

Article

Reduction of DBP Precursors and their THMFPs in Leachate Contaminated Groundwater by PAC Adsorption

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Abstract. This research investigated the reduction of dissolved organic matter (DOM) fractions and their trihalomethane formation potentials (THMFPs) by powder activated carbon (PAC) adsorption. Leachate contaminated groundwater around an inactive open-dumping landfill was selected as the raw water. The PAC adsorption reaction was proven to be the pseudo second order kinetic reaction and the Freundlich isotherm. The dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and THMFP removals were 55%, 57%, and 73%, respectively. The hydrophobic (HPO) fraction exhibited a higher THMFP compared to the hydrophilic (HPI) fraction. The results of DOM fractionation show that the use of PAC adsorption produced an efficient 87% reduction of the HPO fraction, which is characterized as having a high reactivity toward THMFP.

Keywords: Adsorption, dissolved organic matter, leachate, powder activated carbon, trihalomethane formation potential.

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1. Introduction

Groundwater is a major natural water source that is used for human consumption. Households in Thailand used up to 18.6 percent of groundwater for various household purposes and 6.7 percent of it for drinking [1]. In the past, groundwater contamination was not as severe. Groundwater was easily treated using conventional processes such as coagulation, flocculation, sedimentation, and boiling. At present, groundwater has been contaminated by human activities, agriculture, and the livestock industry as well as leachate from open-dumping landfills. As a result, the conventional processes are unable to treat contaminants in groundwater successfully.

From 1958 to 1989, Chiang Mai Province in Thailand utilized an open-dumping landfill in Tambon Mae Hia, located in Muang District, to solve the problem of waste management in the Chiang Mai Municipality. Surrounding communities of the landfill site suffered from its odor and leachate [2]. It led to resistance from the surrounding communities. Finally, the open-dumping site was closed. However, the surrounding communities continue to be affected by the leachate contaminated groundwater. Common compounds present in the leachate include natural organic matters (NOMs), phenol, ammonia, phosphate, sulfide salts, inorganic salts, toxins, and heavy metals [3]. When the groundwater was contaminated by the leachate, the groundwater quality degraded and could not be used for consumption. Furthermore, conventional treatment processes were unable to produce adequate clean and safe water. Advance treatment processes such as adsorption and membrane filtration have, therefore, been introduced to supplement the current disinfection process.

NOMs are complex compounds present in water. Parameters representing NOMs in water include the total organic carbon (TOC), total organic nitrogen (TON), absorption of ultraviolet light at a wavelength of 254 nm (UV-254), and fluorescence excitation emission matrix (FEEM). Huo et al. [4] conducted a study of dissolved organic matters (DOMs), a dissolved form of NOMs, in leachate from landfills at different ages. The study shows that the leachate from young landfills contains high protein compounds, while the leachate from moderate and old landfills contains mainly humic acid and fuvic acid compounds. Additionally, it was found that aromatic and aliphatic compounds in leachate increased with the age of the landfill.

The disinfection process is used in water treatment to prevent the spread of diseases in water. Common disinfectants include chlorine, chloramines, and chlorine dioxide. Disinfectants can inhibit harmful microorganisms effectively; however, these disinfectants could react with NOMs in water and form disinfection by-products (DBPs). DBPs, in the form of trihalomethanes (THMs), were first detected in 1974 when chlorine reacted with NOMs in water during a disinfection process [5]. More than 600 species of DBPs have been found and reported. Some of them detected in drinking water have been identified as carcinogenic compounds [6]. Major DBPs, aside from THMs, include haloacetic acids (HAA) and haloacetonitrile (HANs) compounds. Zhang et al. [7] studied the relationship between DOMs and DBPs. Their study found that the characteristics of DOMs affected the chances of the formation of DBPs. Organic acids served as precursors to the formation of trihalomethanes (THMs). Jiarsirikul [8] tested the relationship between the trihalomethane formation potential (THMFP) and TOC in water from shallow wells nearby an open dumping landfill. It was found that the THMFP had a good correlation with the TOC concentration as well as chlorine demand and UV-254. Xue et al. [9] showed the effect of changes in the dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) concentrations on THM and HAN formations. Their results show a positive correlation between DOC and THMs, but no correlation between DON and HANs.

