

Enhanced Coagulation of Disinfection By-Products Precursors in Porsuk Water Resource, Eskisehir

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Abstract—Natural organic matter (NOM) is heterogeneous mixture of organic compounds that enter the water media from animal and plant remains, domestic and industrial wastes. Researches showed that NOM is likely precursor material for disinfection by products (DBPs). Chlorine very commonly used for disinfection purposes and NOM and chlorine reacts then Trihalomethane (THM) and Haloacetic acids (HAAs) which are cancerogenics for human health are produced. The aim of the study is to search NOM removal by enhanced coagulation from drinking water source of Eskisehir which is supplied from Porsuk Dam. Recently, Porsuk dam water is getting highly polluted and therefore NOM concentration is increasing. Enhanced coagulation studies were evaluated by measurement of Dissolved Organic Carbon (DOC), UV absorbance at 254 nm (UV_{254}), and different trihalomethane formation potential (THMFP) tests. Results of jar test experiments showed that NOM can be removed from water about 40-50 % of efficiency by enhanced coagulation. Optimum coagulant type and coagulant dosages were determined using $FeCl_3$ and Alum.

Keywords—Chlorination, Disinfection by-products, DOC, Enhanced Coagulation, NOM, Porsuk, UV_{254} .

I. INTRODUCTION

NATURAL organic matter (NOM) is complex mixture of organic materials. Results of degradation of the organic materials, generated by physical, chemical and biological activities both in the watershed surrounding a water source and within the water source itself it can be basically divided as humic and non-humic substances. These organic matters effect water quality and cause some odor, color and taste problems. Chlorine commonly is used as disinfectant in water treatment systems in Turkey and also in Eskisehir. During the chlorination of drinking water, chlorine reacts with NOM to form disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), which are believed to be harmful to human health.

At pre and post-disinfection step, chlorine reacts with the presence of NOM in water source and it causes formation of disinfection by-products (DBPs), such as trihalomethanes (THMs) and Haloacetic acids (HAAs). When the organic load is higher in chlorinated water, DBPs concentrations will be higher because of chlorine reaction with natural organic matter

(NOM) to form disinfection by products (DBPs). Humic materials in surface waters tend to have a significant content and are in hydrophobic groups.

One of the important sources for DBPs is acidic fraction of hydrophobic groups which are generally dominant. As a consequence, during preoxidation step water contains higher loads of organics thus the formation of chlorinated DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), is favoured. The epidemiological studies demonstrated that trihalomethanes (THMs) are potentially harmful to human health [1]. Thus, many developed countries set the maximum contaminant level (MCL) for trihalomethanes (THMs), i.e. 80 $\mu\text{g/L}$ in USA, 250 $\mu\text{g/L}$ in Australia, 100 $\mu\text{g/L}$ in most of the European Countries.

Enhanced coagulation is a treatment technique to aim controlling disinfection by-products (DBP's) with removing natural organic carbon (NOM). NOM is measured as Total Organic Carbon (TOC) or Dissolved Organic Carbon (DOC) in drinking water. Removing organic matter with coagulation depends on TOC concentration, chemical nature of the NOM, type of coagulation, coagulant dosage and pH. Enhanced coagulation is the optimization of coagulant doses and pH levels to improve precursor removal. Enhanced coagulation is valuable method of controlling DBP formation which does not require significant capital investments and it can be useful in developing countries where it is almost impossible to afford high technologies [2].

Aluminium and iron salts are used to remove NOM and there is two accepted mechanisms [3], [4]. In the first positively charged metals neutralize the negatively charged NOM by forming insoluble complexes, follow floc precipitation. In the second NOM adsorbs onto metal hydroxides and precipitates. The most important parameters are coagulant dosages and pH for the process.

Porsuk River starts in Western Anatolia plateau and flows through two big cities namely Kutahya and Eskisehir. The river downstream from Kutahya is heavily polluted by industrial wastes (e.g. sugar beet factory, nitrogen fertilizer factory, magnesite factory and agricultural run-off). Porsuk Dam water is highly polluted water source. A treatment plant, which supplies tap and drinking water to Eskisehir, was build after the Porsuk dam reservoir. This water treatment plant consists of mainly screening, pre-chlorination, coagulation, sedimentation, filtration and disinfection steps with chlorine and has a capacity of 80.000 m^3/d [5].

