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Effectiveness of Trihalomethane (THM) Precursors Removal in Groundwater Using Coagulant-Disinfectant

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Abstract: Trihalomethanes (THMs) is a disinfection byproduct (DBP) which forms when disinfectants react with natural organic matter (NOM) in treated drinking water. The coagulation process using ferric salts was able to remove NOM, a DBP precursor, effectively. This study method included the combination of coagulants (ferric-based) with disinfectant(s), to speed up the treatment process in emergency applications. Groundwater samples were treated using either ferric sulphate or ferric chloride, and chlorine in a series of jar tests. Ferric sulphate application showed a good turbidity removal (50.51%) while UV_{254} removal using ferric chloride was as high as 80.76%. Most conditions at pH 5.5 formed lower THMs compared to other pH levels, although the THM level at this pH still exceeded the limit set by authorities.

Keywords: Coagulation, disinfection, THM formation potential, NOM removal.

1. Introduction

Trihalomethanes (THMs) belong to the chlorinated DBP group which comprises four compounds; chloroform ($CHCl_3$), bromoform ($CHBr_3$), bromodichloromethane, BDCM, ($CHCl_2Br$) and dibromochloromethane, DBCM, ($CHBr_2Cl$) [1]. THMs are currently being regulated in most drinking water standards as they have been classified under Group B carcinogens (carcinogenic) which have reportedly caused bladder cancer and birth defects [1]-[3]. THM formation in treated water is a result of the reaction between the disinfectants, such as chlorine, used for water disinfection, with natural organic matters present in natural waters. THM precursors in water can be determined by quantifying these water quality parameters which include total organic carbon, dissolved organic carbon, UV absorbance at 254 nm wavelength (UV_{254}) or specific UV absorbance (SUVA) parameters [4]. According to the Ministry of Health, Malaysia, the maximum allowable limit for total THMs in drinking water is 1 mg/L and it should not exceed the limit to ensure safe and reliable drinking water [5].

Chlorine is the main disinfectant applied in Malaysian drinking water treatment plants due to its effectiveness in destroying bacteria and other pathogens, besides being more economical when compared with other types of oxidants [1]. Apart from that, using chlorine as a disinfectant at the right dose will ensure chlorine residue at the users' end.

Natural organic matter (NOM) is mostly present in natural water sources which can originate from different sources. Since NOM is a heterogenous mixture of organic compounds from the degradation of plant and animal residues, its content in natural water may vary depending on the sources [6]. NOM presence in natural waters is not toxic, however, it can cause aesthetic problems (colour, odour and taste) while also serving as a medium for other

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harmful contaminants to bind. NOM consists of hydrophobic and hydrophilic parts. Hydrophobic parts, which typically have high molecular weight, contain aromatic carbon, phenolic structures and conjugated double bonds, where hydrophobic acids (also called humic substances) have a major portion in aquatic NOM [7]. Hydrophilic NOM (non-humic substances), which is more polar, consists of aliphatic carbon and nitrogenous compounds and usually have low molecular weight. According to Sillanpaa et al., coagulation process has been the top selection in removing NOM from source water as it has been proven to be efficient in removing DBP precursors [8], where metallic-based coagulants are the popular choice.

Two metal salts; ferric and aluminium salts, are most widely used [9] as they are low-cost and efficient in removing turbidity and colour in water in wastewater treatment plants [10]. Aluminium salts are more efficient in removing colour and turbidity, compared to ferric salts [7]. Nonetheless, a few past researchers found that the latter was more efficient in removing NOM compared to the former [11], [12]. Thus, ferric salts would be a more suitable choice to be applied if the main objective is to remove NOM in source water.

Typically, coagulation-flocculation and disinfectant processes are separated into different stages to ensure that the reaction at each stage has been completed. However, in cases of natural disasters or even in rural areas where source water is available but with no proper treatment plant, it is a better idea to provide a simple and rapid treatment method to generate clean and safe drinking water. Therefore, this study aims to determine the best coagulant dosage to be applied simultaneously with disinfectant under different pH, to remove THM precursors. Apart from that, the formation of THM was compared to the drinking water quality standard to determine if this combination is suitable for rapid water treatment.

2. Methodology

This research involved groundwater sampling and the samples were later subjected to jar testing that applied simultaneous coagulation and disinfection processes as the THM formation potential (THMFP) test.