The control and reduction of DBP formation can be carried out by, for example, removing DBP precursors, changing the disinfectant, and/or removing DBPs directly after the disinfection process. DOC and DON are common DBP precursors, and a method could be solely selected or a combination of methods could be used together [10]. The reduction of DBP precursors prior to the disinfection process has been an effective method in reducing the DBP formation potential. Adsorption, ion exchange, and the membrane filtration have also been recommended [11]. The adsorption process using activated carbon as an adsorbent is highly recognized for its ability to remove DOMs [12]. Many advantages of its use have been reported such as its high DOM removal efficiency, ability to remove a wide range contaminant concentrations, and easy application. Furthermore, the adsorption process can be applied in various ways; for example, activated carbon has been applied to reduce a residual aluminium-dye complex and dolomite has been used for fluoride removal [13-14].

This research studies the effectiveness of activated carbon on DBP precursor removal from leachate contaminated groundwater nearby the closed open-dumping landfill in Tambon Mae Hia, Muang District, Chiang Mai, Thailand.

2. Materials and Methods

This research was conducted at the laboratory of the Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University. Details of the research are listed as follows.

2.1. Water Sample

Groundwater from a shallow-well around an inactivated open-dumping landfill in Tambon Mae Hia, Muang District, Chiang Mai, Thailand was collected in a clean plastic container. The water sample was analyzed for pH (HORIBA, pH METER F-21), temperature, alkalinity (titration method, Standard Method 2320B) [15], conductivity (SCHOTT, handy lab LF1), dissolved oxygen (WTW, Oxi 3205), and turbidity (WTW, Turb 430T). The DBP precursor, namely DOC, was measured by a TOC analyzer (O.I. analytical 1010). Total Kjeldahl Nitrogen (TKN) and ammonia nitrogen ($\text{NH}_3\text{-N}$) were measured by 4500-NH₃ F, the phenate method [15]. DON was determined by subtracting $\text{NH}_3\text{-N}$ from TKN. For the DOC and DON measurements, the water sample was filtered through a 0.7 μm GF/F filter and 0.45 μm nylon membrane filter, respectively, prior to the measurements. In order to avoid the organic matter contaminant from the GF/F filters, the filters were combusted at 550 °C prior to use. The nylon membrane filters were rinsed with 100 ml of pure water following by 50 ml of water sample prior to use. The filtered leachate contaminated groundwater was further measured for UV-254 by using a UV/VIS spectrophotometer (Perkin-Elmer, Model Lambda 25) and FEEM by a spectrofluorometer (JASCO, FP-6200). The filtered leachate contaminated groundwater was kept at 4 °C until analysis and experimental use.

2.2. Activated Carbon

Powder activated carbon (PAC) was used in this research. The surface morphology of the PAC was observed by scanning electron microscopy (SEM). The surface properties of the PAC were analyzed using the Brauner Emmet Teller (BET) method [16]. Before using the PAC in this research, the PAC was washed and soaked in pure water for one week to remove contaminants. Then, the PAC was dried at 105 °C for 48 hours in an oven. After that, it was put in a desiccator and ready for use.