The aim of this study is to determine the changes in NOM that affect THM formation and to enhanced coagulation of Porsuk Dam water. In this context, coagulated water with metallic salts, ferric chloride and alum were compared in

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terms of the parameters that are specific to organic matter content such as DOC, UV₂₅₄, and THMFP as DBP.

II. MATERIALS AND METHODS

The experiments were carried out with Porsuk Dam Water (PDW) which is the major source of public water demand for Eskisehir municipality. Due to upstream discharge of farming, industrial and domestic wastes, the reservoir has become polluted. As a result, the chemical dosage for pre-chlorination is higher and the trihalomethane (THM) concentration of the treated water sometimes exceeded 100 µg/l. Table I presents used water characteristics of PDW during experimental works.

TABLE I
 RAW WATER QUALITY CHARACTERISTICS OF PORSUK DAM

Parameter	Units	Values
pH	-	8.43
DOC	mg/L	4.126
UV ₂₅₄	cm ⁻¹	0.074
THMFP	µg/L	146.13
Alkalinity	mgCaCO ₃ /L	319.8

Jar test were performed using Velp four paddle jar test apparatus. The jars were round beakers with one liter capacity. The reagent grade alum and ferric chloride doses were varied from 20 to 120 mg/L. The jar test mixing conditions were as follows: rapid mix at 150 rpm for 2 minutes, flocculation at 30 rpm for 10 minutes and 20 rpm for 20 minutes. After coagulation, jars were allowed to settle for 30 minutes prior to filtration through a 0.45 µm nylon filter.

Final or maximum THMs formation potential (THMFP) measurements were conducted in accordance with Standard Methods of 5710 B [6]. THM concentrations were determined with liquid-liquid extraction method according to EPA Methods 551.1 [7]. The sum of the four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) mass concentrations was reported as Total THM in µg/L. Samples were analyzed by a Agilent Gas Chromatography (6890 Series) with an micro electron capture detector (GC-ECD), auto sampler and capillary column (J&W Science DB-5.625), 30 m x 0.25 mm I.D.x 0.25 µm film thicknesses. pH measurements were carried out with a WTW-pH meter.

DOC measurements were performed by using a Shimadzu TOC-5000 analyzer equipped with an auto sampler. The inorganic carbon (H₂CO₃*, HCO₃⁻, and CO₃²⁻) was removed by acidifying the sample to pH values between 2 and 3 with 1.0 N hydrochloric acid (HCl) followed by sparging with CO₂ free air. Thus, the measured Total or dissolved carbon is equal to respectively total organic carbon (TOC) or dissolved organic carbon (DOC). DOC was analyzed after filtration through a 0.45 µm membrane filter.

UV₂₅₄ absorbance measurements were performed in accordance with Standard Methods 5910 B [6] by using a Hach-Lange Dr 5000 spectrophotometer at a wavelength of

254 nm with 1cm quartz cell. The samples were first filtered through a pre-washed 0.45 µm membrane filter to remove turbidity, which can interfere with this measurement.

III. RESULTS AND DISCUSSIONS

Selection of coagulant type and its dosage is important factor for enhanced coagulation performance. Two types of coagulant performances were compared considering DOC and UV₂₅₄ as seen in Fig. 1 and Fig. 2 respectively.

Dissolved organic carbon (DOC) data obtained at Porsuk Dam Water was used to compare two types of coagulants of ferric chloride and alum. Fig. 1 shows DOC data for dosage of these two coagulants ranging from 20 to 120 mg/L, when treating Porsuk lake water. It shows that ferric chloride (FeCl₃) has the maximum DOC removal capacity of 52 % and alum has the 44 % at the dosage of 120 mg/L and at similar coagulant dosages, ferric chloride consistently outperformed alum in terms of DOC removal from raw water. In other words there is a greater affinity of a fraction of NOM for ferric hydroxide floc than for aluminium hydroxide floc. Ferric hydroxide floc may have more adsorption active sites than aluminium hydroxide floc [8], [9].