2.1 Sampling Site and Analysis

This study extracted groundwater sample from a borehole located in Universiti Sains Malaysia, Pulau Pinang (coordinate location of 5° 08’ 50.5”N, 100° 29’ 34.7E). The depth of the borehole is 43.575 m with a diameter of 0.2 m. It is located just 1 km away from the Kerian River. It was reported previously in a study by Akbar that this groundwater had elevated organic matter content that might be due to surface water intrusion [14]. Before sampling, the groundwater was purged for two hours to make sure the readings for water quality was stabilised. Submersible pump was used to purge the borehole. This is mainly to make sure the variations in the water quality parameter of the raw water is small (less than 10% differences between the readings). The water sample was stored at 4°C until analysis began. Sampling works were carried out from March till May 2017. The parameters tested for the raw water included pH, temperature, UV_{254}, and turbidity. UV_{254} is a measurement of the amount of light absorbed by organic compounds, specifically aromatic. In water sample, UV_{254} also indicates the concentration of organic matter, especially those containing aromatic rings. All parameters were tested according to the Standard Method for the Examination of Water and Wastewater (Standard Method).

2.2 THM Formation Potential Test

Ferric chloride ($FeCl_3$) and ferric sulphate ($Fe_2(SO_4)_3$) were chosen as coagulants for this study as ferric-based salts were proven to be more efficient in removing NOM [12, 13]. Jar tests were carried out with either $FeCl_3$ or $Fe_2(SO_4)_3$ as coagulants at various pH and coagulant dosages, where the pH range was between 4 – 6 and the coagulant dosage was between 0 – 100 mg/L. Control sample (no coagulant dosage) were carried out for each pH conditions. Coagulants were added simultaneously with chlorine (5mg/L dose) after pH adjustments were carried out. Prior to dosing, chlorine stock solution was prepared from sodium hypochlorite at 1000mg/L and will be tested for the initial condition before dosing. The mixing was carried out as follows: rapid mixing at 300 rpm (30 sec) followed by 250 rpm (2 mins), and later slow mixing at 40 rpm (10 mins) before the samples were left to settle for 20 mins. Then, the supernatant was extracted for THM quantification.

2.3 Sample Extraction and THM Quantification

Before THMs compound can be determined, all samples need to be extracted. 30 mL of sample was extracted following a liquid-liquid extraction (LLE) method as modified from the USEPA 551.1 method [15]. In a 60 ml glass extraction vial equipped with a PTFE-lined screw cap, the sample was adjusted to a pH of~3.5 (under acidic condition) using H_2SO_4 dilution followed by the addition of 1 g copper sulphate and 10 g pre-baked sodium sulphate [15]. 3 mL of Methyl tert-butyl ether (MTBE) with 1 µg/ml bromofluorobenzene (internal standard) was added as the extraction solvent. The extraction vial was shaken vigorously by hand for approximately 4 mins and was allowed to rest for approximately 2 mins to let the water and MTBE phases separate. An aliquot of the extract was removed by using a glass pipette and transferred to a 2 mL GC vial and which was subsequently quantified by gas chromatography with mass spectrometry, GC-MS (Agilent 7890 GC with 5975C MSD ChemStation) [15]. The instrument settings areas seen in Table 1.

Table 1 - GC-MS Settings Details

GC:	Agilent 7890A
Columns:	Restek Rxi-5 Sil MS column of dimensions 30 m x 0.25 mm x 0.25 µM.
Carrier Gas:	Helium constant flow at 1 mL per minute
Injection Volume:	3 mL, splitless
Temperature Programmes:	
Oven:	Initial temperature at 35ºC for 3 min, then 20ºC per minute to 150ºC, 35 ºC per minute to 300ºC and hold for 5 minutes
Injector:	250 ºC
Mass Spectrometer:	Agilent 5975C
MS Quad Temperature:	150ºC
Ion Source:	230ºC

3. Results and Discussion

The groundwater site was selected with prior knowledge from Akbar [14] that it contained higher NOM compared to usual groundwater. This was to allow the maximum THM formation potential that might happen in the presence of elevated NOM levels in source water. Table 2 summarises the characteristics of the groundwater which had been sampled for four times from March till May 2017. pH and turbidity levels were still within the limit stated by the Ministry of Health, Malaysia [5]. When compared with previous research, UV_{254} values in this study were on the higher range compared to other groundwater samples and surface water from past research [16-18].

