# PR MARCH_The Effect of Various Oxidant to Alum Coagulation in Removal Natural Organic Matter in Drinking Water Processes

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# THE EFFECT OF VARIOUS OXIDANT TO ALUM COAGULATION IN REMOVAL NATURAL ORGANIC MATTER IN DRINKING WATER PROCESSES

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## ABSTRACT

Natural organic matter (NOM) is a complex matrix of organic materials and a key component in aquatic environments. As a result of the interactions between the hydrologic cycle and the biosphere and geosphere, the water sources of drinking water generally contain NOM. The amount, character, and properties of NOM vary considerably according to the origins of the waters and depend on the biogeochemical cycles of their surrounding environments. The presence of NOM reduces the quality of raw water for drinking water by altering its organoleptic properties (color, taste, and odor), disrupting the deposition system and increasing the use of coagulant in drinking water production processes, fouling of membranes, blockages on the filter and distribution of drinking water. The presence of organic compound in raw water for drinking water will affect the disinfection process. The addition of chlorine to the disinfection process cause to disinfection by-product (DBPs) formation, such as trihalomethane and chlorophenol compounds which can lead to cancer. NOM can be eliminated through several methods such as coagulation and advanced oxidation processes. The purpose of this research is to know the effect of various oxidant to alum coagulation in removal natural organic matter in drinking water processes.

**KEY WORDS :** Oxidant, Natural Organic Matter, Drinking Water, Organoleptic

## INTRODUCTION

Natural organic matter (NOM) is an organic compound in a healthy environment derived from plants and animals, and animals and microorganisms, and from degradation products from many sources (Baghoth, 2012). The content of natural organic matter in water, specifications, and degradation, depends on the season, weather, microorganism activity, human activity, and eutrophication status of water source (Zazouli et. al., 2007; Matilainen et. al., 2011; Lamsal, 2012).

NOM present in waters consists of both hydrophobic and hydrophilic components. The hydrophobic part mainly contains aromatic carbon, having phenolic structures and conjugated double bonds, while hydrophilic NOM is rich in a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates and proteins, sugars and amino acids (Bhatnagar and Sillanpää, 2017).

NOM in the water treatment process does not allow and cause problems, one of which affects the disinfection process (Zhang and DiGiano, 2002; Liu et. al. 2007; Baghoth, 2012; Cahyonugroho and Hidayah, 2018). The most common disinfection process is to provide chlorine compounds. In disinfection process, NOM which is not removed by previous treatment can reacts with chlorine and form disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Reckhow & Singer, 2011). Require removal of organic carbon compounds, if the Total Organic Carbon (TOC) of treated water is greater than 2.0 mg/L (US EPA, 1999; Liu et. al. 2007).

Before the disinfection process is done, it is necessary to preliminary process to set aside organic material contained in water, so it can minimize the formation of DBPs. NOM can be eliminated through several methods such as coagulation, conventional filtration through different media, coagulation, membrane, ion exchange, adsorption, and advanced oxidation processes (Huang et. al., 2008; Matilainen and Sillanpää, 2010; Lin and Wang, 2011). It has been known membrane technology is the most effective option, but because of its high cost, this technology is not suitable for developing countries (Jarvis et. al., 2008 ; Sillanpää, 2015).

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In addition, one method of removal of organic matter in water is a combination of preoxidation and coagulation. Preoxidation is pretreatment to improve coagulation process. According to these studies, in the conventional drinking water treatment process, preoxidation with chlorine before coagulation can be performed to improve the performance of the drinking water treatment process. Alternative pre-oxidants, such as ozone, chlorine, chlorine dioxide, permanganate, while each of preoxidant has its advantages and disadvantage (Hidayah et. al. 2017).

According to the literature, permanganate preoxidation to assist coagulation has been widely used to improve the removal of turbidity, NOM, and algae cells in subsequent coagulation-filtration process by destroying the organic coating on the surface of particles (Xie et. al., 2016; Hidayah and Yeh, 2018). Meanwhile, chlorine can reduce high molecular and humic substances-like compounds (Hua and Reckhow, 2007). Further, preoxidation provides an excellent effect on improving coagulation performance, easy operation, and low cost (Xie et. al. 2016).

This study knows the effects of preoxidation performance by permanganate and chlorination in removing NOM in drinking water process. The surface water is treated by preoxidation by permanganate and chlorination followed by coagulation of alum.

## MATERIALS AND METHODS

In this study the water samples used were from the Jagir River located near the intake of PDAM Ngagel Surabaya which served as raw water for drinking water production. Preoxidation was conducted with a six-paddle gang stirrer jar test apparatus (Phipps & Bird, Richmond, VA, USA). First, preoxidation was added into the water-filled jar, and the contact time was 60 minute under slow mixing 35 rpm, stock solution of $KMnO_4$ (Merck, Germany) or $CaOCl_2$ (Merck, Germany) was added, with dosage being varied from 0.1 to 1.6 mg/L as $KMnO_4$ and varied from 5 to 30 mg/L as $CaOCl_2$. Second, alum $(Al_2(SO_4)_3.18H_2O,$ Merck, Germany) was added, with dosage 35 mg/L. Alum coagulation was setup under 120 rpm flash mixing for 3 min, followed by 35 rpm slow mixing for 15 min, and settling for 30 min. The supernatants were collected and filtered through 0.45 $\mu$m filter (cellulose acetate, Toyo Roshi, Japan) before further analysis.

