The effect of CaO doping in activated carbon composite as a heavy metal adsorbent in water

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Abstract. Lead (Pb) is a dangerous heavy metal that can settle in marine animals, and it will have a bad impact on our health. One of the efforts to reduce the stream's levels of hazardous metals is by using the adsorption method. This study aimed to determine the effect of CaO doping on activated carbon composites on the physical properties of water and its ability to absorb Pb. Atomic Absorption Spectroscopy was conducted to determine the remaining Pb content after the adsorption process. Based on the results, it was found that the doping of CaO in activated carbon composites affected the physical properties of water-based on parameters of pH, EC, TDS, temperature, and turbidity. The water quality test results have met the PerMenKes standard No: 416/MENKES/PER/IX/1990, with the water quality obtained having a pH value of 7, EC 313.00 µs/cm, TDS 156.50 ppm, temperature 29°C, and turbidity 3.95 NTU. Besides that, the addition of CaO mass to activated carbon composites affects Pb metal's adsorption ability, where CaO doping can increase the absorption of Pb.

1. Introduction

Water in Indonesia is subject to environmental pollution like heavy metal contamination from various sources, mainly through its water supplies from rivers and the coastal seawater [1]. This contaminated water is not only harmful to human beings but also affects marine life [2]. Several conditions must be met physically and chemically so that water can be said to be fit for consumption [3]. This health requirement includes freedom from contaminants such as lead, manganese, iron, and so on.

The content of these contaminants is caused by several factors, such as the lack of environmental hygiene and the disposal of household and industrial waste that empties into rivers. These dangerous substances can be suspended in water so that they can enter the human body and marine animals so that if they are consumed, they will be bad for health. One example is the heavy metal lead. Lead is widely used in industries such as making pipes, batteries, and as a mixture of gasoline. Besides having many benefits, lead also has a harmful impact if it is absorbed into the body, including disrupting kidney function and reducing children's intelligence [4].

There are various techniques that have been used for the treatment of pollution in water. One of the effective ways is the adsorption method [5]. There are several advantages of the adsorption method, namely the process is more straightforward because it only involves two components (adsorbate and adsorbent) and is environmentally friendly. Usually, the adsorbent can be activated carbon. Activated carbon is able to absorb harmful substances such as metals [6]. In addition, activated carbon is also
capable of absorbing colors and odors in water [7]. Activated carbon has a porous structure, so it has a good absorption ability. Activated carbon can be made from wasted waste such as mangroves which are found in coastal areas.

Apart from activated carbon, CaO compounds are have a lot of applications [8,9], and one of them is act as good adsorbents [10]. The shells contain high calcium carbonate (CaCO$_3$), and if they are calcined, they will produce CaO compounds that are good for the absorption of harmful compounds such as metals [11]. One type of clamshell with a high content in a blood clamshell with a content of 98.7%. CaO from the results of calcination has the advantage of being able to increase the pH and can absorb harmful substances [12].

In this study, the potential possessed by activated carbon and CaO is utilized to make composites as an adsorbent for heavy metals. In addition to reducing the content of harmful metals, water quality can also be viewed from pH, EC (electrical conductivity), TDS (total dissolved solid), temperature, and turbidity.

### 2. Material and Methods

#### 2.1. Preparation

The research stages began with preparing tools and materials: blood clamshells, mangrove wood, Pb acetate solution, aquades, H$_3$PO$_4$ 30%, and PEG 6000. The material preparation process was carried out by making activated carbon from mangrove wood and CaO. From the shells of blood clams and Mangrove wood, which is used as a material for making activated carbon, is first cleaned and then dried under the hot sun. Mangrove wood burning is carried out using a furnace at 500 °C temperature for 1 hour.

![Mangrove wood (a) before carbonisation (b) after carbonisation](image)

The mangrove wood used is weighed before and after burning to determine its mass ratio. After the charcoal process, the mangrove charcoal is mashed and then sifted with a sieve size of 600 µm. The next process is activation, which aims to increase the surface area. It is done by soaking the mangrove carbon using 30% H$_3$PO$_4$ solution for 24 hours.