2.3. Adsorption Kinetics and Isotherms

The filtered leachate contaminated groundwater was used to study the adsorption kinetics and isotherms. The adsorption kinetics was analyzed by varying the adsorption time from 0 to 24 hours. The initial DOC concentration in the filtered leachate contaminated groundwater was around 6.0 mg/L with a PAC content of 1,000 mg/L, at an approximate pH of 7.0. Then, the filtered leachate contaminated groundwater mixed with the PAC was shaken at 200 rpm at room temperature. Afterwards, they were filtered through a nylon syringe filter with a pore size of 0.45 μm to separate the solutions. The solutions were further analyzed for their remaining DOC concentrations using a TOC analyzer. The adsorption isotherms were studied by varying the PAC dosages: 100, 500, and 1,000 mg/L, respectively. The initial DOC concentration in the filtered leachate contaminated groundwater was around 6.0 mg/L, with an approximate pH of 7.0. The PAC and filtered leachate contaminated groundwater mixtures were shaken at 200 rpm at room temperature. In addition, the equilibrium time of adsorption was based on the kinetic study results. After the equilibrium time, the samples were filtered through a nylon syringe filter with a pore size of 0.45 mm to separate the solutions. The solutions were further analyzed for their remaining DOC concentrations.

2.4. DBP Precursor Removal by PAC

The filtered leachate contaminated groundwater was used to study the removal of DBP precursors by PAC. The PAC dosage was set at 1,000 mg/L. As mentioned above, the equilibrium time of adsorption was based on the kinetic study results. The DOC and DON concentrations, as well as UV-254 and FEEM,

were measured to determine the efficiency of PAC on DBP precursor removal before and after the PAC adsorption tests.

2.5. Formation Potential of DBPs

The filtered leachate contaminated groundwater both before and after the PAC adsorption tests were examined for their THMFP and haloacetonitrile formation potential (HANFP) following Standard Method 5710 B., 4500-Cl B., 6232 B [15]. The THMs were analyzed for chloroform, bromodichloromethane, bromochloromethane and bromo-form, while HANs were analyzed for monochloro acetonitrile, dichloroacetonitrile, and trichloroacetonitrile. The THMFP and HANFP analyses consisted of three steps: (1) a free chlorine residual measurement, (2) liquid-liquid extraction, and (3) sample analysis. For the free chlorine residual measurement, the residual chlorine was measured until its concentration was within the range of 3-5 mg/L by a portable spectrophotometer (HACH, DR/890 colorimeter). Then, it could proceed to the next step. For the liquid-liquid extraction, pentene was used as the solvent. The extracted solution was further taken out and kept in a refrigerator under 4 °C. Finally, the extracted solution was collected and analyzed by gas chromatography, GC-ECD (Hewlett Packard, HP 6890 GC) with an RTX624 column.

2.6. DBP Precursor Fractionation

DOMs in the filtered leachate contaminated groundwater both before and after the PAC adsorption tests were fractionated into two fractions (i.e., the hydrophobic (HPO) and hydrophilic (HPI) fractions) by using DAX-8 resin. The procedure followed a resin fractionation procedure proposed by Leenheer, Marhaba et al., Kanokkantapong et al., and Rakruam and Wattanachira [17-20]. It was acceptable that the difference between the masses of un-fractionated and fractionated organic matters be in the range of 10-15% (% diff.) using DAX-8 resin [21].

3. Principles of the Adsorption Mechanisms

3.1. Adsorption Kinetics

Kinetic model of a pseudo second order model was used to describe the data of DOM removal kinetics. This model has been the most widely used to describe time evolution of adsorption under non-equilibrium conditions. The kinetic model can be expressed by Eq. (1)-(3) [22].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (1)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where k_2 (g/mg.min) are the rate constants of pseudo second-order. q_t and q_e are the amount of DOC adsorbed (mg/g) at t time and equilibrium, respectively.

3.2. Adsorption Isotherms

Adsorption isotherms were evaluated by comparing the obtained data with the Langmuir and Freundlich models. The Langmuir isotherm describes monolayer sorption onto a surface, with sorption occurring only onto sites. There are no interactions between the molecules. The model's equation is as follows [23]:

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \quad (4)$$

where q_0 is the amount of DOC adsorbed per unit weight of PAC in forming a complete monolayer on the surface (mg/g), q_e is the total amount of DOC adsorbed per unit weight of PAC at equilibrium (mg/g), C_e is the concentration of the DOC in the solution at equilibrium (mg/L), and K_L is the constant of sorption (L/mg).

