

PERFORMANCE OF PRE-CHLORINATION, COAGULATION AND ADSORPTION FOR CONTROLLING THE FORMATION OF CARCINOGENIC COMPOUND IN TREATED WATER

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ABSTRACT

Aquatic organic matters refer to chemical compounds that result from natural processes in the environmental including algae metabolic reactions and decomposition of organic matter. The removal of NOM is the most effective effort to minimize the generation of disinfection by-products (DBPs). Aims of this research are to compare various treatments in controlling aquatic organic matters, which caused the formation of the carcinogenic compound. Combination processes of pre-chlorination, coagulation with alum and FeCl₃ and adsorption with powdered activated carbon (PAC) was applied under different dosage. TOC and UV₂₅₄ were measured to quantify organic matters, Fourier Transform Infrared (FTIR) was applied to identify organics properties, and CHCl₃ was measured to know carcinogenic concentration. The results showed that pre-chlorination only caused the formation of lower molecular weight, pre-chlorination followed by coagulation combined with adsorption showed a better result than coagulation-adsorption only. FeCl₃ coagulant is more effective than alum. Aromatic compounds are a precursor for the formation of CHCl₃, since removal UV₂₅₄ along with CHCl₃ concentration.

Keywords: Organic matters, Pre-Chlorination, Coagulation, Adsorption, Chloroform

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INTRODUCTION

Disinfection has an important role in avoiding the broaden of waterborne diseases. Disinfectants are productive in inactivating deleterious microorganisms, disinfectants are very reactive with organic and inorganic materials in treated water as well and leading to the formation of DBPs.¹ It has been known that DBPs are highly toxic and adverse human health effects.² One method for controlling and minimizing the formation of DBPs is the removal of natural organic matter (NOM). NOM is a mixture of heterogeneous natural organic compounds that exist in water especially surface water.^{3,4} The presence of NOM in waters can cause negative effects on raw water quality such as color, odor, and taste⁵, caused membrane fouling⁶, thus forming disinfection by-products (DBPs) such as trihalomethanes (THMs), haloacetic acids (HAAs), haloketones, haloacetonitriles, haloaldehydes, and halogenated furanones.⁷ The formation of DBPs is affected by the characteristics of NOM such as ultraviolet absorbance, aromatic/aliphatic content, and carboxylic/phenolic acidity. In drinking water treatment plant, enhanced coagulation could remove hydrophobic, aromatic, phenol, conjugated double bond, and degrade high molecular weight (HMW) of NOM^{5,8} whereas PAC adsorption is used to remove low molecular weight (LMW) and cause odor in raw water.⁹ Basically, all treatment processes have different capability to remove organic compounds, and treatment efficiency depends on the characteristics and properties of organic compounds. In addition, it has been developed some numbers of organic matter characterization, for example: using bulk parameters for quantitative analysis in terms of total organic carbon (TOC), ultraviolet at 254 nm (UV₂₅₄). Another is qualitative methods, which is fractioned organic matter based on their properties, for example: using chromatography, fluorescence, spectrophotometer, etc. According to those information, therefore the objectives of this study is compare various treatment, including pre-chlorination, coagulation, adsorption

under different dosage and materials, for controlling the formation of carcinogenic compounds in treated water. This research will help with water treatment regarding the effect of organic matter existence in water, and a chance to be applied in wastewater treatment as well.

EXPERIMENTAL

Water samples were carried out from the outlet of the pre-sedimentation chamber at a water treatment plant in Surabaya, Indonesia. Experimental was divided into eleven (11) various treatment processes, including pre-chlorination, coagulation, adsorption. All of these processes were done by using the jar test (Phipps & Bird PB-700). 20 ppm CaOCl_2 as an oxidant in pre-chlorination was added into the jar contain water sample and mixing 110 rpm for 20 min. Next, 90 ppm $\text{Al}_2(\text{SO}_4)_3$ as coagulant was mixing fast at 110 rpm for 30 seconds, slow mixing 25 rpm for 30 min, and settling for 15 min. PAC has added 10 ppm or 40 ppm and mix under 110 rpm for 30 min. Samples were filtered by using 0.45 μm cellulose acetate (CA) filtered paper before chloroform analysis, functional groups FTIR measurements, TOC, and UV_{254} value. Chloroform (CHCl_3) one of the species trihalomethanes was measured by purge and trap packed column gas chromatographic method (Model 3400 GC, Varian, USA) equipped with a purge and trap module (Model LCS-2000, Tekmar, USA).¹⁰ This study concerned about CHCl_3 due to this species exists in pre-chlorinated water in high concentration. FTIR spectroscopy (Thermo Nicolet NEXUS 670) with wavelengths 4000–400 cm^{-1} was used to identify functional groups of organic matters.¹¹ The TOC measurement was analyzed using Shimadzu TOC analyzer, and UV_{254} was measured by UV/vis spectrophotometer (Agilent 8453).¹²