#### 2.2. Synthesis CaO

The next process is physical activation, namely by simple heating using an oven for the drying process, which is at a 105 °C temperature for 3 hours. Synthesis CaO is done by calcining blood clamshells using a furnace at temperature for 3 hours. Then the finished CaO is sifted with a size of 30 mesh. Composites were made by varying the mass of activated carbon and CaO, where a mixture of 0.6 g of PEG and 5 ml of aquades was used as a filler. In this study, the mass of the composites made was 10 g with a variety of composite compositions, namely 100% activated carbon (AC) (sample A), 75% AC: 25% CaO (sample B), 50% AC: 50% CaO (sample C), 25% AC: 75% CaO (sample D), 100% CaO (sample E). The composites then left at room temperature for 48 hours and then in the oven at 105 °C temperature for 2 hours.
2.3. Measurement the physical properties

The next step is to test the composite characteristics, test the physical properties of water, and test the composite's ability to absorb Pb. The tools used are pH meter, turbidity meter, and AAS spectroscopy. The composite endurance test is done by drop test. The composite is dropped at the height of 1.8 m, then the mass of the composite is measured to see the difference in mass before and after the test.

The physical properties of water tested in this study are pH, TDS, EC, temperature, and turbidity. This stage aims to determine the effect of variations in the composition of activated carbon composites with CaO doping on the results of the adsorption of the physical properties of water. The data collection process was carried out by measuring the initial value of water (sample) in the pH, TDS, EC, temperature, and turbidity parameters. Then, put the composite into the water. The volume of water used was 100 mL, and the adsorption contact time used was 2 hours. After 2 hours, the water is filtered using the prepared filter paper. The adsorbed water is then tested for pH, TDS, EC, temperature, and turbidity values to determine value changes.

The process of testing the composites for Pb absorption was carried out by adsorbing the Pb solution that had been prepared. The Pb solution used was 5 mg/L as much as 100 mL. The activated carbon composite with CaO doping was added to the Pb solution with the adsorption contact time of 2 hours. After the adsorption process, the composites then separated from the solution. AAS characterization was carried out to determine the final concentration of Pb.

3. Results and discussion

3.1. The composite endurance test

Heavy metal adsorbent composites of activated carbon and CaO have been successfully prepared. In the manufacture of composites, there is a difference in each composite color where the color becomes whiter as CaO is added to the activated carbon.

Figure 2. Activated carbon composite with CaO doping

The resistance of this composite was done by using a drop test. Giving CaO doping to activated carbon composites affects the physical properties of the composite.

The composite with CaO doping has a more rigid texture, and when touched, the composite does not melt quickly. It is different from the composite without CaO doping, which is that the composite is not too hard, so the composite breaks easily when touched. Based on the drop test results, it was found that there was no change in the amount of mass, but there was a change in the shape of the composite.

Figure 3 shows that the highest resistance of the composite is found in sample C, and the lowest resistance is obtained in sample A. The addition of CaO can increase the value of the composite
strength and increase the stiffness. Based on the results of the drop test, it appears that the best resistance is in sample C. From the density measurement, the lowest density value is in sample B 72.81 Kg/m$^3$, and the highest value is in sample E 140.62 Kg/m$^3$. This is because CaO powder has a higher density value of 1.38 g/cm$^3$ than activated carbon powder with a powder density value of 0.1 g/cm$^3$ [13].

![Figure 3. Drop test result in composite](image)

![Figure 4. The density results in different composition. 100% activated carbon (AC) (sample A), 75% AC: 25% CaO (sample B), 50% AC: 50% CaO (sample C), 25% AC: 75% CaO (sample D), 100% CaO (sample E).](image)

**3.2 The physical properties of water tested**

Water's physical properties are viewed from temperature, TDS, EC, turbidity, and pH. The value of water's physical properties before adsorption is at the temperature value, namely 29°C, TDS 2.00 ppm, EC 4.00 µs/cm, turbidity 1.73 NTU, and pH 7.00. After the adsorption process, the physical properties of the water are measured again.
Table 1. Measurement of some properties of the solution after adsorption process using composite activated carbon with CaO doping

| Sample | T (°C) | TDS (ppm) | EC (µµs/cm) | Turbidity (NTU) | pH  |
|--------|--------|-----------|-------------|----------------|-----|
| A      | 28     | 6308.50   | 10000       | 2.20           | 0   |
| B      | 28     | 461.00    | 923         | 29.05          | 5   |
| C      | 29     | 156.50    | 313         | 3.95           | 7   |
| D      | 29     | 1301.50   | 2644        | 3.52           | 11  |
| E      | 28     | 2755.00   | 5510        | 3.33           | 12  |