The Freundlich isotherm can be applied with non-ideal sorption on heterogeneous surfaces and multilayer sorption. The model is expressed by the following equation [23]:

$$q_e = K_F C_e^{1/n} \quad (5)$$

where q_e is the total amount of DOC adsorbed per unit weight of PAC at equilibrium (mg/g), C_e is the concentration of the DOC in the solution at equilibrium (mg/L), K_F is the Freundlich constant which can express the capacity of the adsorption process (L/g), and n is the Freundlich constant, which explains the intensity of adsorption (dimensionless).

4. Results and Discussion

4.1. Leachate Contaminated Groundwater

The characteristics of the leachate contaminated groundwater are reported in Table 1. DOC, DON, UV-254, and specific UV absorbance (SUVA) values were 3.4-7.5 mg/L, 0.17-0.60 mg/L, 0.128-0.161 cm⁻¹, and 1.71-4.20 L/mg·m, respectively.

Table 1. Characteristics of the leachate contaminated groundwater.

Water parameter	Range (min-max)
pH	6.52-6.94
Temperature (°C)	24.6-27.0
Alkalinity (mg/L as CaCO ₃)	179-202
Conductivity (µS/cm)	520-675
TKN (mg/L)	0.36-1.09
NH ₃ -N (mg/L)	0.04-0.49
UV-254 (cm ⁻¹)	0.128-0.161
DOC (mg/L)	3.4-7.5
DON (mg/L)	0.17-0.60
SUVA (L/mg·m)	1.71-4.20

A high value of conductivity in the groundwater might be due to the large amount of ions in the leachate. The DOC concentration was relatively higher than the common DOC concentration (<1.0 mg/L) found in groundwater [24]. This could be from leachate contamination. In addition, the results show a low value of UV-254. This implied that the leachate contaminated groundwater contained a small number of aromatic and double-bond organic compounds. The SUVA value was calculated by dividing the UV-254 value with the DOC concentration and multiplying it by 100. The SUVA resulting value was utilized to indicate which type of treatment process was appropriate for the DOMs in the water [25]. When the SUVA value is higher than 4, a high amount of hydrophobic organic matters are present, and the coagulation process would be the suggested approach. In this research, the SUVA value was in a range of 1.71-4.20 L/mg·m. Hence, the adsorption process was preferred over coagulation.

4.2. Properties of PAC

The surface morphology of the PAC is illustrated in Fig. 1. It shows the SEM images of the PAC at different magnifications: 50 (a), 500 (b), and 2500 (c). The PAC provided an unsmooth porous structure.

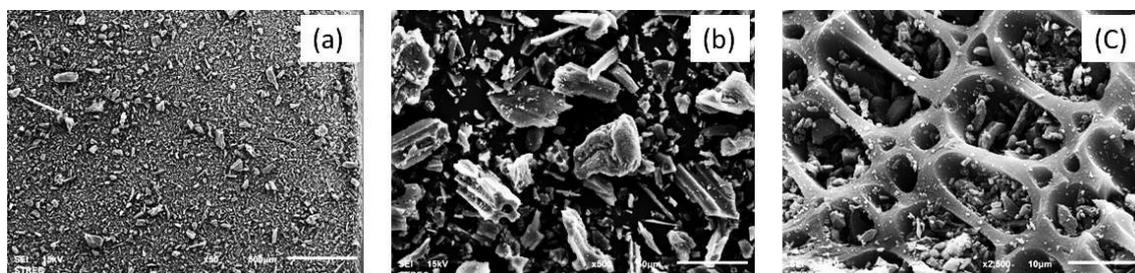


Fig. 1. SEM images of PAC.