RESULTS AND DISCUSSION

Characteristics of Raw Water

The raw water from effluent prasedimentation plant had a very high TOC concentration, about 9.645 mg/L as high as UV_{254} . The high TOC concentration indicated high organic matters compound, it could be as aromatic, non-aromatic compound, humic-like and non-humic substances-like compound, soluble microbial products, etc.⁷ According to UV_{254} value, it presented high aromatic compound in the effluent of pre-sedimentation process. Raw water from the effluent of pre-sedimentation still contain high organic matters, it is probably due to raw water from surface water was contaminated from human activities, such as from domestic and industrial wastewater discharged into surface water.⁵ It seems that organic matter concentration in raw water could not be removed in physical treatment, such as in pre-sedimentation.³ The raw water also has high turbidity due to the rainfall experienced prior to sampling, and neutral pH¹⁰. The characteristics of organic matter in raw water are presented in Table-1.

Table-1: Characteristics of raw water

Sample	pH	Turbidity (NTU)	TOC (mg/l)	UV_{254} (cm^{-1})
Raw water	7.51	65.9	9.645	0.077

Comparison Between CHCl_3 Removal and Organic Matters Removal in Various Treatments

Carcinogenic compounds are represented as CHCl_3 or chloroform, one of the species of trihalomethanes (THMs), and it is known as disinfectant by-products (DBPs). Organic matters, mostly represented as TOC concentration and UV_{254} value parameters, are precursors for disinfectant by-products (DBPs) generation.¹³ Comparison between CHCl_3 and organic matter removal could describe the effect of organic matters on the formation of CHCl_3 . Figure-1 shown removal TOC and UV_{254} compare with CHCl_3 removal in all treatment processes. Firstly, it shows that UV_{254} removal is higher than TOC removal. It indicated that aromatic compounds are more amenable removed during water treatment processes through coagulation and adsorption. Aromatic compounds contain a humic substances-like compounds and it is more hydrophobic and easy to be removed.^{3,10} Secondly, the removal of carcinogenic CHCl_3 shows a higher removal along with UV_{254} removal. It seems that aromatic compounds are organic precursors of CHCl_3 formation. This result shows consistency with previous studies.^{3,11-14} Third, treatment comparison between coagulant combined with PAC presented that alum shows a higher removal (about 85%) of CHCl_3 concentration than FeCl_3 . However, the FeCl_3 coagulant showed its effectiveness in removing

almost 40% organic aromatic compounds, as shown in the UV_{254} value. Both coagulants have a similar capability to remove organic matter in terms of TOC concentration, about 20-25%.

Further, treatment comparison under pre-chlorination indicated that pre-chlorination could help to enhance organic matter removal. The results show a combination of pre-chlorination-coagulant-activated carbon resulted in a higher removal for all parameters than others. As shown in Fig.-1, alum coagulant performed better efficiency than $FeCl_3$, about 90%, 60% and 40% removal of $CHCl_3$ concentration, UV_{254} value, and TOC concentration, respectively. It seems that if pre-chlorination is applied as pretreatment and activated carbon as post-treatment, then alum is a suitable coagulant for removing organic matter in order to control the formation of $CHCl_3$, which has been known as a carcinogenic compound.