Sample was analyzed for TOC by using total organic carbon analyzer (Model TOC-500, Shimadzu, Kyoto, Japan). $UV_{210}$ was measured using UV/vis spectrophotometer (HP 8452A Diode Array Spectrophotometer) with a 1-cm quartz cell (APHA et al., 2012). FTIR spectroscopy (Perkin Spectrum One FTIR Spectrometer) was used to identify the functional groups, in term of their structural and organic characteristics of organic matter in raw water and treated water. KBr pellets were prepared by grinding the samples with spectrographic grade KBr in an agate mortar utilizing a fixed amount of sample (1%, wt%). FTIR was setup with scanning from 4000 $cm^{-1}$ to 400 $cm^{-1}$.

## RESULT AND DISCUSSION

### Characteristics of Raw Water

Table 1 shows the characterisitics of Jagir River water quality as raw water of the study. The results demonstrated that the Jagir River has a neutral pH, but based on the Regulation of the Minister of Health of the Republic of Indonesia Number 32 Year 2017 on Standard of Environmental Health Quality Standard and Water Health Requirements for Sanitation Hygiene, Swimming Pool, Solus Per Aqua and Public Baths, the standard of turbidity standard is 25 NTU, so that Jagir River water exceeds the quality standard.

**Table 1.** Characteristics of Jagir River water quality

| Parameter | Unit | Jagir River |
|---|---|---|
| pH | – | 7 |
| Turbidity | (NTU) | 37,84 |
| Total Organic Carbon | (mg/L) | 11,67 |
| Ultraviolet Absorbance 210 nm | $(m^{-1})$ | 1,4983 |

In natural waters TOC values typically range from 1-30 mg/L, in groundwater the TOC value is usually smaller, $\pm$ 2 mg/L and the TOC value of waters that have received waste, either domestic or industrial, or waters in swampy areas (swamp) can be more than 10-100 mg/L (Effendi, 2003), it is indicated TOC concentration Jagir River which is in acceptable range. Based on the value of TOC and Ultraviolet Absorbance, it is known that Jagir River has an SUVA value of 0.934 L/mg/m indicating low hydrophobic character with low molecular weight and most not humic is the dominant composition. SUVA value > 4 L/mg/m means high organic material with high molecular weight and mostly aquatic humid, while SUVA value < 2 L/mg/m is low hydrophobic character with low molecular weight and mostly non humic. The SUVA values between them are hydrophobic and hydrophilic mixtures and mixed molecular weights (Baghoth, 2012).

This is probably due to human activities around the river, domestic and industrial wastewater discharged directly to the river contribute more dominantly to the organic matter contained in Jagir River. It has been well known that wastewater treatment from indutrial activities might contributed to the quantity and quality of organic matter in the river bodies, or it is known as effluent organic matter (Shon et al., 2012).

## Effect of Preoxidation on NOM Removal

The preoxidation effect on NOM removal with total organic carbon (TOC) parameter can be show in Figure 1a and 1b. Preoxidation by permanganate and chlorination was found to enhance alum coagulation of TOC, but no significant effect was observed on TOC after permanganate preoxidation followed coagulation. There existed an optimum permanganate and chlorination dosage, 1.2 mg/L and 25 mg/L in this case, as higher dosages could not further improve coagulation.
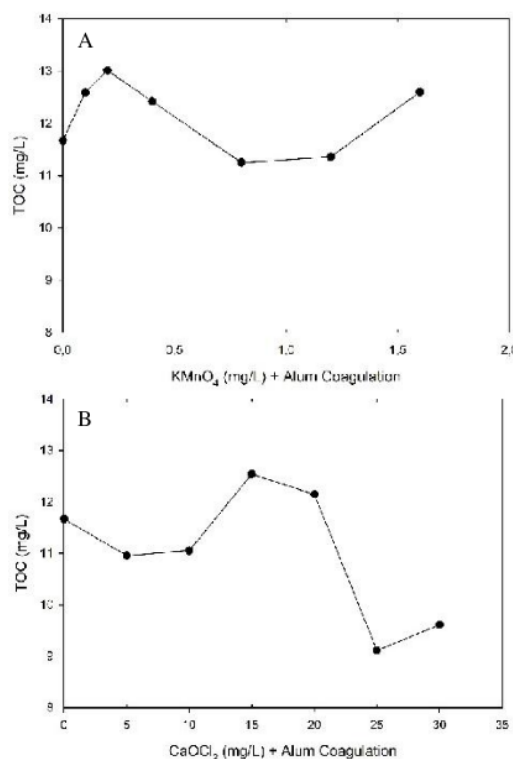


