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Article

Calcium Reduction Using Variations of Thickness and Retention Time of Cocoa Shell Activated Carbon

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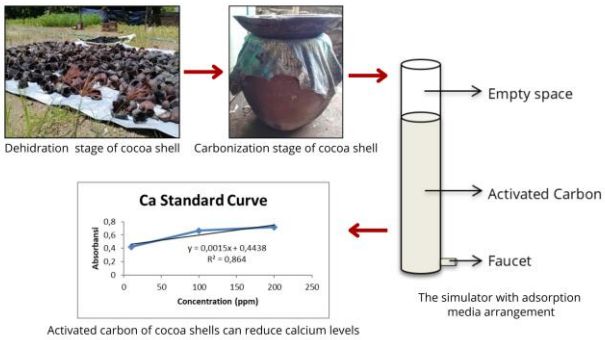
Abstract

High levels of hardness can lead to increased cases of kidney stones. Hardness levels can be reduced by using activated carbon from the cocoa rind as an adsorbent. The purpose of this research was to determine the variation of activated carbon thickness and optimum retention time in reducing the calcium content of dug well water, to determine the percent decrease in calcium ion levels at the optimum variation, and to determine the significance of the difference in the decreased in calcium levels between the treatment groups. The research method used the principle of adsorption of activated carbon from cocoa shells to calcium ions, which are activated by KOH. There were ten treatment samples with different variations of activated carbon thickness and retention time. The results showed that the thickness of activated carbon of 60 cm with a retention time of 50 minutes had the optimum ability to reduce the calcium content of dug well water. The percentage decrease in calcium levels reached 89,041 % with a decreased concentration of 234 ppm. The result of the statistical test showed a significance value of 0,05. The conclusion of the research is that activated carbon of cocoa shells can reduce calcium levels to the levels of soft water hardness, with variations in activated carbon thickness and retention time having a significant effect.

Keywords: *activated carbon; calcium; cocoa; retention time; spectrophotometer UV-Vis*

Graphical Abstract



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Introduction

Water is a natural resource that has an important role in the continuation of life, so it is necessary to have water quality parameters [1]. There are several factors that can affect water quality, such as geological conditions, aquifer properties, lithology and soil type [2]. One factor that can reduce water quality is the geological condition of an area (Jahanshahi & Zare, 2016). An area with a limestone rock composition will potentially have high water hardness levels [3]. Based on the Regional Environmental Status Report of Tulungagung Regency in 2007, 40% of the total area of Tulungagung Regency is composed of limestone. This allows high levels of calcium in water sources. According to Ministry of Health Regulation RI [1], the maximum limit of water hardness level with the function as consumption water is 500 mg/ml. The high level of hardness that exceeds the maximum limit can affect public health, namely cardiovascular cases [4]. Further, Ministry of Health Regulation RI number 492 [1] states that diseases that can be caused by hard water are cardiovascular disease (blockage of heart blood vessels) and urolithiasis (kidney stones). Based on Jain et al. (2010) hardness levels above 300 mg/ml can increase the risk of kidney stones with long-term consumption. From several statements that support the cause of the increase in cardiovascular cases, Tulungagung Regency recorded cases of hypertension in 2016 reaching 21,214 cases which ranked fourth out of the ten most common diseases [5]. The high number of cases is due to a trigger factor, namely high hardness levels. In accordance with research conducted by Kristina (2013) in Semarang, it is known that there is a relationship between the hardness of dug well water (p-value = 0.001) with the incidence of kidney stones in the community in the working area of the Margasari Health Center, the results showed that dug well water with high hardness is a risk factor for kidney stone disease (OR = 4.795). Another study conducted by Bobihu in Gorontalo (2012) showed that the hardness level of drinking water for people with urinary tract stones was 1375.172 mg/L, while the hardness level of drinking water sources for people without urinary tract stones was 429.7415 mg/L [6].