The specific surface area, average pore diameter, and total pore volume of the adsorbent were determined using the BET technique. The specific surface area, total pore volume, and average pore size of the PAC were observed at $647 \text{ m}^2/\text{g}$, 0.46 cc/g , and 28.5 \AA , respectively. The specific surface area of PAC used in this study was in the range between 500 and $3000 \text{ m}^2/\text{g}$, which was consistent with others [26-27], while PAC pore size of 28.5 \AA was considered as mesopores. The high specific surface area of the PAC allowed it to have a high organic matter adsorption capacity. This was reported in a study by Leyva and co-workers, who found that adsorbents with higher specific surface areas and total pore volumes could reach higher adsorption efficiencies [28].

4.3. Adsorption Kinetics and Isotherms

Figure 2 illustrates the kinetic adsorption of DOC by the PAC. The PAC adsorbed DOC rapidly in the first 30 minutes. For instance, the DOC adsorbed on PAC was increased with increase contact time to around 2.0 mg/g and then the adsorption gradually slowed until it reached equilibrium after 3 hours.

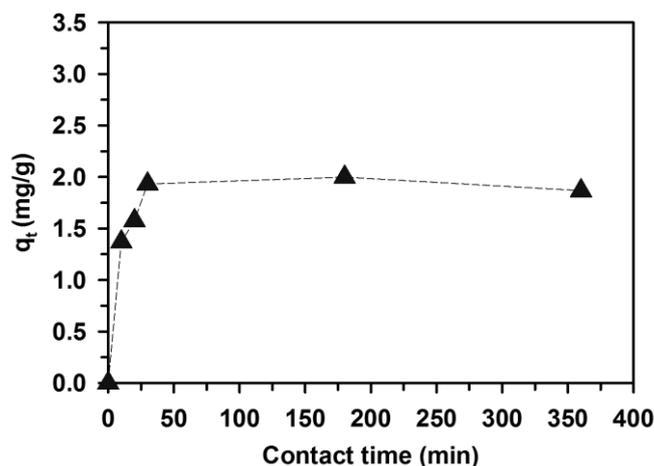


Fig. 2. Kinetic adsorption of DOC adsorbed on PAC.

Kinetic adsorption processes could be divided into three main steps: (i) diffusion across the solute film surrounding the surface of adsorbent; (ii) intra-particle diffusion and (iii) physical adsorption or chemical adsorption at active site of adsorbent [29]. Our result reveals that the pseudo second order model suitably described the DOC adsorption by PAC using leachate contaminated groundwater with coefficients of determination and rate constant of 0.998 and $0.73 \text{ g/mg}\cdot\text{min}$, respectively. It suggests that rate-limiting step of the DOC adsorption probably relates to the chemisorption, involving valence forces through then sharing or exchange of electrons.

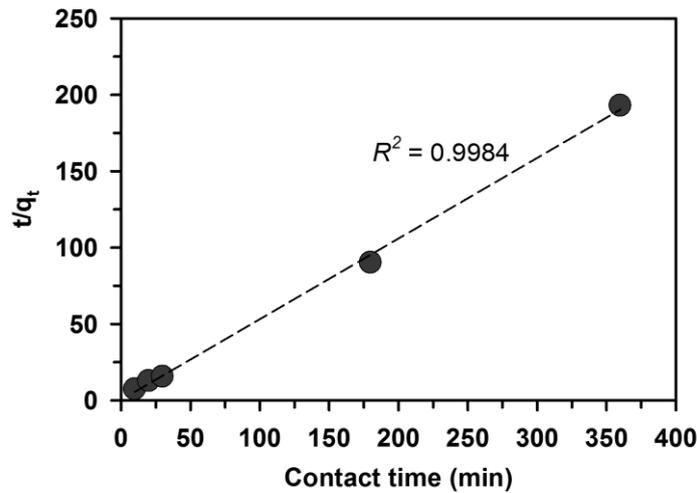


Fig. 3. A plot of the pseudo second-order kinetic model.

