The Changing of Dissolved Organic Matter Based on Its Molecular Weight Through Alum Coagulation and Adsorption Activated Carbon

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Abstract. Surface water may contain dissolved organic matter (DOM), which is derived from microbial activities in water and discharged from the watershed. Source water is mainly used as raw water for clean and drinking water, and DOM in water could affect the treated water quality. Therefore, it is necessary to remove DOM in water. This study aims to know the efficiency of removal of DOM by using alum coagulation followed by adsorption with activated carbon. In addition, this study applied the chromatograms method to identify the changing of DOM based on its molecular weight. The results show that raw water was composed of two main organic fractions: humic substances and low molecular weight acids and neutral. The humic substances organic fractions have been removed through alum coagulation up to 48%, and removal increased up to 85% through adsorption with activated carbon. The low molecular weight acids and neutral organic compounds have been removed about 85% and 40% in alum coagulation and adsorption, respectively.

Keywords. Dissolved Organic Matter, Humic Substances, Low Molecular Weight, Water Treatment

1 Introduction

Dissolved organic matter (DOM) is a heterogeneous mixture of organic existing in water, which is derived from microbial activities in water and discharged from the soil. DOM has been identified based on its properties, including its molecular weight, hydrophobicity or hydrophilicity, aromaticity or aliphatic compounds, etc. Water containing DOM mostly applied as source water for drinking water. However, the processes should perform to remove DOM in order to prevent the formation of disinfectant by-products (DBPs) [1]. It has been well known that chemical disinfectant is very reactive with DOM, the reaction that will generate by-products. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the main species of DBPs compounds formed through chemical disinfection [2,3]. Some research has found that water treatment processes could remove DOM.

However, the efficient removal of those processes depends on the characteristics of DOM. Coagulation is the most applied process for removing DOM because coagulation has some mechanisms for removal, such as entrapment, destabilization, adsorption, and coagulation. Adsorption could remove hydrophobic and aromatic with high molecular weight organic matters, though it depends on the type of coagulants [4]. Adsorption is one of the advanced treatment technologies that could remove DOM due to the capacity of its pore size to adsorb those organic matters [5]. Adsorption could remove hydrophilic and aliphatic with low molecule weight organic matters, though it depends on the type of adsorbent, which has a different pore size [3]. Some characterization methods have been improved to dig out the characteristic of organic matter through various treatment processes [3,6]. Characterization has been conducted by using various methods which could be related to the specification of organic matter. Those methods identified organic matters primarily based on the properties of their molecular weight [4], fluorophores compounds [7], functional groups, aromaticity, and hydrophilicity [5]. High-performance size exclusion chromatography (HPSEC) is one of the primary methods that has been applied to identify DOM based on its molecular weight, which is separated based on differential of its molecule’s sizes into a porous matrix. A higher molecular weight will elute first than the lowest molecular weight [8]. Fluorescence spectroscopy has considered as a regards tool for detecting aquatic organic matter. This technique can provide information on the structure and humification (formation of humus) of DOM. Fluorescence occurs when chromophores are
excited and then relax to a ground state through the radiation photons [9]. According to aromaticity compound, UV/Vis spectroscopic method provides information about compounds with unsaturated bonds (e.g., aromatics), which is considered at lowest wavelength 220 - 280 nm most relevant for DOM measurements [7]. It has been explored that various wavelengths are known to define various number chromophores of DOM [10]. The combination between the bulk parameters with phytoplankton abundance and spectroscopy methods, could be applied to explore the characteristic of DOM, while the combination of these methods could be applied to control the surface water quality [11]. This study demonstrates the effect of coagulation using alum, followed by adsorption with activated carbon to remove DOM and to identify the changing of DOM based on its molecular weight. The outcome of this study could be applied to predict the efficiency of alum coagulation, adsorption with activated carbon, and a combination of both processes in removing DOM based on its molecular weight.

2 Research Method

Source water from Kali Surabaya was used as raw water, and the sample was filtered through 0.45 µm filter paper to identify the properties of DOM based on its molecular weight. The first experiment was alum coagulation under an alum dosage of 40 mg/L in raw water. Jar test was conducted under 150 rpm in 1 min, 30 rpm in 15 min, and settling time in 30 min [4]. In addition, adsorption with activated carbon was applied under an activated carbon dosage of 20 mg/L into raw water. The jar test experimental of adsorption with activated carbon was similar to the alum coagulation. The supernatant of both treatment processes was filtered to remove particulate organic, followed by characterizing DOM based on its molecular weight. Next, high-performance liquid chromatography (HPLC, LC-20 ATV, Shimadzu, Japan)-size exclusion chromatography (SEC) was conducted with an online ultraviolet detector (UVD) [4,9]. Finally, chromatograms were solved using the technique for peak fitting to present the quantitative data of efficiency removal DOM [12]. Peak-fitting interprets a hidden peak as one not responsible for a local maximum in the data stream. One method in peak-fitting is Residual Method for finding hidden peaks [4,13].