The high level of hardness requires an effort to improve public health by applying a method that works to reduce hardness levels. One effective method is the adsorption process using cocoa shell activated carbon. Some studies on activated carbon used as an adsorbent include the use of activated carbon from palm shells as a filtration medium for physical characteristics of water covering turbidity, odor, pH and taste. The use of palm shells and corn cobs as a heavy metal absorber in batik waste [7], adsorption of lead metal (Pb) from its solution using corn cobs [8], the use of adsorbents from cocoa shells (*Theobrema cacao L*.) to reduce chemical oxygen demand in palm oil mill effluent [9], study of the adsorption of hazelnut shell charcoal (*Aleorotes moluccana*) on Iron (III) and Lead (II) ions [10], the effectiveness of activated carbon from kluwek (Pangium edule) fruit shells and coffee bean shells (*Coffea arabica L*.) on CO and CO gas adsorption on the absorption of CO gas and Pb particles from motor vehicle emissions [11], the use of cocoa shell activated charcoal (*Theobrema cacao L.*) as an absorber of lead metal in used oil [12], the use of cocoa fruit shells as an adsorption medium for iron (Fe) and manganese (Mn) metals in well water [13], and the effectiveness of using cocoa shell waste charcoal (*Theobrema cacao L.*) to reduce water hardness, salinity and organic compounds [14]. The adsorption process is an event of substance absorption on a solid surface with an attractive force [15]. The occurrence of the ion absorption mechanism causes activated carbon to be able to reduce hardness levels. The utilization of cocoa shell as activated carbon is based on the content of organic compounds in it. Cocoa shell contains 23-54% cellulose[16] while cellulose is composed of 44.44% carbon. The high carbon content in cocoa shells can produce activated carbon with good quality. In previous studies, tests have been carried out related to the utilization of cocoa shell activated carbon including as a lead metal sorbent [12], iron and manganese metal adsorption [13], and reducing total hardness [14]. This study was conducted to determine the effectiveness of cocoa shell activated carbon in reducing calcium levels in dug well water based on activated carbon thickness and retention time.

The ability of cocoa shell activated carbon to bind metal ions, especially calcium, is expected to reduce water hardness levels so as to improve water quality which in turn can improve the quality of public health.

Experimental Section

Materials

The materials used include dug well water as a sample, cocoa shell activated carbon, murexide indicator (ACS), 96% ethanol (ACS), NaOH (EMSURE), KOH (Merck) and $CaCl_2.2H_2O$ (Merck).

Instrumentation

The instrument used to test calcium levels using a UV-Vis spectrophotometer brand Inesa UV-Vis N4S to increase accuracy with a high degree of precision.

Procedure

The research method is experimental with quantitative identification of the decrease in calcium levels. Several stages were carried out as follows.

Sample and simulator preparation[13]

The sample used is dug well water taken from one of the houses in Bulus Village, Tulungagung Regency. Based on the profile of Bulus Village, geographically Bulus Village is located right on the border of Tulungagung Regency and Trenggalek Regency (Figure 1), topographically located in the lowlands with an altitude of 100 m from sea level with an administrative area of 148,290 Ha. Sampling is a complete random series of the population of dug wells in the village. Sampling points in the dug wells were taken from five spots in the well.

The simulator used is a series of pipes with adsorption media arrangement. There are three simulators with different thickness of activated carbon used.

Cocoa shell carbonization[13]

Carbonization is done by a simple method of burning cocoa shells in a closed furnace. The carbonization process lasts for 2 hours in an airtight place. To obtain an airtight condition, treatment is given by covering the surface of the furnace with wet banana stem fronds, then covering it again using a cloth, and the outermost layer is covered with soil while the hole cavity that can still be penetrated by the burning smoke is covered with clay [17].

Activation of cocoa shell carbon[18]

The activation process of cocoa shell carbon is carried out chemically with a 5 M KOH solution soaked for 24 hours in a tightly closed container. then filtered and washed using distilled water until a neutral pH is obtained. The last stage was oven drying at 200 °C for 2 hours. Based on SNI (Standar Nasional Indonesia—Indonesian National Standard) 06-3730-1995 on technical activated charcoal, good quality powdered activated charcoal has a maximum moisture content of 15%, a maximum volatile substance content of 25%, a maximum ash content of 10% and a minimum carbon content of 65% [19].