**Figure 1.** Effect of preoxidation to TOC concentration by: (A) permanganate; (B) chlorine

Combination chlorine as preoxidation and alum is more effective than combination permanganate as preoxidation and alum in degrading TOC. Chlorine with a dose of 25 mg/L decreased TOC from 11.67 mg/L to 9.11 mg/L, whereas permanganate with a dose of 1,2 mg/L only decreased TOC from 11.67 mg/L to 11.25 mg/L. Preoxidation using oxidants such as chlorine, permanganate, chlorine dioxide, ozone, and ferrates is affected by a fairly high redox potential. Redox potential for oxidants used in water and wastewater treatment such as chlorine 0.841-1.482 E°V, permanganate 0.6-1.679 E°V, chlorine dioxide 0.954 E°V, ozone 2.076 E°V, ferrate (VI) 2.2 E°V (Xie

et al., 2016). Such low levels of TOC removal by preoxidant permanganate were probably due to its low redox potential than preoxidant chlorine.
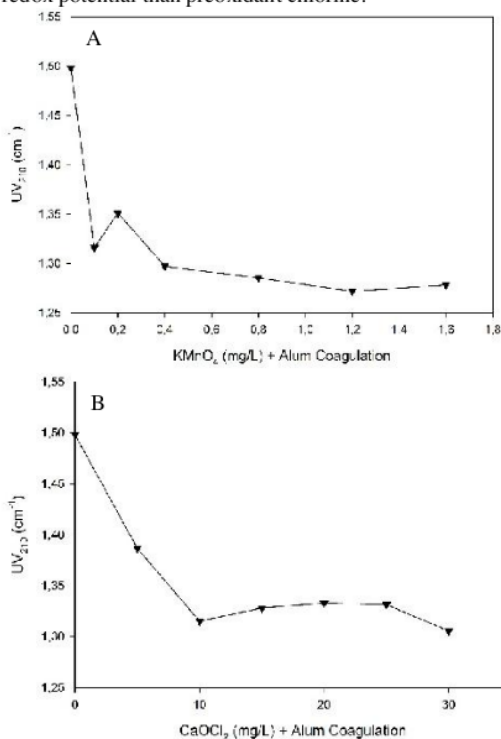


**Figure 2.** Effect of preoxidation to $UV_{210}$ value by: (A) permanganate; (B) chlorine

Figure 2 showed NOM concentration in term of $UV_{210}$ value. $UV_{210}$ indicates water containing aromatic compounds with double bonds C=C conjugate. The $UV_{210}$ value shows a decrease concentration in in all treatment processes. $UV_{210}$ detected aromatic compound, therefore decreasing $UV_{210}$ concentration indicated that aromatic compound have been reduced. It has been well established that aromatic and humic substances is easy to be degraded by coagulation only, preoxidation, and combination of water treatment processes (Edzwald and Tobiason, 2011).

Figure 3 showed the spectrum from FTIR analysis of the source water and treated water from different treatment process. The results indicates that source water contain four peaks, which identify four major functional groups including: O–H and N–H compounds at wavelength 3200-3600 $cm^{-1}$, triple bond C☰C compounds at wavelength 2100-2600 $cm^{-1}$, double bond C=C and C=O compounds at wavelength 1630 $cm^{-1}$, and C–X compounds at wavelength 500-800 $cm^{-1}$ (Sing, 2010).

According to the literature, O–H and N–H compounds

at wavelength 3200-3600 cm$^{-1}$ are indicative of amides and amines compounds, triple bond C☐C compounds at wavelength 2100-2600 cm$^{-1}$ are indicative of alkynes, nitrile, and thiols compounds, double bond C=C and C=O compounds at wavelength 1630 cm$^{-1}$ are indicative of alkenes, arene, imine, and nitro compounds, and C–X compounds at wavelength 500-800 cm$^{-1}$ are indicative of amides, anhydrides (2bands), carboxylic acids, acid chlorides, ketones (Sorrell, 1988).

All treatment processes identify the decreasing of functional groups compound. This results is consistent with TOC concentration and UV$_{210}$ value. Preoxidation by chlorine followed by alum coagulation showed a higher reduction of percentage transmittance of organic matter, it means that preoxidation by chlorine-alum coagulation could be considered as an alternative process to remove NOM in water.
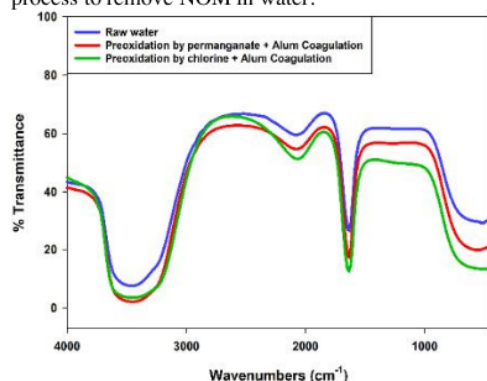


**Figure 3.** Spectrum FTIR of the source water and treated water from different treatment process

## CONCLUSION

Source water Jagir contains of high TOC concentration, aromatic compound and mainly composed by single, double, and triple bond organic matter. Preoxidation by chlorination more effective than preoxidation by permanganate to be used as a pretreatment of the coagulation process. But, the effectiveness of preoxidation in removing organic matter contained in water is still low. This is probably due to the diverse characteristics of source water, which vary by place and season.

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