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Improve Coagulation Process To Control The Disinfection By-Products In Water Treatment Plant

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ABSTRACT

This paper describes a laboratory study comparing three coagulants (alum, ferric chloride, and ferric sulfate) to determine which coagulant would not only remove NOM but DBP precursors as well. Experiments were conducted to compare the effectiveness of three coagulants in removing DBPs precursors from raw water samples. The results show that the removal of total organic carbon (TOC) which is mean NOM here, was dependent on the coagulant type and was enhanced with increasing coagulant dose, but ferric chloride, and ferric sulfate have no further considerable effect in case of increasing to high levels. For all the treated samples coagulation with ferric chloride proved to be more effective than alum and ferric sulfate at similar doses and the mean values of treatment efficiencies were 30%, 37%, and 45% by ferric sulfate, alum, and ferric chloride respectively. The range of TOC removal rates obtained using ferric sulfate (18-48%), (14-50%) for alum, and (21-59%) for ferric chloride. Ferric chloride was therefore considered the better chemical for enhancing the coagulation process.Fair removals of turbidity were observed (86%) for ferric chloride, (78%) for alum, and 65% for ferric sulfate. Mean TOC removal using alum was determined to be 61% and much more than results of water coagulation by ferric sulfate which was reported to be 53% in experiments performed for treating Euphrates river water.

Among the Trihalomethanes compounds, chloroform was the common detected Trihalomethanes in the samples collected from Euphrates Riverwere generally below the guideline values, but some samples displayed levels which exceeded the level of WHO Standards for chlorinated compounds. Based on preliminary jar test experiments, ferric chloride at concentrations of 20-30 mg/L was found as an efficient coagulant for disinfection by- products and turbidity reduction.

Keywords: natural organic matter, coagulation, trihalomethane, alum, ferric chloride, ferric sulfate, treatment plant.

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تحسين عملية التخثير للسيطرة على النواتج العرضية لعملية التعقيم بالكلور في محطات معالجة المياه

الخلاصة:

يهدف البحث لدراسة افضل الظروف التشغيلية التي تؤدي الى اعلى كفاءة للمفاعل في تكسير وازالة المواد العضويةالسامة (صبغة المثيل البنفسجية) في المياه الملوثة. المفاعل الشمسي يتكون من لوحة مسطحة من زجاج شفافةعديمة اللون بابعاد(1000x750 x 4 mm) . قاعدة المفاعل مصنعة من الالمنيوم . هذا التصميم يسمح لضوء الدخول الى طبقة السائل من اي اتجاه تقريبا ومن ثم الانعكاس من على طبقة الالمنيوم . تم دراسة تاثير المتغيرات التشغيلية المختلفة على سلوك المفاعل في ازالة الصبغة مثل تركيز المادة العضوية من 10 الى50 ملغم/لتر, تركيز العامل المساعد النانوي (TiO_2) من 200الى 800ملغم/لتر, تركيز (H_2O_2) من 200 الى 1000 ملغم/لتر, حامضية المحلول (pH) من 5 الى 9, تدفق جريان المحلول من 0.3 الى 2 لتر/دقيقة . وجد ان افضل الظروف التشغيلية التي تؤدي الى اعلى كفاءة للمفاعل هي عندما يكون تركيز العامل المساعد 400ملغم/لتر, تدفق جريان المحلول 0.5 لتر/دقيقة, تركيز العامل المؤكسد 400ملغم/لتر وحامضية المحلول (pH) هي 5. تم الحصول على نسبة ازالة 95.27% بعد ساعة واحدة من التشغيل ونسبة ازالة99.95% بعد ثلاث ساعات من التشغيل عند افضل الظروف التشغيلية . ثم تم تحليل المياه الناتجة باستخدام FTIR,UV-spectrophotometer. حيث ان تحليل النتائج أكدت أن المياه المنتجة من نظام مفاعل الشمسي يمكن إعادة تدويرها وإعادة استخدامها بأمان.