Table 2 Groundwater characteristics

Parameters	Unit	Min value	Max Value	Average
pH		6.58	7.64	6.92
Temperature	°C	28.33	29.09	28.47
Turbidity	NTU	9.06	42.53	23.7
UV_{254} nm	cm^{-1}	1.002	1.328	1.161

Fig. 1 shows the trends in turbidity removal at different pH levels and $FeCl_3$ dosages. The trends indicated that a higher dosage produced higher percentage of removal; however optimum dosage could not be determined as the percentage of removal kept increasing with the dosage. The highest percentage removal was 44.61% with $FeCl_3$ at 100 mg/L at a pH of 5.5 (control sample – 44.31 NTU, final turbidity – 26.29 NTU). To achieve higher removal, higher coagulant dosage should be tested in order to obtain the optimum pH and dosage. The highest removal at 44.61% was still far from reaching the allowable Malaysian drinking water standard (5 NTU). However, with higher dosage it will be less economical. Thus, using $FeCl_3$ as coagulant simultaneously with chlorine at the tested pH might need additions/alterations of some other conditions to boost the turbidity removal.

Fig. 2 shows the percentage of turbidity removal using $Fe_2(SO_4)_3$ as the coagulant. There is a difference in the removal trend compared to $FeCl_3$. By using $Fe_2(SO_4)_3$, the optimum value obtained was when the pH was 5.0 at the dosage of 80 mg/L. During optimum conditions, the percentage of removal was slightly higher than removal rates recorded when using $FeCl_3$, at 50.51% (final turbidity – 23.49 NTU). However, the initial turbidity for the $Fe_2(SO_4)_3$ experiments were at 46.06 NTU, just slightly higher than the initial turbidity for $FeCl_3$, 44.31 NTU. Thus, when comparing both coagulants, the percentage of removal obtained showed only a slight difference. However, $FeCl_3$ showed the percentage turbidity removal continued to increase even at the same coagulant dose (100 mg/L) compared to ferric sulphate. It can be concluded that the application of $Fe_2(SO_4)_3$ is more economical due to higher removal of turbidity at lower dosage, however higher turbidity removal can be expected with higher dosage of $FeCl_3$. According to a study by Ibrahim and Aziz [14], overdosing the coagulant results in a substantial increase in the amount of generated sludge and a decrease in pH. This might explain the decreases in removal after 80 mg/L for all cases when applying $Fe_2(SO_4)_3$ as coagulant.

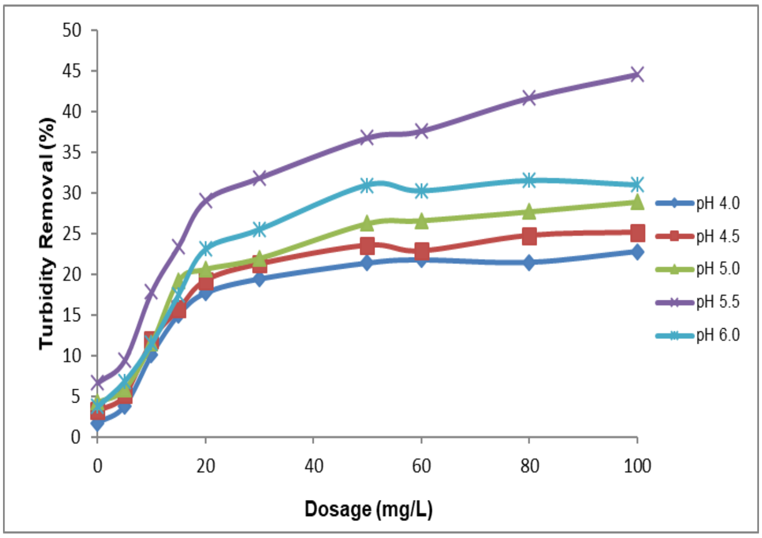

Fig. 1 - Percentage of turbidity removal using $FeCl_3$ as coagulant at various conditions pH and coagulant dose