Figure 1. Map of Bulus village, Bandung sub-district.

Preparation of the simulator[13]

The simulator used comes from a paralon pipe with a length of 150 cm and a diameter of 2 inches which is assembled in such a manner. Then the preparation of adsorption media is carried out. The media that functions as adsorption is activated carbon which is arranged according to thickness variations.

Adsorption process

The adsorption process is differentiated by the thickness of activated carbon and the retention time of water with activated carbon. There are three variations of activated carbon thickness used, namely 40, 60, and 80 cm. While the retention time variations are 30, 40, and 50 minutes.

Calcium level test

Calcium level test was conducted on the control group and test group after treatment. The test was carried out using a UV-Vis spectrophotometer with the addition of murexide indicator in an alkaline environment.

a. Preparation of murexide solution

The preparation of the solution was carried out by weighing 50 mg of murexide and then dissolved in 10 mL of distilled water, so that a concentration of 0.5% was obtained. Next, 25 mL of ethanol was added.

b. Preparation of calcium standard solution

Calcium standard solution will be utilized with a level of 1000 ppm. The preparation of the solution was by dissolving 50 mg of CaCl2.2H2O with distilled water up to 50 mL so that a concentration of 1000 ppm was obtained.

c. Determination of maximum wavelength

From a standard solution with a concentration of 1000 ppm, 1 mL was taken and put in a 50 mL volumetric flask. Then 1 mL of murexide solution and a little distilled water were added. After that, 2 mL of 0.1 N NaOH was added and then distilled water was added until the limit mark. The solution was mixed until homogeneous then put in a cuvette and the absorbance was read at a wavelength between 400-800 nm [20].

d. Standard curve determination

From 1000 ppm of calcium standard solution, 3 variants of concentration were made, namely 10, 100, and 200 ppm. Each concentration was put in a 50 mL volumetric flask. Each volumetric flask was added with 1 mL of murexide solution then a small amount of distilled water. After that, 2 mL of 0.1 N NaOH was added and then distilled water was added until the limit mark. The solution was mixed until homogeneous then put into the cuvette and the absorbance was read at the maximum wavelength, with the linear regression equation $y = bx + a$ [20].

e. Determining calcium content in dug well water

1 mL of dug well water sample was taken and put into a 50 mL volumetric flask. 1 mL of murexide solution and enough distilled water were added. Then, 2 mL of 0.1 N NaOH was added to distilled water until the limit mark. The solution was shaken until homogeneous then put into a cuvette and the absorbance was read at the maximum wavelength. The levels were determined with 3 replications.

Analysis of results

To see the significant difference in calcium content reduction between treatment groups, statistical analysis is needed. The statistical analysis used the Kruskal-Wallis comparative test to see the difference between variations in activated carbon thickness and retention time on the decrease in calcium levels in the sample, followed by the Mann-Whitney Post Hoc test. Before conducting the Kruskal-Wallis comparative test, a normality test was performed, requiring normally distributed data if both variables or at least one variable had a $p>0.05$ value.

Results and Discussions

Sample and test media preparation

Sample selection was based on a complete randomized series from the population of dug wells in Bulus Village.

The sampling technique was done with a polypropylene (PP) plastic bucket that had previously been rinsed using water from the same dug well as the sample. In Indonesia, the standard requirements for sample containers that can be used are made of glass or polyethylene plastic (PE) or polypropylene (PP) or Teflon (Poly Tetra Fluoro Ethylene, PTFE) [21]. Samples were taken ± 20 cm below the water surface by visual means. Sampling points are at five spots of the well. Samples taken as much as 20 L were then placed in the same plastic container to be homogenized.