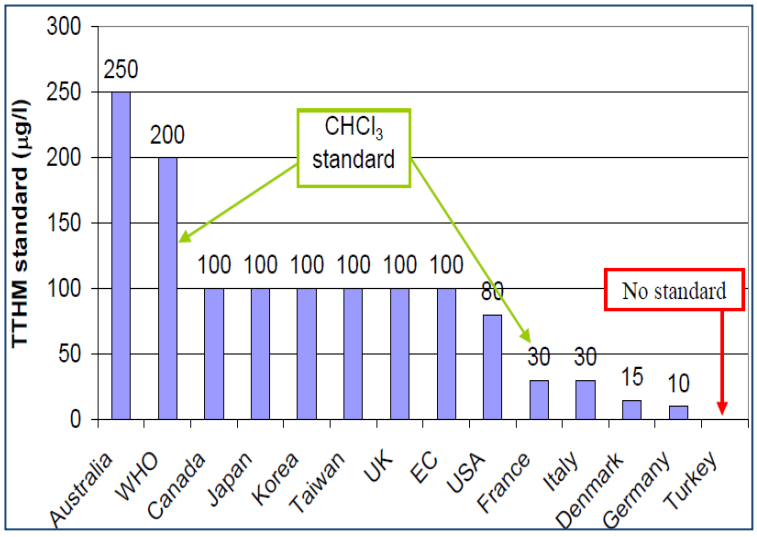
INTRODUCTION

Disinfection byproduct (DBP) is a term used to describe a group of organic and inorganic compounds formed during water disinfection. These byproducts are formed by the reactions between disinfectants and natural organic matter (NOM) or inorganic substances in water. The removal of natural organic matter (NOM) to reduce the formation of disinfection by-products (DBPs), is growing in importance. Enhanced coagulation is thus introduced to most water utilities treating surface water. Disinfection byproducts (DBP) are formed during water disinfection when disinfectants such as chlorine react with the NOM. Many of DBPs are halogenated compounds such as trihalomethanes (THMs), which are suspected to have adverse health effects [1]. A concern regarding the potential health effects of DBPs have resulted in a number of regulations developed by US Environmental Protection Agency This agency has set maximum contaminant levels for total THMs of 0.08 mg/L [2].

Enhanced coagulation is the practice of using coagulant dose in excess of what is normally required for turbidity removal, to achieve a specific reduction of TOC. The enhanced coagulation requirements of TOC reduction are based on the TOC and alkalinity of the source water. In practicing enhanced coagulation, water systems are not expected to optimize or maximize the removal of DBPs precursors. So as not to be cost

prohibitive, systems must meet target percent removals of TOC, where TOC serves as a surrogate for identified and no identified DBPs precursors. The percent removal was developed with recognition of the tendency for TOC removal to become more difficult as alkalinity increases and TOC decreases. In higher alkalinity waters, pH depression to a level at which TOC removal is optimal (e.g., pH between 5.5 and 6.5) is more difficult and cannot be easily achieved through the addition of coagulant alone [3]. NOM removal is higher at low pH values for all coagulants. To achieve the NOM removals, coagulation may be accomplished by increased coagulant dosages, lower coagulation pH values, or both [4]. At several utilities, pH is controlled by the addition of the coagulant. Some utilities, however, focus on independent control of pH through separate addition of acids. Some plants required to implement enhanced coagulation which will not be achieved the removal levels because their water quality characteristics are not unique. The objectives of this investigation were to: compare the effectiveness of alum, ferric chloride, and ferric sulfate in removing DBPs precursors.

The occurrence of THMs and other volatile organics in Iraqi surface water resources were investigated by the previous and present data obtained on raw, coagulated, chlorinated, water samples. The present drinking water directives/ regulations in developed countries set maximum contaminant level (MCL) for THMs at different levels. In Iraq, where the 100% of water demand is supplied by surface water, there is still no regulation for the THMs. The characterization of chlorinated by-products, particularly THMs, is detailed according to raw water origin and treatment technologies currently applied. Fig. 1shows the TTHMs standards in different countries.



Figure(1): TTHMs standards in different countries.

The term "enhanced coagulation" refers to the modification of the coagulation process to achieve greater or maximum NOM removal [5]. Higher doses of coagulant are

used and the pH may be controlled during the coagulation/flocculation stage compared with conditions that maximize turbidity removal. The control of pH during coagulation is one of the most important factors controlling NOM removal [6]. Earlier studies using natural waters in southern Australia have demonstrated that the use of enhanced coagulation (controlled at pH 6) achieved greater removal of dissolved organic carbon (DOC) compared with conventional coagulation(without pH control) at the same alum dose [7].Although conventional water treatment processes (coagulation with alum, sedimentation and filtration) were often designed and operated for turbidity and color removal, and not targeted on the organic precursor removal, they were illustrated to have potential for the removal of some organic contaminants [8;9].