The adsorption isotherms of the Langmuir and Freundlich models were evaluated. It was found that the adsorption data of DOC on the PAC best fit with the Freundlich isotherm model with regard to R^2 ($R^2 = 0.97$) as shown in Fig. 4. The K_F and n constants were 2.51 mg/g and 0.336, respectively.

In this study, the DOC adsorption by PAC followed the Freundlich isotherm, which was assumed to have a heterogeneous surface consisting of active sites with different adsorption potentials. Furthermore, the experimental data indicated that DOC adsorption was not restricted to the formation of the monolayer. The result demonstrated that PAC had adsorption capacity to adsorb DOC with K_F value of 2.51 mg/L. It was similar to K_F value of antrazine adsorption by PAC (K_F of 2.59 mg/L) [30]. DOC removal by PAC was possibly associated to the interaction between carboxylic function group of DOM and positive charged reactive site of PAC.

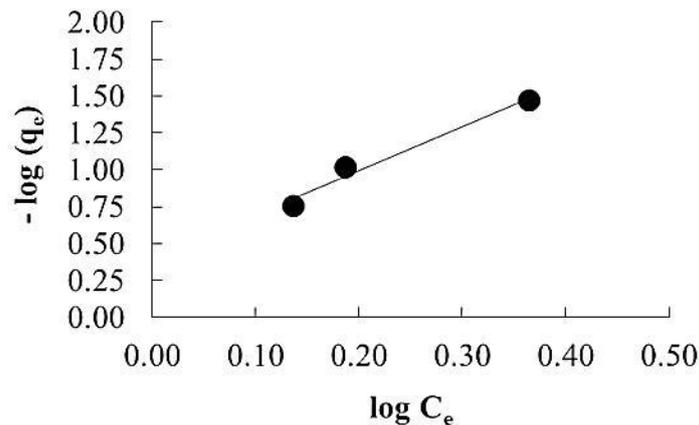


Fig. 4. A plot of the Freundlich model.

4.4. Treatment of Leachate Contaminated Groundwater by PAC

4.4.1. DBP precursor fractionations

The DBP precursors were reported in terms of their DOC and DON. The DOC, DON, and UV-254 values of the leachate contaminated groundwater before PAC adsorption were 7.5 mg/L, 0.60 mg/L, and 0.128 cm⁻¹, respectively. After PAC adsorption, those values were observed at 3.4 mg/L, 0.26 mg/L, and 0.009 cm⁻¹, respectively. The DOC and DON reductions were calculated to be 55% and 57%, respectively. This implied that the PAC could moderately remove the DBP precursors DOC and DON.

With regard to the fractionation of DOC, the leachate contaminated groundwater before and after PAC adsorption was fractionated into the HPO and HPI fractions as shown in Fig. 5. Before PAC adsorption, the DOC concentrations of the HPO and HPI fractions were 2.3 and 4.1 mg/L, respectively. Hence, the HPO and HPI fractions were observed at 36% and 64%, respectively. After PAC adsorption, the DOC concentrations of the HPO and HPI fractions were 0.3 and 2.8 mg/L, respectively. Thus, the HPO and HPI fractions were observed at 11% and 89%, respectively. These results elucidated PAC's ability to adsorb the HPO fraction efficiently [31]. It furthermore provided a significant reduction in the UV-254 value. In addition, the concentration of DON was quite low, when DON was separated into DON fraction as HPI and HPO. The DON concentration of HPI and HPO fractions were non-detectable. Therefore, a fractionation based on DON was not achieved.