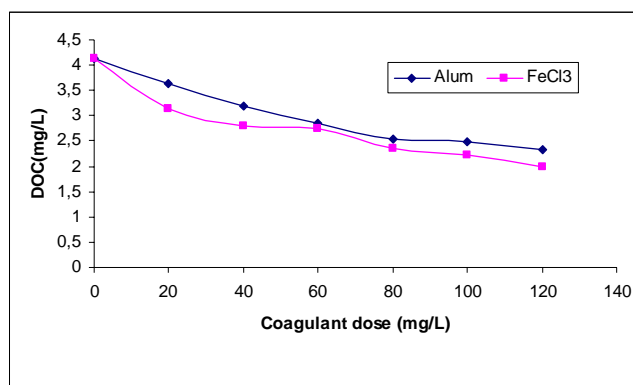


Fig. 1 Changing of Dissolved Organic Carbon (DOC) concentration according to Alum and FeCl₃ coagulant dosages

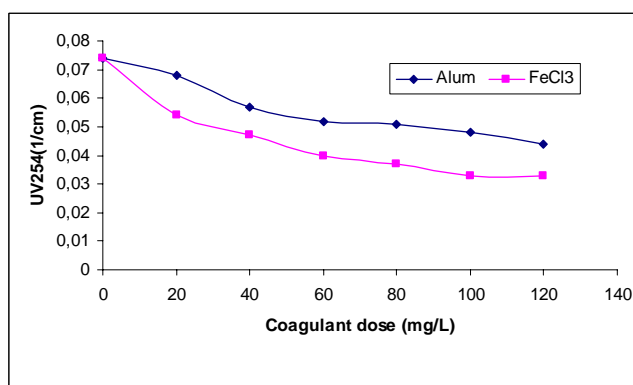


Fig. 2 UV₂₅₄ absorbance as a function of ferric chloride and alum

The absorbance of ultraviolet radiation at 254 nm by natural waters is a good indicator of the aromatic structure of NOM in water. Fig. 2 shows the results of UV₂₅₄ absorbance values as

a function of alum and ferric chloride dosages. Ferric chloride reduced the UV_{254} level to 0.033 cm^{-1} and alum reduced the UV_{254} level to 0.044 cm^{-1} from the 0.074 cm^{-1} with the dosage of 120 mg/L . The percent removal of UV_{254} with ferric chloride and alum was about 55, 41%, respectively. It can be seen that the removal of UV_{254} absorbance values decreases when the coagulant dosage increases. Ferric chloride consistently outperformed alum increasing dosage. This is probably due to the high cationic charge of ferric chloride in contrast to alum. Furthermore, ferric chloride solution is more acidic than alum solution. Also, the alkalinity consumed during the formation of the metal hydroxides is higher for ferric chloride than alum. As a result, for a similar coagulant dosage, the coagulation pH would be lower with ferric chloride than with alum. The lower pH by increasing the positive charge of the coagulant species, favors the adsorption of organics onto metal hydroxides [10], [11].

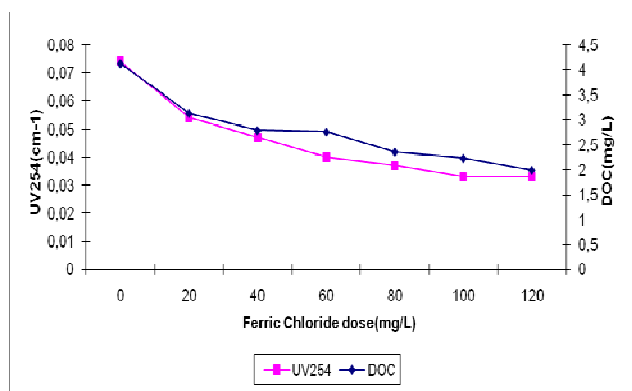


Fig. 3 Removal of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV_{254}) as a function of ferric chloride dose

Fig. 3 shows the two parameters of DOC and UV_{254} for different ferric chloride dosages. It can be seen that maximum DOC and UV_{254} was achieved at 100 mg/L ferric dosage. At this dosages the percent removal of DOC and UV_{254} were 46 % and 55 % respectively. As ferric chloride increased 100 to 120 a not further reduction in DOC an UV_{254} . This experimental data show that the removal amount of UV_{254} washigher than that of DOC for a given jar test. The aromatic materials of PDW are removed more effectively by ferric chloride than other NOM fraction [9], [12].