Coagulation with alum was reported to be quite effective in removing hydrophobic and high molecular weight organics. Past reports demonstrated that enhanced coagulation, process of improving the removal of DBP precursors in a conventional water treatment plant could be an effective method for organic matter removal [10;11].

THM measurement assesses the four common THMs with chloroform usually constituting the largest proportion due to being the principal disinfection by-product in chlorinated drinking water [12]. Several chlorination studies have been conducted for THMs as mentioned above. However, this is the first investigation in Iraq related to the formation of a wide range of chlorination by-products including individual species of THMs. The results presented here provide more insight to the THMs concentration which is a necessary objective in minimizing the exposure to THMs in drinking water.

This work was set out to investigate the mechanism of the coagulation with alum, ferric chloride, and ferric sulfate in controlling the generation of THMs in the chlorination process which provided an insight into the use of alum for the removal of THM organic precursors.

NOM removal prior to chlorination is one strategy to reduce the DBP formation is to reduce the concentration of NOM prior to chlorination. Therefore, reducing DBP formation is highly dependent on treatment processes that not only reduce the concentration of NOM but the specific components that contribute to DBP formation (i.e., DBP precursors).

This work was aimed to investigate the influence of using different coagulants of alum, ferric chloride, and ferric sulfate in controlling the formation of DBPs (THMs) in water which provided an insight into the use of coagulant for the removal of THM organic precursors.

Experimental Work

Sample collection and preservation

The tested samples of water used in our experiments were collected from Euphrates River / Iraq. The characteristics of the samples of raw water are shown in Table 1 below:

Table 1: Characteristics of Euphrates river water.

Parameter	Value,	Parameter	Value,

	Average.		Average.
Temperature, ^{o}C	28	Ca, mg/L	98
Turbidity, NTU	22	Mg, mg/L	42
pH	8.2	Chloride, mg/L	129
EC, µms/cm	1234	Sulfate, mg/L	345
Alkalinity, as $CaCo_3$, mg/L	142	TDS, mg/L	834
Total hardness, mg/L	417	TSS, mg/L	60
TOC, mg/L	2.8	Al, mg/L	0

Chemicals

The characteristics, theadvantages and disadvantages of each coagulant and brief explanations of their functioningwere illustrated in Table 2.

Table (2): The advantages and disadvantages of each coagulant.

Chemical Class	Chemical	Advantages	Disadvantages
Hydrolyzing Metallic Salts	Alum (Aluminum Sulfate) $Al_2(SO_4)_3 \cdot 18\ H_2O$	A standard in coagulation /flocculation. Attracts inorganic suspended solids very effectively.	Fast mixing is critical to proper functioning. Non-optimal pH leads to excessive dosage requirements, should be used between pH 5.5 and 7.5, typically requiring alkaline additives to achieve optimum pH. Performance substantially degrades at lower temperatures. Poor efficiency for attracting organic suspended solids. [2] Relatively large dosage required when used alone.
	Ferric Chloride $FeCl_3 \cdot 6\ H_2O$	Alternative to Alum. Ferric chloride is good at attracting inorganic SS. Gives more compact sludge. pH sensitivity is somewhat less than alum. Suitable for usage in the lime-softening process (pH 9).	Lower efficiency for removing organic suspended solids than alum. Fast mixing is critical to proper functioning. Should be used between pH 5.5 – 8.5, typically requiring alkaline additives to achieve optimum pH. Generally large dosage required.
	Ferric Sulfate $Fe_2(SO_4)_3 \cdot 9\ H_2O$		

Jar test experiments

The three coagulants were used to compare their NOM removal capacity. Aluminum sulfate (Alum), ferric chloride, and ferric sulfate were chosen due to their wide-spread use in the water treatment industry. The coagulants were first rapid mixed using a Phipps and Bird stirrer at 100 rpms for 1 minute, then 30 rpms for 30 minutes to promote flocculation, and allowed to settle for 1 hour. Jar tests were all accomplished by use of a standard six paddle gang stirring apparatus with 7.6 cm diameter flat paddle impellers and Gator jars was used at ambient temperature. Addition of coagulant (alum, ferric chloride, or ferric sulfate) was done during rapid mixing and doses applied were 10, 20,

30, 40, 50, and 60 mg/L. Doses above 60 mg/L were not chosen since they were not customary for use in actual plants and had not significant efficiencies. After the end of the jar tests, sampling of the supernatants was conducted by an appropriate tip pipette from the depth of 10 cm below the water surface in the jar, so it was possible to sample the small quantities of settled water for analyses. Samples from treated and raw waters were analyzed for TOC, pH, and turbidity, and measured according to the procedures outlined in Standard Methods immediately after chlorination process [13]. An analysis of TOC was conducted at the private lab (Scientific Research Lab/Al-Diwanya Province), Iraq. Water samples were preserved with sulfuric acid at pH less than two.