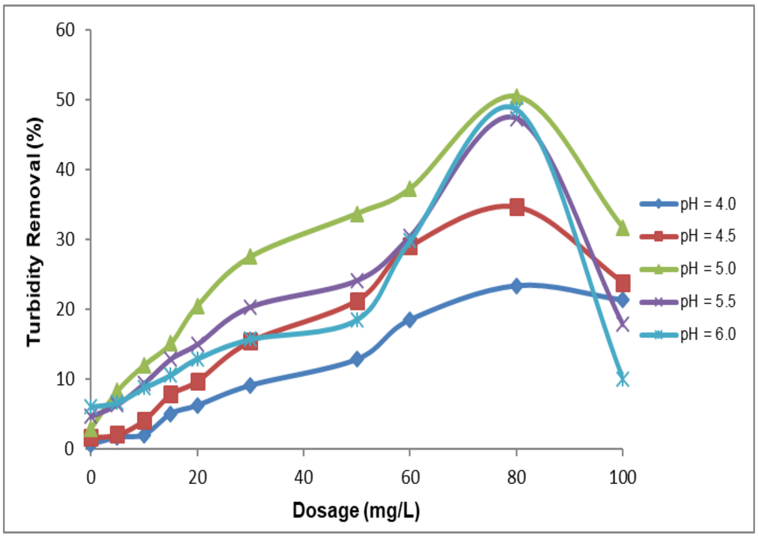

Fig. 2 - Percentage of turbidity removal using $Fe_2(SO_4)_3$ as coagulant at various conditions pH and coagulant dose

Fig. 3 shows the percentage of UV_{254} removal, which produced two peaks at 10 mg/L and 50 mg/L. The first peak shows a low removal rate compared to the second peak illustrating that $FeCl_3$ was effective with only 10 mg/L as it had removed almost 40% of UV_{254}. However, the best value for UV_{254} removal was chosen at pH 5.5 set at a dosage of 50 mg/L, due to higher removal. The highest percentage removal was at 80.76%. As compared to previous research, $FeCl_3$ reached until 55% UV_{254} removal at dosage of 80 mg/L [4]. Furthermore, according to Sulaymon et al. [19], $FeCl_3$ obtained UV_{254} removal about 54% at dosages greater than 40 mg/L. It showed that, UV_{254} removal obtained in this study achieved higher removal rates than previous studies.

Based on Fig. 4, $Fe_2(SO_4)_3$ shows lower percentage removal compared to $FeCl_3$ but at a higher coagulant dose. At pH 5, about 57.63% of UV_{254} was removed when using $Fe_2(SO_4)_3$ compared to 78.84% when using $FeCl_3$. Optimal removal obtained was at pH 5.0 and dosage of 80 mg/L. At lower pH of 4.0 and 4.5, $Fe_2(SO4)_3$ recorded removal trend of less than half the amount of removal at the higher pH, at all dosage. By comparing both coagulants, $FeCl_3$ was a more effective coagulant as it removed higher percentage of UV_{254}. According to Crittenden et al. [20], it was recorded that for treatment plants $Fe_2(SO_4)_3$ application mainly needs higher dosage, on weight basis, (20 – 250 mg/L) compared to $FeCl_3$ (5 – 150 mg/L), which shown that normally $Fe_2(SO_4)_3$ are needed in higher quantity to obtain good removal.

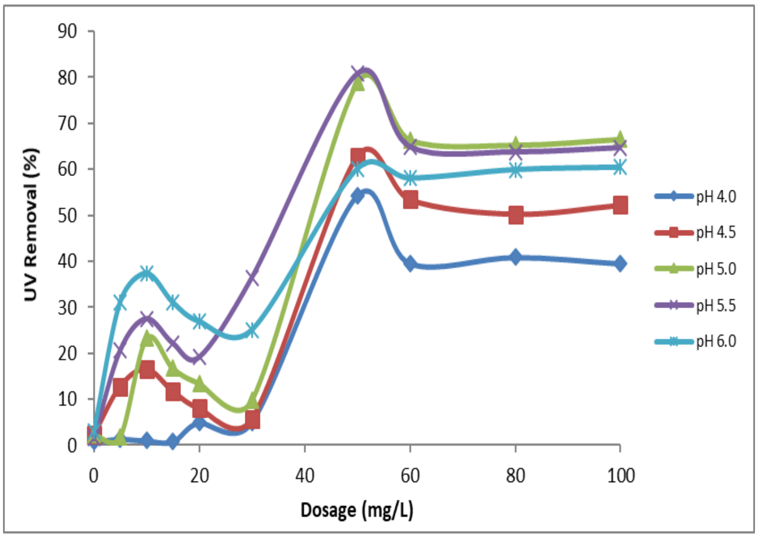

Fig. 3 - Percentage of UV_{254} removal using $FeCl_3$ as coagulant at various conditions pH and coagulant dose

