction between the adsorbent and the adsorbate, so that more and more adsorbate is adsorbed by the adsorbent, but if it is too long it can reduce the absorption rate (Magfiroh et al, [19]).

In this study, various mass variations of coffee grounds activated charcoal as an adsorbent adsorb Ca²⁺ and Mg²⁺ in hard water at the optimum contact time and pH. The results of the analysis of the effect of the adsorbent mass in adsorption of hardness in water can be seen in Figure 2.

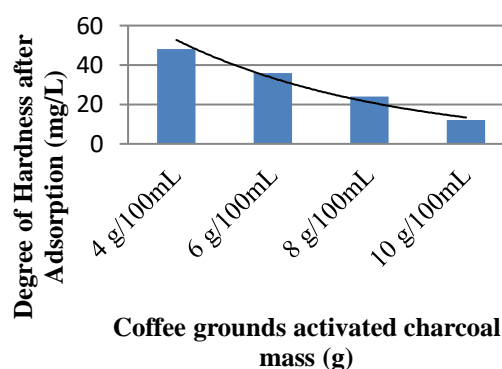


Figure 2. Relationship of Water Hardness to Coffee Ground Adsorbent Mass

Figure 2 shows that there was a decrease in hardness in water after the adsorption process by activated charcoal with variations in the mass of the adsorbent. The greater the mass of activated charcoal used, the greater the adsorption, which is indicated by the decrease in the level of hardness in the water. The relationship between the mass of coffee grounds activated charcoal and the decrease in hardness is inversely proportional to the equation: $Y = 83.13e^{-0.45X}$, with a coefficient of determination, $R^2 = 0.960$. Y = hardness and x weight of coffee grounds activated charcoal per 100 mL of hard water. The decrease in hardness at the addition of 10 grams/100mL resulted in water hardness of 12 mg/L and the % recovery was 100%. The decrease in hardness at the addition of 10 grams/100mL resulted in water hardness of 12 mg/L and the % recovery was 100%. According to Yustinah et al [20], the higher the amount of adsorbent used, the more metal will be adsorbed. This is understandable because the more adsorbents are used, the greater the surface area that can be used as a site for the adsorbate to be adsorbed in the adsorbent.

4. CONCLUSION

Activated charcoal of coffee grounds can be used as an adsorbent in adsorption of hardness in water. The optimum pH and contact time of coffee grounds activated charcoal in adsorption of hardness in water was at a contact

time of 75 minutes and pH 7 with a hardness level in water of 565.17 mg CaCO₃/L decreasing to 56 mg CaCO₃/L. The optimum weight of coffee grounds activated charcoal in adsorption of hardness in water is 10 grams with hardness levels in water from 565.17 mg CaCO₃/L decreasing to 12 mg CaCO₃/L.