Analytical methods

- pH was measured using a Cyborscan (Eutech Instruments).
- TOC measured by a Gas Chromatography (GC, BUCK, USA).Samples for total organic carbon (TOC) analysis were collected from the jars and placed in amber, 40-mL glass vials with Teflon-lined screw caps. They were preserved by addition of phosphoric acid to pH less than two and refrigerated at 4°C until analyzed. Prior to analysis, the samples were purged with oxygen to remove carbon dioxide.
- Turbidity: A 6035 turbid meter (Jenway)was used to give a direct reading of the turbidity of a sample in nephelometric turbidity units (NTU).
- Trihalomethane Test: 60 ml of treated water was chlorinated at 3 mg/L in an amber bottle. After incubation at the above temperatures for72 hours the sample was quenched with ascorbic acid and analyzed for THMs. THMconcentrations were determined using a gas chromatograph with a headspaceautosampler and volatile compounds were detected by an electron capture detector(ECD).

Results and Discussion

The data of all coagulants alum, ferric chloride, and ferric sulfate were used in this study are shown in Fig. 2. This Figure shows a plot of turbidity readings versus dosage that reveals the optimum dose. The flocs resulting from aluminum salts are less dense and slower to form than those from iron salts. However, the advantage of aluminum compounds is shown in a higher efficiency in the neutralization of surface charges and hence in coagulation/flocculation processes (e.g. removal of turbidity) [14]. The effects of coagulant dose on turbidity and TOC removal from a water sample with initial of average turbidity and TOC of 22 NTU and 2.8 mg/L, respectively. There are several important points about the optimum dose. First, it may change from day to day. If there are high raw water turbidity fluctuations, a jar test will be required with each major change. Further, the optimum dose does not always refer to the dose that achieves maximum turbidity removal. If a 10 mg/L increment in dosage produces only a slight improvement in turbidity removal. [15], also observed that turbidity removal was decreased with an increase in pH. They found that 94% of turbidity had been removed when ferric chloride was used as coagulant. About the same results were obtained by several authors in their coagulation-flocculation experiments. The differences in results may be due to different experimental conditions and characteristics of raw water used as most of their studies involved. Nevertheless, the decrease in pH can be explained by the

acidic character of Fe^{3+} or Al^{3+}. When reacting with OH^- ions, aluminum or iron will precipitate in the form of $Fe(OH)_3$ or $Al(OH)_3$ [16].

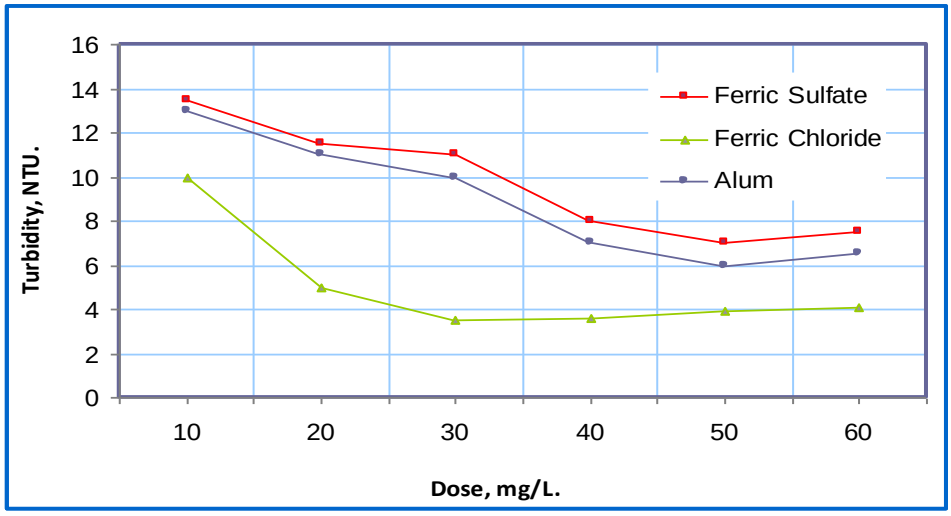


Figure (2): Removal of turbidity at different coagulant dose.