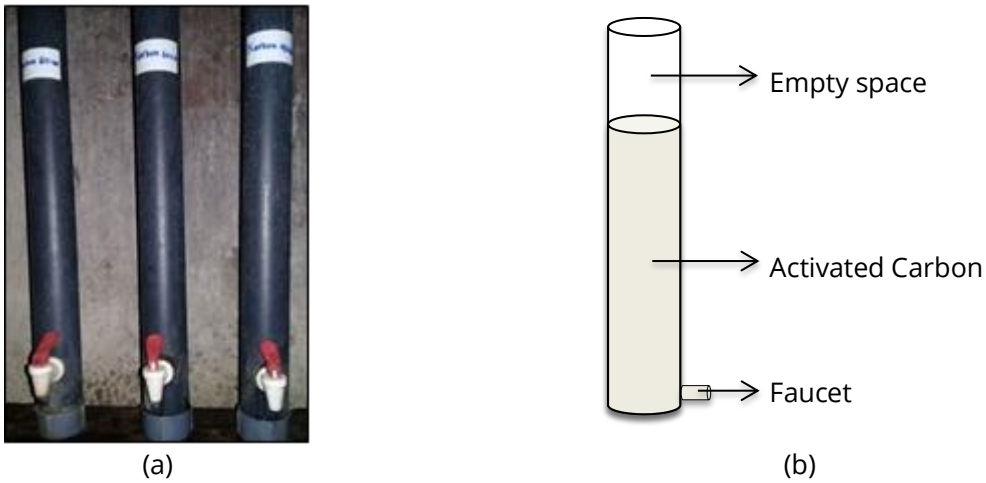
The simulator used is a series of PVC pipes with a diameter of 2 inches equipped with a faucet at the bottom of the pipe in a vertical position. The inside of the pipe is set up with adsorption media in the form of cocoa shell activated carbon as per the thickness variation used. The results of the media arrangement are presented in Figure 2.

Carbonization of carbon shells

Carbonization is a method to obtain charcoal or carbon as the main product [22]. Referring to the research of Shofa[23], the carbonization process is divided into two stages, namely dehydration and carbonization. Cocoa shell waste used as media was taken from a plantation in Bulus Village, Tulungagung Regency. The dehydration stage was done by drying the cocoa pods with the help of sunlight. The carbonization stage was carried out by burning in a closed furnace. The carbonization process was conducted for ±2 hours to produce perfectly burned carbon. The carbon formed was cut into pieces and then activated. The dehydration and carbonization process are shown in Figure 3.

Activation of carbon

The activation process uses a chemical activation method. Chemical activation is the process of breaking the carbon chain in organic compounds with the help of chemicals. The activating agent used was a 5 M KOH solution. The selection of KOH as an activating agent is based on research conducted by Nurfitria et al.[24] that KOH is a good chemical activator for carbon because it can increase the surface area up to 3000 m2/g. The activation process was carried out by soaking the pieces of cocoa shell carbon with 5 M KOH solution for 24 hours. After being soaked, it is then washed with distilled water until the pH is neutral, then continued with an oven at 200 °C for 2 hours. The results of curing are in the form of activated carbon that is black, odorless, has a smooth, shiny surface, is more fragile and lighter.



(a) (b)

Figure 2. a) Simulator dan (b) Scheme of the inside of the simulator.

(a)

(b)

Figure 3. Processes of (a) Dehydration dan (b) Carbonization.

Preparation of test media

The test media used is an arrangement of activated carbon as an adsorbent. The simulator circuit with adsorbing agent was divided into three media based on the difference in activated carbon thickness of 40, 60 and 80 cm. Measurement of the density of the activated carbon pieces was done visually.

Adsorption process

The adsorption process was carried out without repetition in each treatment. The sample adsorbed in each simulator is equalized in volume of 2 L. The filtering results in each treatment produce black colored water. This is due to the ability of activated carbon to bind calcium ions chemically by forming a suspension in the sample so that a black color is produced [25]. The adsorption process begins with the movement of adsorbate molecules towards the surface and diffuses on the surface of the adsorbent pore forming covalent bonds and ionic bonds [26].

Calcium level test

Calcium level test was conducted on the negative control group and treatment group with three repetitions.