REFERENCES

- [1] International Coffee Organization (ICO). 2017. Total Production By All Exporting Countries. [Www. Ico.org/prices/po-production.pdf](http://www.ico.org/prices/po-production.pdf).
- [2] Najiyati S and Danarti. 2001. Coffee Cultivation and Post-Harvest Processing. Self-help spreader: Jakarta.
- [3] Khusna, Dwi., and Joko Susanto. 2015. Utilization of Coffee Solid Waste as Alternative Fuel in the Form of Biomass-Based Brickets (Case Study At PT. Santos Jaya Abadi Instant Coffee). National Seminar on Applied Science and Technology III. Pages 247-260.
- [4] Aman, Fakhrol., Mariana., and Mahidin., and Farid Maulana. 2018. Absorption of Ammonia Liquid Waste Using Coffee Ground Activated Charcoal. *Industrial R&D Journal*. 8(1) : 47-52.
- [5] Ristianan, Nana., Dwi Astuti., and Tri Puji Kurniawan. 2009. The Effectiveness of Combination Thickness of Zeolite with Activated Charcoal in Reducing the Hardness Level of Well Water in Karang Tengah Weru, Sukoharjo Regency. *Journal of Health*. 2(1) : 91-102.
- [6] Marsidi, Ruliasih. 2001. Zeolite To Reduce Water Hardness. *Journal of Environmental Technology*. 2(1) :1-10.
- [7] Sulistyani., Sunarto., and Annisa Fillaeli. 2012. Test of Groundwater Hardness in the Area Around the Coast, Rembang District, Central Java Province. *Journal of Basic Science*. 1(1) : 33-38.
- [8] Budiman., and Cahya Mentarianata. 2015. Effectiveness of Rice Husk Ash as a Biofilter of Lime (CaCO₃) in Dug Well Water on Jalan Domba, Talise Village. Volume. 1(1) : 9-13.
- [9] Samosir, Asnita Fraselina., Bambang Yulianto., and Chrisna Adhi Suryono. 2019. Activated Charcoal from Coffee Grounds as Dissolved Cu Metal Adsorbent in Laboratory Scale. *Journal of Marine Research*. 8(3): 237-240.
- [10] Imawati, Anita., and Adhitiyawardman. 2015. Maximum Adsorption Capacity of Pb(III) Ions by Activated Charcoal of Coffee Grounds HCl and H₃PO₄. *Journal of Chemistry and Packaging*. 4(2):50-61.
- [11] Astuti, Dian Wuri., Muji Rahayu., and Dewi Sri Rahayu. 2015. Determination of Total Hardness (CaCO₃) of Well Water in Cekelan Kemusu Boyolali Hamlet using Complexometric Method. *Public Health*. 9(2): 119-124.
- [12] Prabarini, Nunik., and DG Okayadnya. 2014. Removal of Iron Metal (Fe) in Well Water with Activated Carbon from Candlenut Shell. *Scientific Journal of Environmental Engineering*. 5(2) : 33-41.
- [13] Sulaiman, Nurul Huda., Latri Aryani Malau., Fadhillah Husna Lubis., Nurhailani B. Harahap., Fadly Rikki Manalu., and Agus. Processing of Candlenut Shell as Activated Carbon with Variations of Phosphoric Acid Activator. *Journal of Research Results in Physics*. 5(2): 37-41.
- [14] Kusdarini, Esthi., Agus Budianto., and Desyana Ghafarunnisa. 2017. Production of Activated Carbon from Bituminous Coal with Single Activation of H₃PO₄ Combination of H₃PO₄-NH₄HCO₃ and Thermal. *Reactor*. 17(2):74-80.
- [15] Permatasari, Anugrah Rizqi., Lia Umi Khasanah., and Esti Widawati. 2014. Characterization of Cassava Peel Activated Carbon (Manihot utilissima) with Variation of Activator Types. *Journal of Agricultural Products Technology*. 7(2):71-75.
- [16] Fessenden and Fessenden. 1982. *Organic Chemistry*. Jakarta : Erlangga.
- [17] Alya, Siti Nor., Abdul Hafidz Yusoff., Siti Koriah Zakaria., and Pao Ter Teo. 2019. Preliminary Assessment of Utilizing Treated Arabica Coffee Waste as Adsorbent for Heavy Metals Removal From Aqueous Solution. *International Journal of Advanced Science and Technology*. 28(16):1879-1887.
- [18] Lestari, Sri. 2010. Effect of weight and contact time for lead(II) adsorption by adsorbent from guava (Psidium guajava L.) stem bark. *Jurnal Kimia Mulawarman*. 8(1):7-10.
- [19] Maghfiroh, Lu'luatul., F. Widhi Mahatmanti, dan Ella Kusumastuti. 2017. Remazol Brilliant Blue Adsorption Using Zeolite Synthesized from Coal Fly Ash. *Indonesian Journal of Chemical Science*. 6(1):43-49.
- [20] Yustinah, Hudzaifah., Maya Aprilia., dan Syamsudin AB. 2019. Equilibrium Adsorption of Heavy Metals (Pb) with Diatomite Earth Adsorbent in Batch. *Jurnal KONVERSI*. 9(1):17-27