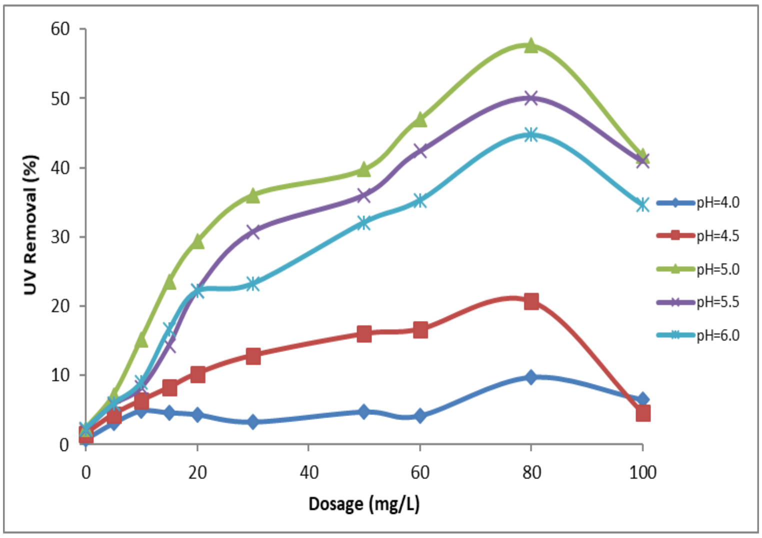

Fig. 4 - Percentage of UV_{254} removal using $Fe_2(SO_4)_3$ as coagulant at various conditions pH and coagulant dose

With regards to the removal of turbidity and UV_{254}, pH 5.0 and 5.5 are the best condition for removal for both $FeCl_3$ and $Fe_2(SO_4)_3$. Thus, THM formation potential experiments were carried out for these two pH levels to determine if THM formation would exceed the standard limits. Fig. 5 shows THM formation at pH 5 for both coagulants. All THM compounds were formed at this stage and BDCM was the dominant compound for both coagulants. For $Fe_2(SO_4)_3$, BDCM formed the highest concentration which exceeded the limit specified by the Ministry of Health and WHO; as more than 0.060 mg/L formed, followed by chloroform, DBCM and bromoform. For $FeCl_3$, BDCM was the major compound formed at the set concentrations which almost exceeded the limit at all dosages except at 5 mg/L (0.087 mg/L) while chloroform and bromoform were not as high. Even though the percentage removal for $FeCl_3$ was lower compared to $Fe_2(SO_4)_3$, the dosage to reach the optimum removal was found to be lower for $FeCl_3$ compared to $Fe_2(SO_4)_3$.

By referring to Fig. 6, higher chloroform formed in groundwater at pH 5.5 for $Fe_2(SO_4)_3$ application (0.16 mg/L at 50 mg/L), whereas when $FeCl_3$ was applied BDCM had higher concentrations. At the same dose of 50 mg/L chloroform was reduced to less than 0.01 mg/L, while BDCM formed was at 0.060 mg/L, which is close to the maximum detection limit. However, BDCM shows a gradual decrease after reaching the highest peak. For $FeCl_3$, all THM compounds formed at lower concentrations compared to $Fe_2(SO_4)_3$. Only BDCM exceeded the limit while other THM compounds did not. Based on Fig. 5 and Fig. 6, the application of $FeCl_3$ with chlorine might have the ability to reduce chloroform formation in the treated water. However, BDCM might be slightly elevated in most cases.

At both pH levels, mostly all four THM compounds were formed, though at different concentrations. By comparing both coagulants with various conditions of pH and dosages, pH 5.5 showed the least formation where most of the compounds formed were still under the limit specified by the two guidelines. This means that THMs formation potential was the least at pH of 5.5. With regards to total THM (TTHM) weight basis, it is still considered unsafe for prolonged use as the TTHM weight exceeded the limit stated (>1 mg/L of TTHM). If consumers drink or use this water for other purposes at an extended period, there is a high health risk.