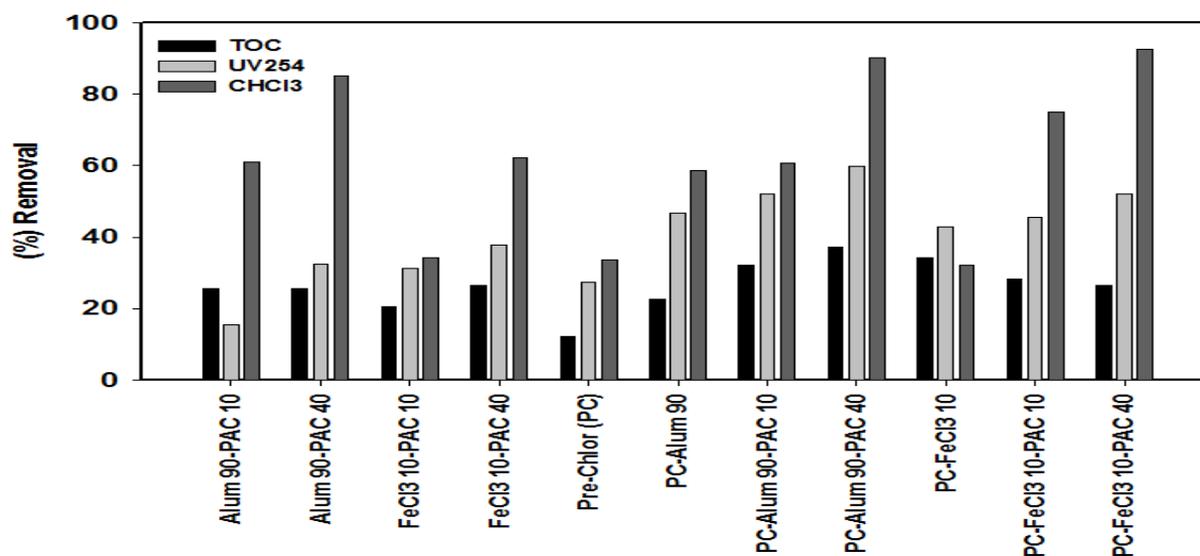


Fig.-1: Performance of Various Treatments in removing TOC, UV_{254} and $CHCl_3$ Concentration

Pre-chlorination could reduce organic matters because the hypochlorite (hydrolysis of chlorine in the water) oxidized the layer of organic matters to the smallest weight molecule or transformation aromatic.^{11,13,14} It is supported by decreasing UV_{254} . Chlorine reacts strongly with donating groups of electron such as $-OH$, $-OR$, $-NH_2$, $-R$, phenol to activate the aromatic ring and causing THMs.¹³ In addition, the adsorption process could enhance organic matter removal, especially with high dosage. In pre-chlorination, comparison between alum with and without PAC presented that PC-alum with a low dosage of PAC (10 ppm) has similar removal of organic matters to PC-alum only. However, coagulant $FeCl_3$ showed gradually increasing the removal of organic matters and $CHCl_3$ under without PAC, with a low dosage of PAC and a high dosage of PAC. This results conjectured that $FeCl_3$ coagulant has an effective performance under different treatment processes, it is consistent with the previous studies.^{3,4,10,15} Natural coagulants have been developed in the previous studies, and it seems have the opportunity to be applied in this study, since natural coagulant is environment-friendly and biodegradable nature in water. In addition, those natural coagulants could be applied as adsorbent as well.¹⁶⁻¹⁸

Functional Groups Properties of Organic Matters Under Pre-Chlorination, Coagulation and Adsorption

Figure-2 and Fig.-3 described the FTIR spectra of functional group organic matters in raw and treated water. The functional group dominant in treated water were alcohols, phenols, aromatic amines, amides, alkenes, and halogen. At a wavelength of $3600-3200\text{ cm}^{-1}$ is identified as functional groups OH and NH (alcohols, phenols, and aromatic amines). Amide group and alkenes identified at $1800-1600\text{ cm}^{-1}$ and $1650-1500\text{ cm}^{-1}$, whereas halogen groups are known at $650-550\text{ cm}^{-1}$ and $570-500\text{ cm}^{-1}$. Fig.-2 presented percentage transmittance of organic matters after pre-chlorination only and coagulation combined with adsorption. The results showed that pre-chlorination caused decreasing transmittance of functional groups OH and NH at $3600-3200\text{ cm}^{-1}$ wavelengths and amide, alkenes groups at $1650-1500\text{ cm}^{-1}$ wavelength. It

conjectured that pre-chlorination caused the formation of those compounds, which could be precursors of carcinogenic CHCl_3 . Pre-chlorination could breakdown high molecular weight organic matters into lower molecular weight fractions.^{10,14} Meanwhile, coagulation combined with adsorption could increase the transmittance of all functional groups. It indicated that coagulant and adsorption could interact with organic fractions through its mechanism. Charge neutralization, complexation, sweep coagulation is probably one of the mechanism to remove organic fractions during coagulation, while pore mechanism is the main role in adsorption.^{9,15}