3 Result and discussions

Fig. 1 demonstrates the variations of the chromatograph of each treatment sample, including raw water, alum coagulation, and adsorption with activated carbon. First, the chromatographs indicated 2 peaks: Peak 1 with an average molecular weight (AMW) of 1800 Da and Peak 2 with an AMW of 650 Da. All samples have a similar number of peaks, which means that raw water contains various molecular weights of organic matter. Peak 1 represents humic substances compounds, and Peak 2 indicates a low molecular weight (LMW), including LMW acids and LMW neutral [14]. Peak 1 is higher than Peak 2, suggesting that raw water contains organic matter of humic substances at higher composition than LMW acids and neutral. The high composition of humic substances in surface water indicated that the sources of DOM could be derived from the terrestrial watershed. It is suggested as a kind of allochthonous organic matter. Secondly, after treatment, all peaks showed a lower height of peak than the height peak of raw water. It means that both processes could remove organic matters with particular molecular weight. Previous studies have conjectured that alum coagulation could remove humic compounds. It is probably due coagulation process having various mechanisms for removing organic pollutants [3,4]. Meanwhile, adsorption with activated carbon has been well known for its good performance in removing lower molecular weight. Organic pollutants were probably attached to the surface pore of activated carbon. Therefore, the adsorption efficiency was affected by the pore size of adsorbent [5]. The peak fitting technique was implemented to quantify the area of Peak 1 and Peak 2 for knowing the removal percentage of DOM in alum coagulation and alum coagulation combined with adsorption.

Fig. 2 shows the area of Peak 1 and Peak 2 in raw water in the sample after alum coagulation and after adsorption. The results show that raw water has the highest peak area, followed by alum coagulation and adsorption with activated carbon. After treatment, reducing Peak Area 1 and Peak Area 2 indicates that alum coagulation and adsorption with activated carbon could remove AMW 1650 Da and 650 Da under various capacities. According to the peak area of raw water, this study found that the efficiency removal of alum coagulation is 48% in removing humic substances and 18% in low molecular weight compounds.

![Figure 1](https://example.com/figure1.png)

**Fig. 1.** The chromatograph of the organic fraction in raw water, after alum coagulation and followed by adsorption with activated carbon.

![Figure 2](https://example.com/figure2.png)

**Fig. 2.** Peak area of of three main component, such as humic substances and low molecular weight acids and neutral after alum coagulation and adsorption with activated carbon.
Further, after adsorption with activated carbon, the removal of humic substances increased significantly to 85%, and low molecular weight removal was removed up to 40%. In other words, the removal percentage of humic substances increased by 37%, and the removal of low molecular weight increased by 22% after alum coagulation. Comparison between those processes conjectured that alum coagulation performs more efficiently to remove humic substances, while adsorption works efficiently for removing low molecular weight fraction. It seems that alum coagulation could not remove the lower molecular weight, and those compounds were adsorbed or attached to the pore surface of activated carbon [5,6]. The mechanism of removal of DOM in alum coagulation could be a integration mechanism among adsorption, entrapment, charge neutralization, and complexation with coagulant ions into insoluble particulate compounds. It has been well known that coagulation is more effective for removing a high molecular mass of organic matter than a low molecular mass because the high molecular matter is more hydrophobic and consists more of aromatic compounds [4,12]. The organic compounds that existed in water after alum coagulation could not be bound by the alum coagulation because those compounds probably as low molecular weight. Therefore, the low molecular weight could be reduced by attaching to the adsorbent surface [5,9].

4 Conclusion

This study identifies DOM in surface water, mainly composed of humic substances, low molecular weight acids, and neutrals. The source water is categorized as allochthonous organic matter. After the treatment, alum coagulation could remove about 48% of humic substances fractions and 18% of low molecular weight fractions. Further, adsorption with activated carbon provided a higher efficiency removal of humic substances up to 85% and 40% of low molecular weight. Comparison between alum coagulation and adsorption with activated carbon conjectures that alum coagulation performs more efficiently in removing humic substances, while adsorption works efficiently for removing low molecular weight fractions. This study concludes that a combination of alum coagulation followed by adsorption could be applied to remove DOM. It is a mitigations efforts to diminish the formation of carcinogenic compounds in treated water.

References