Determining the maximum wavelength

Determination of the maximum wavelength is done by measuring the absorbance of the standard solution of CaCl2.2H2O in 1000 ppm. The 1000 ppm standard solution was diluted by pipetting 1 mL into a 50 mL volumetric flask and then adding 1 mL of murexide solution and 2 mL of 0.1 N NaOH solution. The addition of murexide solution to the standard solution formed a brick red color then the addition of NaOH formed a concentrated burgundy color. The addition of 0.1 N NaOH will form a solution with a pH of 12-13 so that the solution is in a stable state to form a complex. Then distilled water is added to the limit mark so that a burgundy-colored solution is formed.

The prepared solution was put into a cuvette and the absorbance was read in the wavelength range of 400-800 nm. The absorbance readings were repeated three times in the visible area. The reading results obtained a maximum wavelength of 507 nm with an average absorbance of 1.340. The spectra of the calcium standard solution formed are shown in Figure 4.

Standard curve set up

Calcium standard curve was made using three concentration variations of 10, 100, and 200 ppm diluted from 1000 ppm calcium standard solution. Then each concentration was added 1 mL of murexide solution and 2 mL of 0.1 N NaOH solution and then marked using distilled water. The solution was homogenized then put into a cuvette and the absorbance was read at a wavelength of 507 nm.

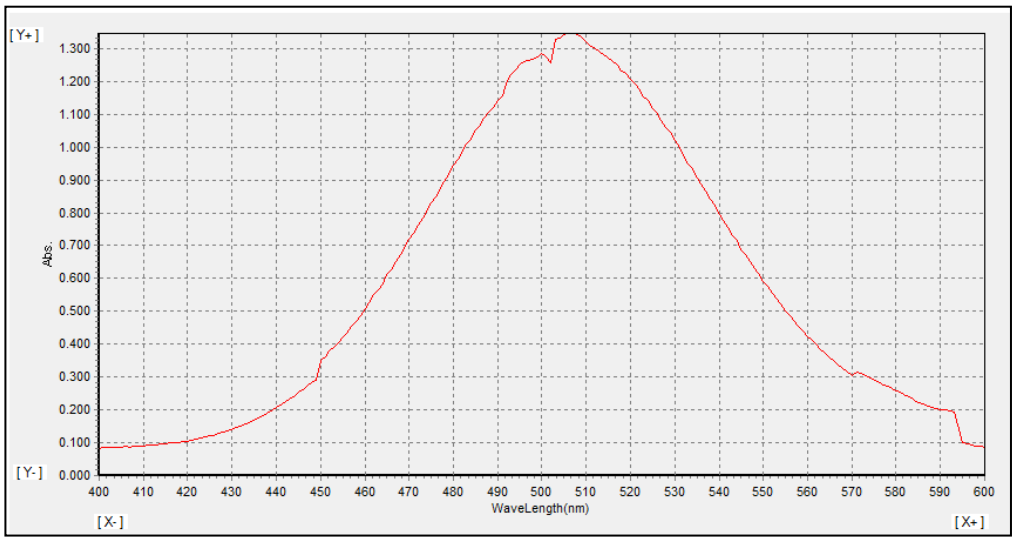


Figure 4. The spectra of the calcium standard solution.

Absorbance readings at each concentration variation were repeated three times. The results of the standard curve absorbance will be shown in Table 1.

Table 1 shows the absorbance value of each variation of calcium standard solution concentration. There is an increase in absorbance value as the concentration of the solution increases. The average absorbance results will be presented in the form of a curve shown in Figure 5. Figure 5 shows the calcium standard curve obtained from the absorbance of various calcium concentrations. Presentation with a standard curve aims to acquire a linear regression equation that will be used to calculate the concentration of calcium in the sample. From the standard curve formed, a linear regression equation y = 0.0015x + 0.4438 was obtained with a value of R2 = 0.864.

Determining calcium content in dug well water

Calcium content was determined on 10 samples consisting of 1 negative control group sample and 9 treatment group samples. Each sample was prepared for absorbance reading. 1 mL of each sample was taken and placed in each 50 mL volumetric flask and then added 1 mL of murexide, 2 mL of 0.1 N NaOH and marked with distilled water.

Tabel 1. The standard curve absorbance.