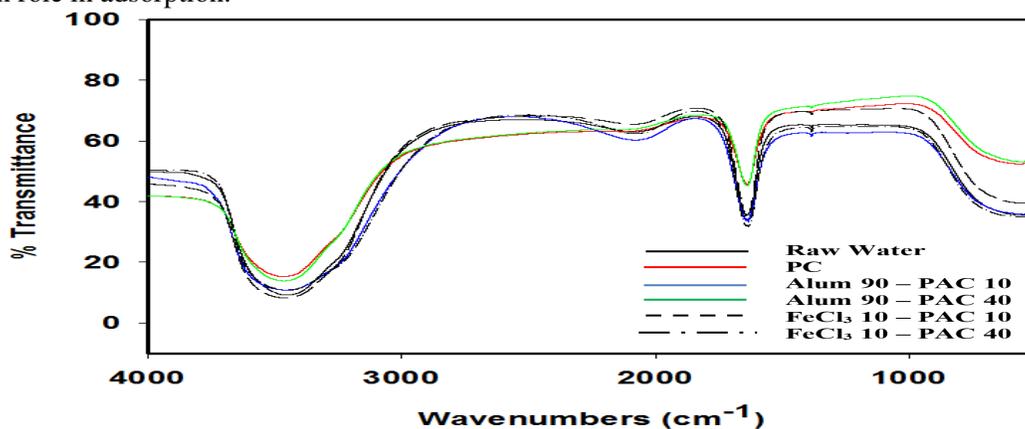


Fig.-2: FTIR Spectrum of Organic Matters in Raw Water and Treated Water using Coagulation-Adsorption

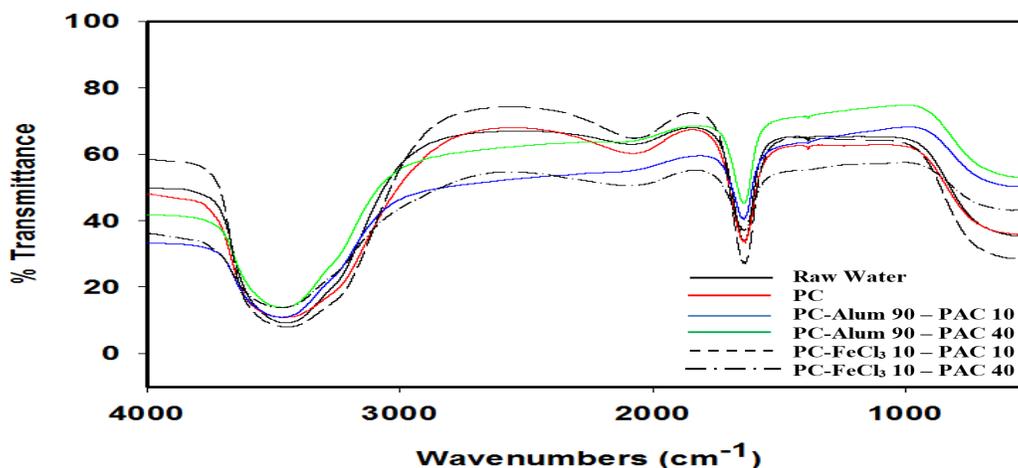


Fig.-3: FTIR Spectrum of Organic Matters in Raw Water and Treated Water using Pre-Chlorination-Coagulation-Adsorption

Figure-3 presented percentage transmittance of organic matters after pre-chlorination as pretreatment, followed by coagulation and adsorption. Shortly, the mechanism of organic fractions removal is almost similar to the previous experiment. The results showed that pre-chlorination caused decreasing transmittance of functional groups OH and NH at $3600\text{--}3200\text{ cm}^{-1}$ wavelengths. It conjectured that pre-chlorination caused the formation of those compounds, which could be precursors of carcinogenic CHCl_3 , even those functional groups existed after coagulation and adsorption. Pre-chlorination could breakdown high molecular weight organic matters into lower molecular weight fractions.^{10,14} It seems that the formed lower molecular weight fractions is a kind of non-aromatic, and hydrophilic compounds, which is difficult to be removed through coagulation and adsorption. The highest percent of transmittance halogen was 39.43% at a wavelength of 557.39 cm^{-1} . The number of halogen groups shows the presence of THMs in the water. THMs are halogen-substituted single carbon mixtures with general formula CHX_3 while X can represent halogen F, Cl, Br, I or another combination. Enhanced coagulation-adsorption could remove NOM and be implemented as an alternative method to reduce and control NOM and THMs in water.

CONCLUSION

According to the treatment process, UV₂₅₄ removal is higher than TOC removal. Removal of carcinogenic CHCl₃ shows a higher removal along with UV₂₅₄ removal. It seems that aromatic compounds are organic precursors of CHCl₃ formation. Pre-chlorination as pretreatment could enhance coagulation-adsorption for controlling the formation of a carcinogenic compounds, such as trihalomethanes. The addition of adsorption could remove more trihalomethanes formation potential precursors than coagulation only. Organic matter measurement has consistency results with FTIR measurement. Sustainability of pre-chlorination could be considered as pretreatment in order to remove the carcinogenic compound. However, for future work, a different kind of pre-oxidant could be compared with pre-chlorination to see which pretreatment will generate lower disinfectant by-products. This similar study could be carried out for wastewater treatment, since some of the wastewater treatment have been applying chlorination at the end of treatment.

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