This work was aimed to study the chemical coagulation of NOM. Based on preliminary jar test experiments, ferric chloride at concentrations of 20–30 mg/L was found as an efficient coagulant for TOC and turbidity reduction. The experiments resulted in turbidity removal (86%) for ferric chloride, (78%) for alum, and 65% for ferric sulfate as shown in Fig. 3.

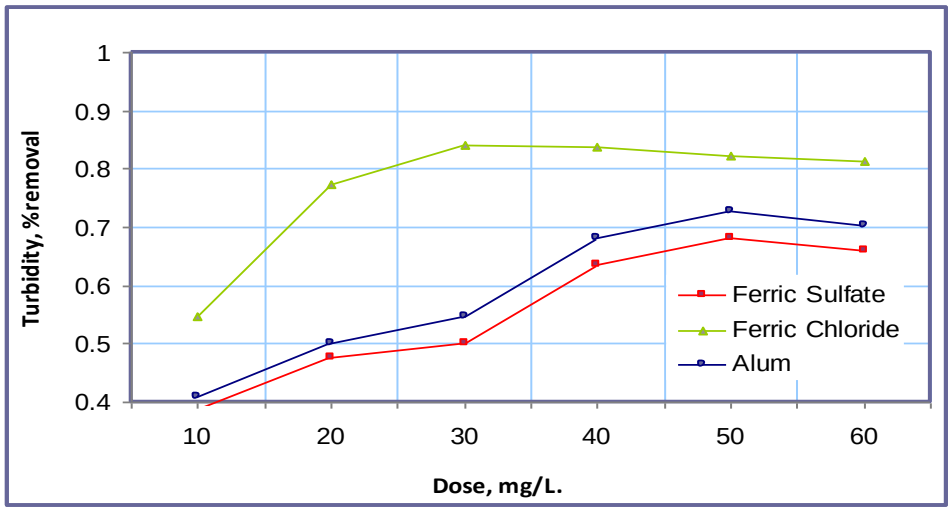


Figure (3): Percent of removal of turbidity at different coagulant dose.

The influence of pH on the removal of suspended solids is important in coagulation process. According to [17], pH is the most important variable in the coagulation process for water treatment. The extent of pH range is affected by the types of coagulant used and by the chemical composition of water as well as by the concentration of coagulant. All common iron and aluminum coagulants are acid salts and, therefore, their addition consumes alkalinity and lowers the pH of the treated water. This is important because pH affects both particle surface charge and floc precipitation during coagulation [5;18]. Fig. 4 shows the effects of coagulant dose on the pH value.

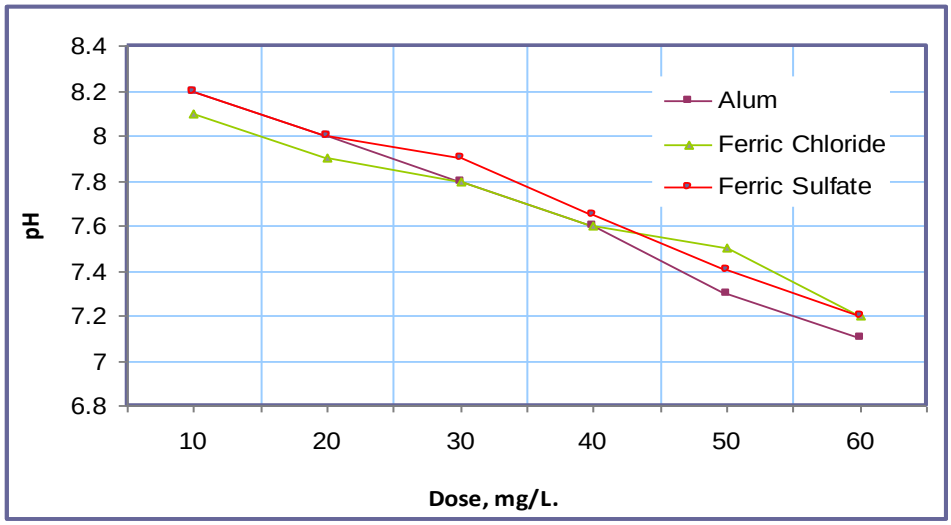


Figure (4): dose pH relationship.