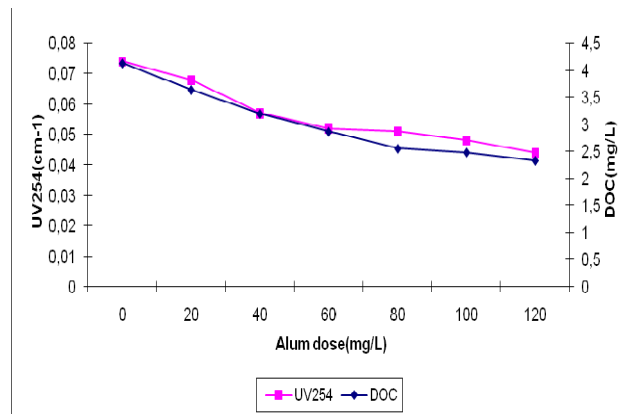


Fig. 4 Removal of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV_{254}) as a function of alum dose

A comparison of DOC versus UV_{254} is shown for alum coagulation in Fig. 4 the removal of DOC and UV_{254} are very close to each other. In this study, proper and acceptable DOC and UV_{254} removal was achieved at 80 mg/L alum dosage because the higher dosages, 100 and 120 mg/L , increased a few numbers. At this dosage the percent removal of DOC and UV_{254} were 38 % and 31 % respectively. When alum increased 80 to 120 mg/L not much further reduction in DOC an UV_{254} .

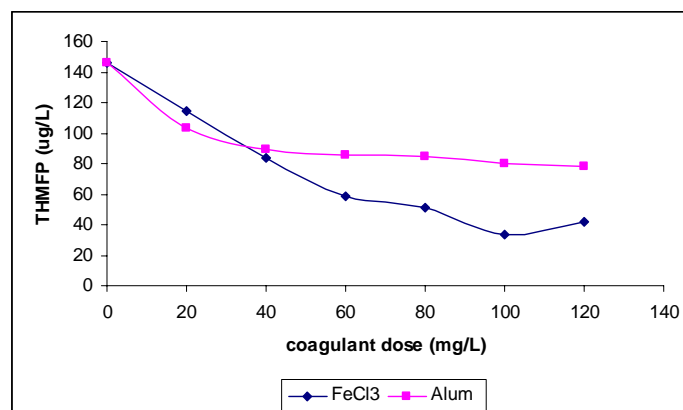


Fig. 5 THMFP as a function of coagulant dose

The total THM (sum of $CHCl_3$, $CHBrCl_2$, $CHClBr_2$ and $CHBr_3$) formed as a function of ferric chloride and alum dosage are shown in Fig. 5. Reduction in THMFP is attributed to removal of THM precursors. The jar test results indicated that ferric chloride was found to be more effective than alum in terms of THMFP removals. The maximum THMFP removal with ferric chloride coagulation was 71 % for 120 mg/L ferric chloride dosage and 47 % for 120 mg/L alum dosages, respectively. The difference between ferric and alum reduction levels of THMFP is attributed to a greater affinity of a fraction of NOM for ferric hydroxide floc than for aluminium hydroxide floc. Moreover, the reduction in THMFP increased with increasing both coagulant dosages.

IV. CONCLUSION

In this study, DOC removal and reduction in UV₂₅₄ absorbance increased with increasing ferric chloride and alum coagulant dose for Porsuk Dam Water. However, ferric chloride proved to be consistently more effective than alum in removing NOM in water as determined by the other researches in literature. Jar test results of Porsuk Dam water can be given as follows;

- Proper FeCl₃ dosage 100 mg/L and DOC removal and UV₂₅₄ removal were 46 % and 55 % respectively.
- Proper Alum dosage 80 mg/L and DOC removal and UV₂₅₄ removal were 38 % and 31 % respectively.
- Ferric chloride is more proper coagulant for PLW.
- UV₂₅₄ removal is bigger than DOC for Ferric chloride and almost same for Alum.
- THMFP reduction was 71 % by using 120 mg/L Ferric chloride.

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