Calcium concentration	Absorbance			Average Abs.
	R1	R2	R3	
10 ppm	0.422	0.420	0.429	0.424 ± 0.005
100 ppm	0.668	0.665	0.659	0.664 ± 0.005
200 ppm	0.725	0.716	0.716	0.719 ± 0.005

Notes:
R: replication
Abs.: absorbance

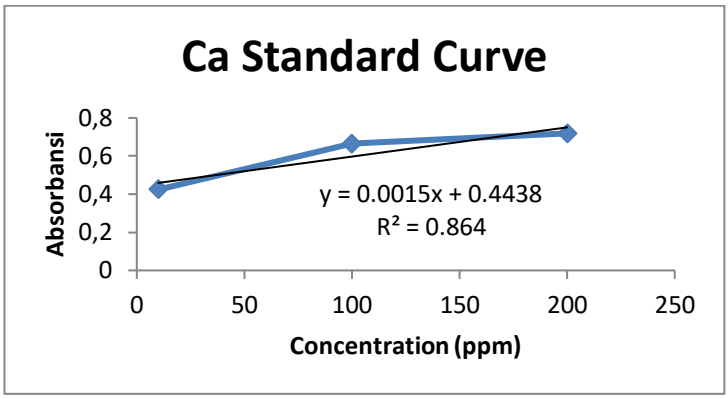


Figure 5. Ca Standard Curve.

The absorbance reading of each sample was done in three repetitions which will be presented in Table 2. Table 2 presents the average absorbance data of the treatment samples conducted in three replications. Based on the absorbance value, the negative control group has an absorbance value of 0.838 while the treatment group shows a decrease in absorbance. This means that the thickness of activated carbon and retention time influence reducing calcium levels.

Based on the average absorbance data, the calculation of calcium concentration levels and the percentage decrease in levels in each treatment was carried out. The results of the calculation of calcium concentration and percentage reduction are presented in Table 3.

Tabel 2. Sample Absorbance.

Treatment		Absorbance			Average Abs.	Calcium Level (ppm)
Thick (cm)	RT (minute)	R1	R2	R3		
40	30	0,688	0,690	0,703	0,694 ± 0,008	166,800
	40	0,570	0,567	0,585	0,574 ± 0,01	86,800
	50	0,842	0,843	0,908	0,875 ± 0,04	287,467
60	30	0,784	0,790	0,809	0,794 ± 0,01	233,467
	40	0,613	0,611	0,638	0,621 ± 0,02	111,467
	50	0,483	0,487	0,485	0,484 ± 0,002	28,800
80	30	0,565	0,564	0,586	0,572 ± 0,012	85,467
	40	0,516	0,518	0,543	0,526 ± 0,015	54,800
	50	0,576	0,577	0,577	0,577 ± 0,001	88,800
Control (-)		0,828	0,831	0,854	0,838 ± 0,014	262,800

Notes:
Thick: Thickness of activated carbon
RT: retention time
R1: 1st replication
R2: 2nd replication
R3: 3rd replication

Tabel 3. Calcium level and level decrease percentage.

Thick (cm)	RT (menit)	Ca Concentration (ppm)	Concentration Decrease (ppm)	% Decrease
K -	0	262,800	0	0
40	30	166,800	96	36,530
	40	86,800	176	66,971
	50	287,467	-24,667	-9,386
60	30	233,467	29,333	11,162
	40	111,467	151,333	57,585
	50	28,800	234	89,041
80	30	85,467	177,333	67,478
	40	54,800	208	79,148
	50	88,800	174	66,210

Notes:
Thick: thickness of activated carbon
RT: retention time

Based on Table 3, there are eight samples from the treatment group that have decreased calcium levels when compared to the negative control group. The negative control group has a calcium level of 262.800 ppm, indicating that the water is classified as hard. According to Sutrisno (2007) water is classified as hard if it has calcium levels of 150-300 mg/L [27].