According to Figs. 5 and 6, the results of this research are similar to those found by [6], in their studies concerning NOM removal. Some investigators have reported that iron was superior to alum salts. For example, in Fig. 6, mean TOC removal using alum was determined to be 61% and much more than results of water coagulation by ferric sulfate which was reported to be53% in experiments performed for treating Euphrates river water. Simultaneously, [6;19], reported that the efficiency of organic matter removal can be more increased using ferric chloride as compared with alum. According to above discussion, it appears that colloidal destabilizations as well as humates and fulvates formation both were better accomplished by ferric chloride in dosages much less than the required amounts of alum. In addition, standard ferric chloride solution (40- 45%) is more acidic than 50% alum and so more alkalinity is consumed for formation of ferric hydroxides [19]. Consequently, coagulation pH would be much less with ferric chloride at similar coagulant doses. More favorable pH is undoubtedly the most important reason for better removal of TOC by iron salts. This indicates that the total coagulant demand can be decreased with ferric chloride as shown in Fig. 2. Based on the literatures the solubility of different species of aluminum and iron are least at pHs 6 and 8, respectively.

Fig. 5 indicates that NOM concentration sharply increased to its initial amount by reduction of coagulant dose. Similar results and discussions would also be mentioned about residual iron concentration in drinking water. Accordingly, increasing coagulant dose should not always be considered as a trouble since better NOM removal can occur and so much better water quality would be expected.

Although total organic carbon reduction was chosen as the coagulation goal, removal of other parameters including DBPs was tested. Ferric chloride displayed a considerable better efficacy for NOM removal than ferric sulfate and alum. The mean values of TOC removal were 30%, 37%, and 45% by ferric sulfate, alum, and ferric chloride respectively. The range of TOC removal rates obtained using ferric sulfate (18-48%), (14-50%) for alum, and (21-59%) for ferric chlorideas shown in Fig. 6. In ferric chloride coagulation negative turbidity removal at the lower doses increased with decrease in pH. Alum removed turbidity and colloidal particles at a relatively narrow pH range of 6–9, best at pH 6–7 whereas ferric chloride performs well is larger being 3–10, [19].

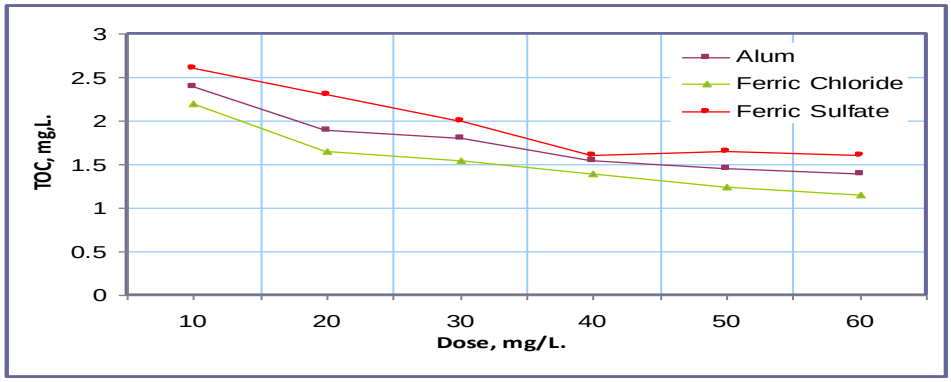


Figure (5): Removal of TOC at different coagulant dose.

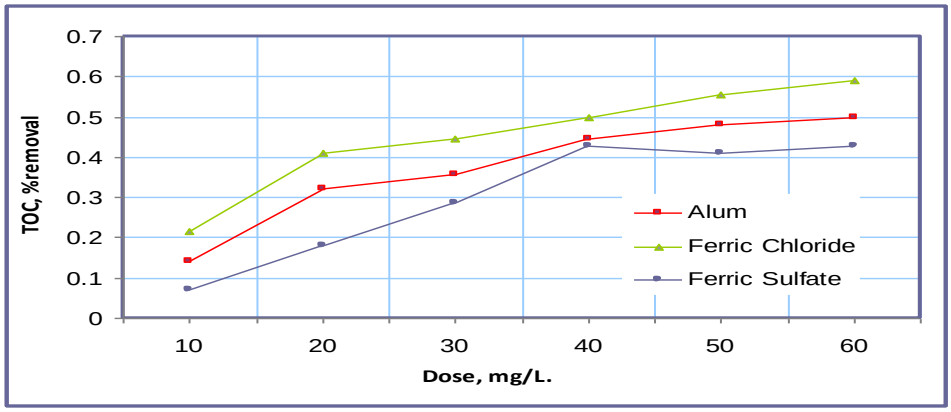


Figure (6): Percent of TOC removal.