One of the determinants of water quality is pH. Based on the regulation of the Minister of Health No: 416/MENKES/PER/IX/1990, it states that the requirements for drinking water quality for a pH range between 6.5 and 8.5. In this study, it was found that the increase of pH related to the addition of CaO. The pH value of water before adsorption was 7. Table 1 shows that the pH value has decreased to 0 (zero) in sample A, indicating that water has a high acidity level. With the addition of CaO in sample B, the pH value decreased further to 5. In sample C, the pH value became normal again. However, in sample D and E, the solution becomes alkaline with pH>9. Therefore, from pH measurement, sample C gives the best result. The increase in pH value that occurs is consistent with the research conducted by Hanafi (2015) [12], where the solution pH increase along with the addition of CaO from blood collar shells. It contains 98.7% calcium carbonate (CaCO₃), and if dissolved in water, it will release hydroxide OH⁻. The release of OH⁻ can increase pH.

In this study, EC testing was carried out on the sample solution before and after adsorption. The greater the number of dissolved solids, the more likely the number of ions in a solution will also be more significant so that the EC value will also increase. Table 1 shows that when the EC value is high, the TDS value obtained is also high and vice versa. The highest EC value was obtained in sample A 1000 µs/cm. The lowest EC is in sample C 313 µs/cm, where it has met EC standards for drinking water.

TDS is the level of solids dissolved in a solution. The dissolved substances can be either organic or mineral compounds. In this study, the TDS value obtained increased after adsorption. The highest TDS value was obtained in sample A. The addition of CaO to the composite can reduce the TDS value, but the higher the addition of CaO can also increase the TDS value. The addition of the number of adsorbent results in an increase in dissolved particles in the solution. This indicates that the adsorbent contains minerals and organic materials [14]. Compared to the composition of A and B, it shows that activated carbon has higher organic compounds than CaO. In Table 1, it can be seen that the adsorption with samples B and C shows that the water has met the standards issued by PerMenKes No: 416/MENKES/PER/IX/1190, where the maximum allowable TDS value is 1000 mg/L.

The level of turbidity in water shows the number of suspended substances in the water. In this study, the results of the turbidity test showed that the turbidity value had increased. Where the turbidity value before adsorption is 1.73 NTU, and after adsorption has increased. The increase in turbidity value is caused by the presence of substances contained in water-soluble composite materials. Based on Table 1, the temperature value has decreased in samples A and B. In samples C and D, the solution's temperature has not changed, and in sample E, the solution's temperature has decreased again. The test results on the temperature value show insignificant results because the occasional outside temperature can affect the temperature measurement results.

3.3 Test for Pb adsorption

From the AAS characterization results, the amount of Pb content in water was obtained after adsorption. The maximum permissible level of Pb in water is 0.01 mg/L.

From these results, it can be seen that the activated carbon composite with CaO doping is able to absorb Pb metal well. In sample A, Pb metal concentration after adsorption was 2.94 mg/L. The adsorption results of Pb obtained in sample B to sample E is almost 100%. This is because CaO is able to absorb heavy metals exceptionally well and in measurements used Pb concentrations that are too
small compared to CaO concentrations so that the Pb remaining after the adsorption process is almost zero.

Table 2. Pb concentration result in solution before and after adsorption using composite activated carbon with CaO doping.

| Sample | Initial Concentration of Pb (mg/L) | Final Concentration of Pb (mg/L) | Adsorption ability (%) |
|--------|----------------------------------|---------------------------------|------------------------|
| A      | 5                                | 2.94                            | 41.2                   |
| B      | 5                                | 0                               | 100                    |
| C      | 5                                | 0                               | 100                    |
| D      | 5                                | 0                               | 100                    |
| E      | 5                                | 0                               | 100                    |

4. Conclusions
Based on the research results, it can be concluded that CaO doping in activated carbon composites can absorb heavy metals. From the test results, the water quality that meets the standards of PerMenKes No: 416/MENKES/PER/IX/1190 is adsorption using composite sample C with a ratio of activated carbon and CaO is 1:1. The addition of CaO mass to activated carbon composites affects the adsorption ability of Pb.

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