Metal adsorption of Pb and Fe in refillable drinking water in Semarang City using Powdered Activated Carbon (PAC) based on coconut shell and ozonation technology

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Abstract. Drinking Water Refilling Depot (DAMIU) is one of the most common sources of drinking water. Drinking water quality standards have been regulated in PERMENKES No. 492 Year 2010 concerning Drinking Water Requirements. Drinking water samples were taken at two DAMIUs, which using a reverse osmosis process, located in Semarang. The sample contained metal contents (Pb and Fe) that exceeded the quality standards. The Pb metal content ranged from 0.17-0.18 mg/L with a quality standard of 0.01 mg/L and Fe metal content ranged from 0.43-0.48 mg/L with a quality standard of 0.3 mg/L. In this study, to reduce the levels of Pb and Fe metals are using adsorption and ozonation technology. Adsorption was carried out using powdered activated carbon from coconut shell with a particle size of 100 mesh, variations of dose used were 2, 3, 4, and 5 g. The variation of adsorption and ozonation contact time were 20, 40, and 60 minutes. The highest adsorption method efficiency with a 2 g dose and a 60 minutes time, with Pb and Fe levels are 97.2% and 97.0%, respectively. Meanwhile, the highest ozone efficiency was at 60 minutes with Pb and Fe levels of 90.7% and 92.3% respectively.

1. Introduction
Drinking Water Refilling Depot (DAMIU) is one of the sources of drinking water that is relied on by the community. The need for drinking water also increases along with the increase in community growth. Therefore, monitoring and checking DAMIU quality standards need to be carried out regularly. However, in its application, there are still many DAMIUs that do not receive supervision and investigation. For example, as stated on the TribunJateng.com website newspaper, there are still many DAMIUs in Semarang City that do not yet have sanitation and hygiene certificates. DAMIU inspection that is not thorough causes the quality of drinking water to be inappropriate with the Minister of Health Republic Indonesia Regulation Number 492/MENKES/PER/IV/2010 concerning the requirements for drinking water quality, which are physical, chemical, and biological parameters such as odour, water hardness, metal content, nitrate content, E. coli bacteria, and coliform bacteria.

Based on the Minister of Health Republic Indonesia Regulation Number 492/MENKES/PER/IV/2010 concerning requirements for drinking water quality, the maximum concentrations of Pb and Fe that are allowed in drinking water are 0.01 mg/L and 0.3 mg/L. Excess heavy metal levels in refillable drinking water can have a negative impact on human health if consumed
continuously. According to Kesumaningrum et al [1] heavy metals Pb and Fe if consumed for long term can cause vomiting, rapid respiration, tired easily, blood vessels inhibition, hypertension, liver disease and even reproduction disturbance.

The study was carried out to determine the metal content of Pb and Fe also reducing its metal content by adsorption and ozonation technology methods. The adsorption method is an option to reduce Pb and Fe metal levels because of their high efficiency and reusability [2]. In addition to the adsorption method, the ozonation method is also used to reduce the levels of heavy metals contained in refillable drinking water [3]. This study aims to determine metal content of Pb and Fe that were still contained in refillable drinking water, to reduce metal content of Pb and Fe, and to compare between the method of adsorption and ozonation technology to determine which method is better.

2. Material and Method

2.1 Material

The materials used in this study were refillable water, Haycarb powder activated carbon (PAC) 100 mesh size from coconut shell, HNO₃, Pb(NO₃)₂, Fe(NO₃)₃, buffer solution pH 8 and pH 3.6, Alizarin Red S (ARS) reagent, NaOH, ozone generator and UV-Vis spectrophotometer.

Refillable drinking water. Refillable drinking water is one type of drinking water that can be consumed directly without being boiled first. The refillable drinking water used in this study came from DAMIU near Elisabeth Hospital and DAMIU in the area of Sekaran, Semarang City, the purification process carried out from both DAMIU was Reverse Osmosis (RO). In the previous study, they have only analysed the content of heavy metal in drinking water. Therefore, in this study, adsorption and ozonation technology will be applied for the reduction of heavy metal content in drinking water.

Activated carbon. The trademark used in this experiment is Haycarb activated carbon in the form of powder derived from coconut shell biomass. Haycarb activated carbon has hydrophobic functional groups (i.e., C = C and CH) and hydrophilic functional groups (i.e., CO, C = O and OH) on the surface. These functional groups play a role in binding adsorbate, which will be absorbed during the adsorption process. In addition to various functional groups, Haycarb activated carbon also has a large specific surface area of 1270 m²/g and is suitable for treatment in water purification because it has an iodine value of 800 mg/g [4].

Adsorption. Adsorption is the process of absorbing some substances on the solid surface of the adsorbent [5]. The adsorbent that is used in this probe is activated carbon.

Ozonation. In this study, the ozonation process is carried out using a PURETREX brand ozone generator. The ozone generator has several advantages, such as: relatively affordable price, can be used for home scale because the operation is uncomplicated. However, besides that this ozone generator only has a maximum timer of up to 30 minutes, the ozone dose cannot be adjusted, and cannot be used for large-scale ozonation.

2.2 Method

To determine metal content of Pb and Fe, 10 mL of sample mixed with 1 mL of HNO₃ solution until homogeneous, then the adsorption value was checked using UV-Vis spectrophotometer which will be used to calculate the concentration of Pb and Fe that were contained in the sample.