Effect of Water Treatment Parameters (Chlorine Dose, pH, and Raw Water TOC Concentration) onTHM Occurrence

Many researchers had stated that the chlorine dosage and reaction time, pH, and raw water organic content as TOC; influence the detected concentration and formation rate of THM within water treatment plants. THMs are formed as soon as chlorine is dosed to water with highest evolution at water treatment plants. [19], reported that the highest TTHM concentrations were found at the water treatment plant, and an expecting increase of these concentrations as contact between the free chlorine residual and naturally occurring organic materials continued throughout the distribution system.

An important factor influencing BP formation is the type of water treatment process the source water is subjected to. THMs are presents in water and through this experiment we can now approve that the concentration of trihalomethanes compound decreases if we use alum as a coagulant and from the results above we can see that the dose of alum of 28mg/L results in minimum concentration. Also we can see that chloroform is the most compound present in water followed by Bromodichloromethane then Chlorodibromomethane and Bromoform is the less one as shown in Figs. 7 to 11.

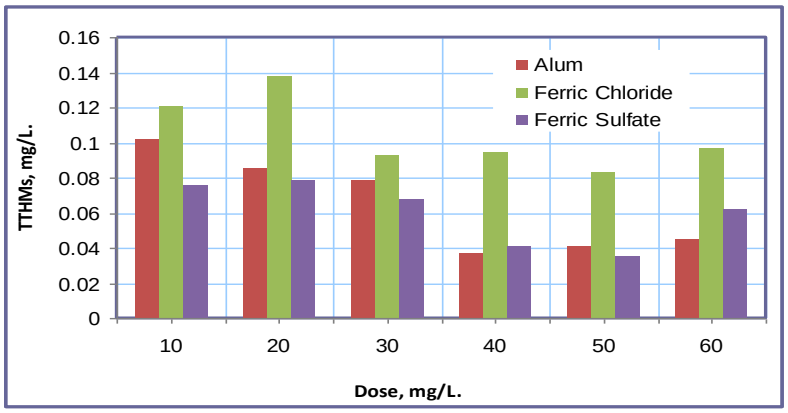


Figure (7): Dose concentration relationship for TTHMs.

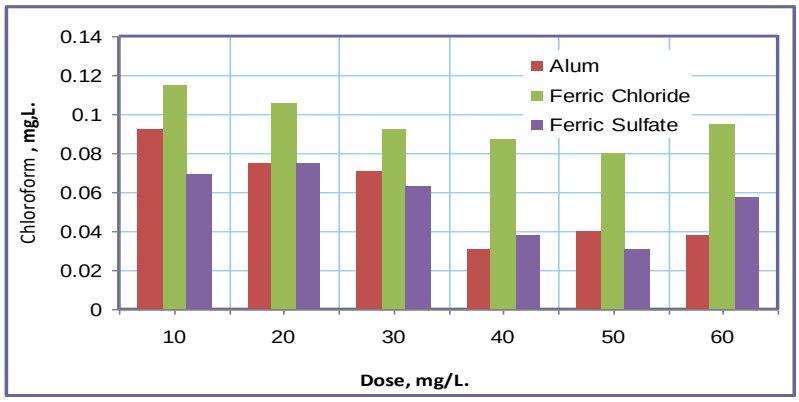


Figure (8): Dose concentration relationship for Chloroform.