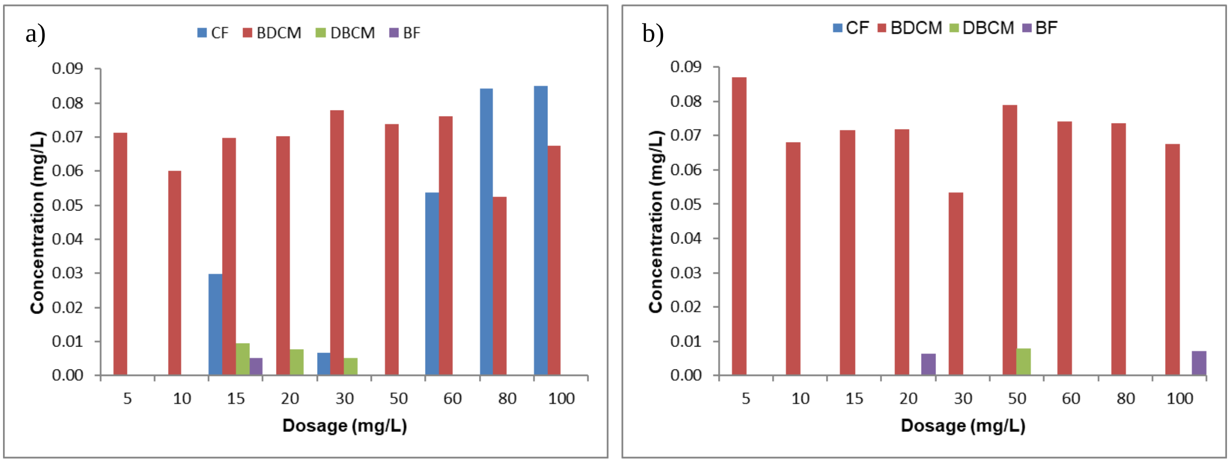

Fig. 5 - Occurrence of THM compound in groundwater at pH 5 using a) $Fe_2(SO_4)_3$ and b) $FeCl_3$

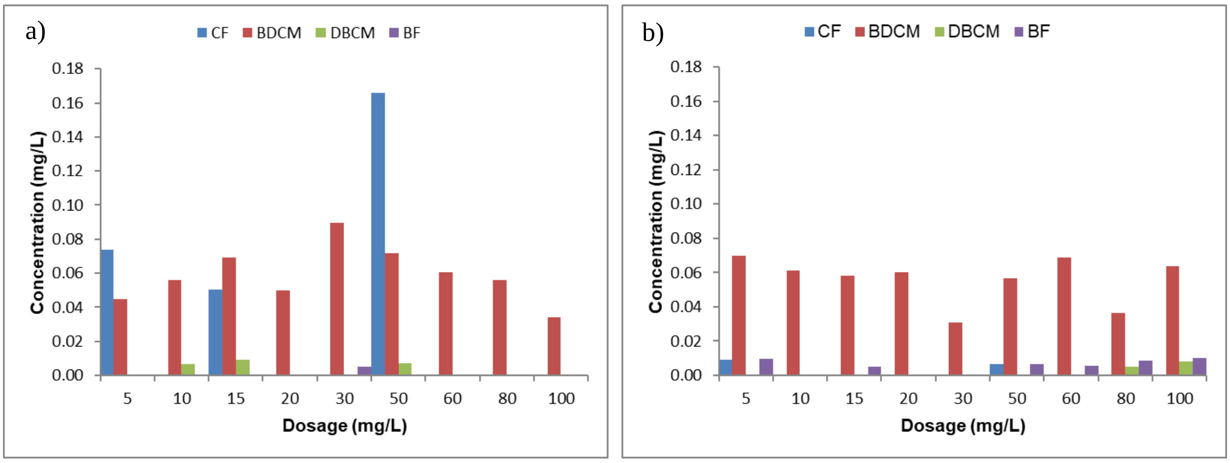

Fig. 6 - Occurrence of THM compound in groundwater at pH 5.5 using a) $Fe_2(SO_4)_3$ and b) $FeCl_3$

4. Summary

This study was conducted to determine the effectiveness of removing THM precursors by using simultaneous coagulant-disinfectants. Groundwater was tested at different pH levels and coagulant dosages. Generally, $Fe_2(SO_4)_3$ application at all the pH tested shown pattern with optimal conditions, however $FeCl_3$ application shown better removal with increment of dosage until 100 mg/L. For $Fe_2(SO_4)_3$, the highest percentage of removal was at 50.51% and 57.63% which indicated highest turbidity and UV_{254} removal, respectively. This was by applying $Fe_2(SO_4)_3$, at the optimal conditions which was at pH 5 and dosage 80 mg/L for both parameters, turbidity and UV_{254}. For $FeCl_3$, the highest percentage of removal was 44.61% and 80.76% for turbidity and UV_{254}, respectively. However, turbidity removal did not show any obvious peak but it could be concluded from the graph that higher dosage of coagulant produced higher turbidity removal. The optimum condition for UV_{254} removal was at pH 5.5 and dosage of 50 mg/L. It would be better to also have dissolved organic (DOC) data so that the correlation of THM formation can be compared with the DOC value. However, due to certain limitations, the authors were not able to present it here. On weight basis, most of the water samples tested at pH 5 and 5.5, which recorded the best removal rate, exceeded the TTHM limit specified by the Malaysian Drinking Water Quality Standard.

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