Adsorption. 10 mL of standard solutions of 100 ppm Pb and Fe were each diluted with 100 mL of distilled water to obtain 10 ppm solutions of A Pb and A Fe metals. Then, 1.8 mL and 1.7 mL of A Pb metal solution, respectively, were diluted with 100 mL of distilled water to obtain 0.18 ppm and 0.17 ppm B Pb metal solutions. And 4.8 mL and 4.3 mL of metal A Fe solution, respectively, were diluted with 100 mL of distilled water to obtain 0.48 ppm and 0.43 ppm B Fe metal solutions. Variable doses of activated carbon (2, 3, 4 and 5 grams) were mixed with 100 mL of metal solution B Pb and B Fe. Then they were shaken using a shaker at a speed of 140 rpm with adsorption times of 20, 40 and 60 minutes. After that, the solution was filtered using filter paper and analysed for metal concentrations of Pb and Fe using a UV-Vis Spectrophotometer to determine the remaining concentrations of Pb and Fe.
Ozonation. Ozonation was carried out by mixing 100 mL of metal B solution (Pb and Fe) and put in a 250 mL beaker. Then ozonation was carried out with ozonation treatment for 20, 40 and 60 minutes. After getting the ozonation treatment, the solution was analysed using a UV-Vis spectrophotometer to determine the remaining concentrations of Pb and Fe.

3. Result and Discussion

Analysis of refillable drinking water samples from DAMIU near Elisabeth Hospital (as sample A) and from the Sekaran area (as sample B), Semarang City, showed that the analysed refillable drinking water still contained heavy metals Pb and Fe exceeding the permissible threshold, which can be seen in Table 1.

| Metal | Permissible concentration (mg/L) | Initial concentration of sample (mg/L) |
|-------|----------------------------------|----------------------------------------|
| Pb A  | 0.01                             | 0.18                                   |
| Pb B  | 0.01                             | 0.17                                   |
| Fe A  | 0.3                              | 0.48                                   |
| Fe B  | 0.3                              | 0.43                                   |

Based on Figure 1, the more mass of adsorbent added, the lower the removal efficiency will be. Removal efficiency percentage is calculated as following [6]:

$$ R = \frac{c_0 - c_e}{c_0} \times 100\% $$  \hspace{1cm} (1)

The time variable 60 minutes and the adsorbent mass variable 2 g gave the highest removal percentage, which were 96.67-97.64% for Pb metal and 95.56-97.34% for Fe metal. The more we add the adsorbent mass, the higher the removal percentage will be. This happens because the surface area or active site increases [7] so that the interaction with metal ions is greater and causes the removal percentage to be higher [8]. However, the higher adsorbent mass can cause the removal percentage to decrease, due to the clumping anomaly of activated carbon [9]. Activated carbon agglomeration can weaken the surface area or active site [9] due to overlapping of active sites. Furthermore, it can cause the unavailability of active sites for adsorption so that the removal percentage also goes down [10].
Figure 1. Effect of adsorbent dosage on removal percentage with (a) Adsorption time of 20 minutes (b) Adsorption time of 40 minutes and (c) Adsorption time of 60 minutes.

Contact time is one of the factors that affect the value of adsorption efficiency [11]. Figure 1 shows the longer the contact time, the higher the removal percentage will be. The highest removal percentage at 60 minutes was 96.67-97.64% for Pb metal and 95.56-97.34% for Fe metal. This is in accordance with the theory which states that the longer the contact time between the adsorbent and the adsorbate, the more adsorbate will be able to diffuse into the adsorbent [12]. The longer the contact time, it will provide more significant opportunities for metals to adsorb, interact with the activated carbon surface [13].
(a)

(b)

(c)
Figure 2. Effect of contact time on removal percentage with (a) 2 gram activated carbon (b) 3 gram activated carbon (c) 4 gram activated carbon and (d) 5 gram activated carbon.

Figure 2 shows that the longer the contact time using ozonation method, the percentage of decrease in the levels of Pb and Fe in the two refillable drinking water samples increased. The ozonation test with a contact time of 60 minutes gave the highest reduction in Pb and Fe metal levels with the percentage reduction in Pb metal levels in sample A and sample B, which was 90.57% and 90.85%, while for the percentage decrease in Fe metal content in sample A and sample B are 93.81% and 93.59%, respectively. This is because the length of time the ozone is in contact with metals greatly affects the level of metal reduction [14,15].

Figure 3. Effect of ozonation contact time on removal percentage of Pb and Fe.

The decrease in metal content between adsorption using activated carbon and ozonation technology, indicates that activated carbon is more efficient in reducing metal content. It can be seen in Table 2, that after the activated carbon treatment, the metal content decreased far from the initial level and was below the quality standard. Meanwhile, in the ozonation treatment, Pb was still above the quality standard.
Table 2. Comparison of Metal Content Reduction Between Adsorption Using Activated Carbon and Ozonation Technology

| Metal | Permissible concentration (mg/L) | Initial concentration of sample (mg/L) | Activated carbon treatment (mg/L) | Ozonation Treatment (mg/L) |
|-------|---------------------------------|--------------------------------------|----------------------------------|---------------------------|
| Pb A  | 0.01                            | 0.18                                 | 0.004                            | 0.016                     |
| Pb B  | 0.01                            | 0.17                                 | 0.005                            | 0.015                     |
| Fe A  | 0.3                             | 0.48                                 | 0.012                            | 0.029                     |
| Fe B  | 0.3                             | 0.43                                 | 0.019                            | 0.027                     |

4. Conclusion

Treatment using adsorption with powdered activated carbon and ozonation technology, metal adsorption on refillable drinking water in Semarang City has been achieved satisfactorily with the most effective adsorbent dose of 2 g/L and a time of 60 minutes. The result of adsorption treatment, the highest removal percentage for Pb metal was 96.67–97.64% and 95.56–97.34% for Fe metal. Whereas when using ozonation technology, the highest removal percentage in Pb and Fe levels was obtained at a contact time of 60 minutes, which were 90.57–90.85% and 93.59–93.81%, respectively.

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