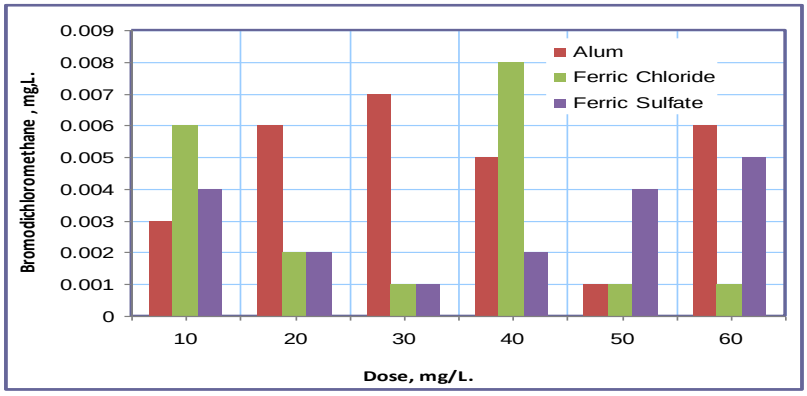
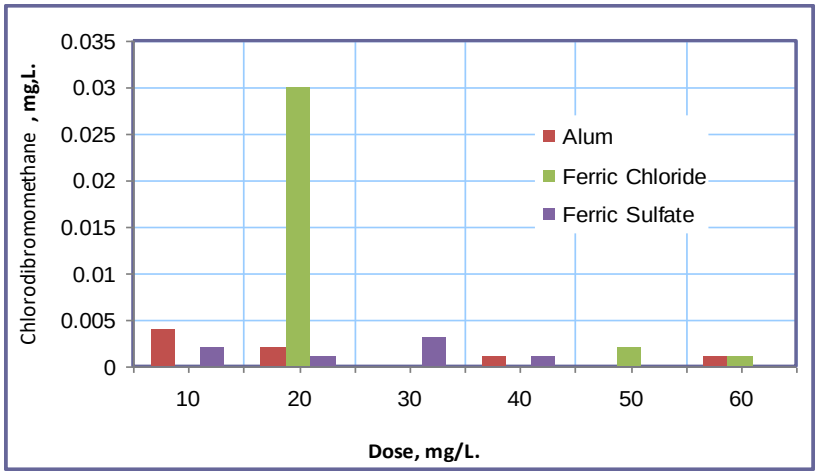
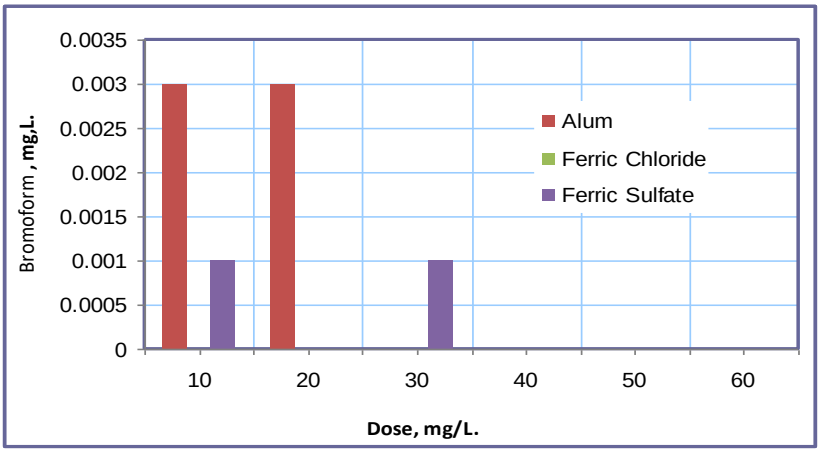


Figure (9): Dose concentration relationship for Bromodichloromethane.



Figure(10): Dose concentration relationship for Chlorodibromomethane.



Figure(11): Dose concentration relationship for Bromoform.

CONCLUSIONS

Although total organic carbon reduction was chosen as the coagulation goal, as overall conclusions:-

1. It could be noted that ferric chloride was one of the best chemicals for enhancing the coagulation process, since it could meet the TOC removal requirements without need to pH adjustment by acids mainly due to provision of higher acidity that results in higher removal of NOM.
2. It was determined that ferric chloride in the range 20 to 30 mg/L showed the greatest removal of THMs.
3. Ferric chloride was found to be generally superior to the other two coagulants in removing all the parameters.
4. Fair removals of turbidity were observed (86%) for ferric chloride, (78%) for alum, and 65% for ferric sulfate. Mean TOC removal using alum was determined to be 61% and much more than results of water coagulation by ferric sulfate which was reported to be 53% in experiments performed for treating Euphrates river water.
5. Ferric chloride displayed a considerable better efficacy for NOM removal than ferric sulfate and alum. The mean values of TOC removal were 53%, 61%, and 74% by ferric sulfate, alum, and ferric chloride respectively. The range of TOC removal rates obtained using ferric sulfate (32-62%), (34-90%) for alum, and (42-88%) for ferric chloride.
6. In ferric chloride coagulation negative turbidity removal at the lower doses increased with decrease in pH. Alum removed turbidity and colloidal particles at a relatively narrow pH range of 6–9, best at pH 6–7 whereas ferric chloride performs well is larger being 3–10.
7. An important factor influencingDBP formation is the type of water treatment process the source water is subjected to. The concentration of trihalomethanes compound decreases if we use alum as a coagulant and from the results above we can see that the dose of alum of 28 mg/L results in minimum concentration. Also we can see that chloroform is the most compound present in water followed by Bromodichloromethane then Chlorodibromomethane and Bromoform is the less one.

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