Furthermore, Table 3 also shows that the thickness of activated carbon at 40 cm with variations in retention time has an optimal reduction rate at a retention time of 40 minutes. The 30-minute retention time has a decreased level below the 40-minute retention time; this is due to the lack of contact time between the water sample and activated carbon so that the calcium adsorption process is not optimal. While at a retention time of 50 minutes there was an increase in calcium concentration when compared to the negative control. This is likely to occur due to the saturation of activated carbon against the binding of calcium ions. Referring to the quality standard of technical activated charcoal of SNI 06-3730-1995, the absorption capacity of carbon is ≥750 mg/g. The increase in hardness levels is a result of several factors, one of which is the mismatch between the ratio of activated carbon thickness and retention time to the volume of sample adsorbed. In addition, the presence of CaO content in cocoa shells allows the release of Ca ions in the sample so that the calcium content of the treatment sample is higher than the negative control. This is in accordance with the statement of Bujawati (2014) that if the activated carbon is saturated, there will be a re-release so the sample after treatment shows an increase in hardness [15].

At a thickness of 60 cm, activated carbon with variations in retention time has an increase in reducing calcium levels. With variations in retention time of 30, 40 and 50 minutes, there was an increase in the reduction of calcium levels by 11.162%, 57.585% and 89.041%, respectively. In accordance with research conducted by Bujawati (2014) which compared the thickness of activated carbon, the optimum thickness was obtained at a thickness of 60 cm with an increase in the ability to reduce as the retention time prolonged. [15] A similar research conducted by Ristiana et al. (2009) on the effect of activated carbon thickness on hardness reduction showed the results of a decrease in hardness levels at a thickness of 60 cm activated carbon by 71.54% [28]. While another research conducted by Nurullita et al. (2010) which compared the effect of contact duration showed an increase in the percent reduction in levels as the contact duration increased [4].

Tabel 4. Statistical test significance value.

Treatment	Comparative Treatment	P	Meaning
K-	RT 30 Thick 40	0,050	Significant
	RT 30 Thick 60	0,050	Significant
	RT 30 Thick 80	0,050	Significant
	RT 40 Thick 40	0,050	Significant
	RT 40 Thick 60	0,050	Significant
	RT 40 Thick 80	0,050	Significant
	RT 50 Thick 40	0,275	Not Significant
	RT 50 Thick 60	0,050	Significant
	RT 50 Thick 80	0,046	Significant

Notes:
Thick: thickness of activated carbon
RT: retention time

Similar research was conducted by Lustiningrum (2013) by comparing the effect of the length of contact of activated carbon on the decrease in hardness levels. The results showed that the longer the contact time, the lower the hardness levels [29].

Meanwhile, at a thickness of 80 cm with variations in retention time, the optimal reduction rate is reached at 40 minutes with a percent reduction of 79.148%. The 50-minute retention time shows a decrease in the percentage of calcium content reduction. This is due to the saturation of activated carbon at a retention time of 50 minutes. This is in accordance with the research by Masitoh and Sianita (2013) that increasing the retention time above the optimal time causes an insignificant decrease in calcium levels, because the active side of the activated carbon reaches a saturated condition so that the adsorption ability decreases [30]. The decrease in calcium levels with variations in activated carbon thickness and retention time has a significance value of ≤0.05 as shown in Table 4.

The significance value of ≤0.05 indicates that the variation of activated carbon thickness and retention time has an influence on the ability to reduce calcium levels of dug well water which is significantly different. This is as shown in Table 4.3 regarding the percentage of decrease in calcium levels with variations in activated carbon thickness and retention time. The optimal variation is obtained at a thickness of 60 cm and a retention time of 50 minutes with a percent decrease reaching 89.041% or 234 ppm.

Conclusions

Variations in activated carbon thickness and retention time can reduce calcium levels of dug well water with optimal results at 60 cm activated carbon thickness with 50 minutes retention time. Percentage decrease in levels reached 89.041% with a concentration decrease of 234 ppm and has a significance value ≤0.05. Further research on the effectiveness of cocoa shell carbon can be done by considering the weight of carbon, the need to characterize activated carbon with SEM or determination of functional groups with FT-IR, and the need for comparison with the control group +.

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