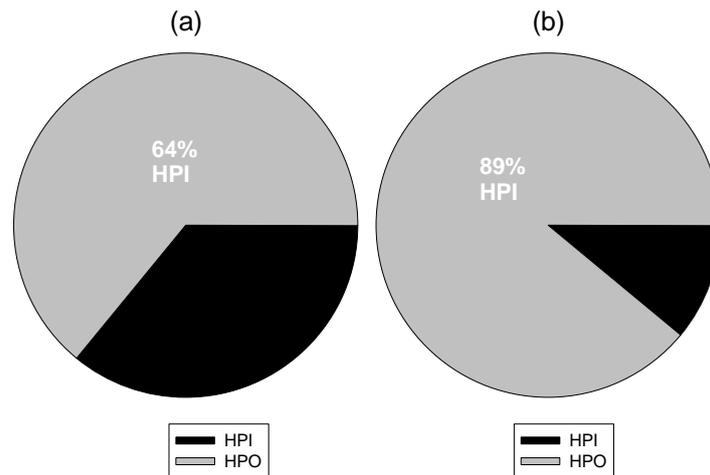


Fig. 5. DOC distribution of HPO and HPI fractions of (a) the leachate contaminated groundwater and (b) after PAC adsorption.

4.4.2. FEEM results

FEEM of water samples were analyzed by spectrofluorometer. The spectra of FEEM in which fluorescence intensity (arbitrary units) was represented as function of excitation wavelength of 220–600 nm and emission wavelength of 200–600 nm. The FEEM spectra of all water samples were subtracted with the FEEM spectra of pure water. Three-dimensional contour plots were produced by plotting fluorescence intensity as a function of emission (x-axis) and excitation (y-axis) wavelength using statistical analysis software [20]. Three fluorophores, labeled A, B, and C, were observed in the leachate contaminated groundwater before (a) and after (b) PAC adsorption, as presented in Fig. 6.

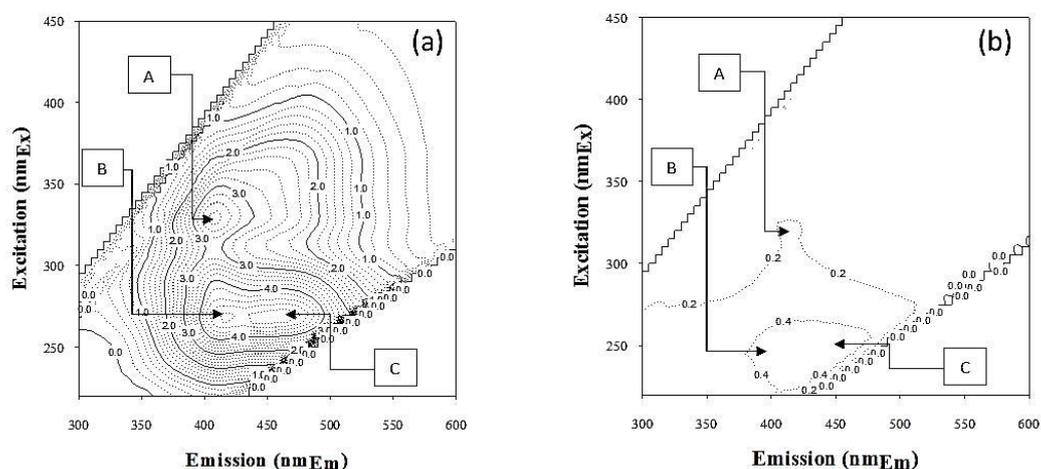


Fig. 6. FEEM results of the leachate contaminated groundwater before (a) and after (b) PAC adsorption.

Peak A occurs at an excitation wave length of 325 nm and an emission wavelength of 410 nm (Ex: 325 nm/Em: 410 nm). Peak A was assigned to fulvic-like substances [32]. Peak B occurs at an excitation wave length of 270 nm and an emission wavelength of 420 nm (Ex: 270 nm/Em: 420 nm), while Peak C occurs at an excitation wave length of 270 nm and an emission wavelength of 440-470 nm (Ex: 270 nm/Em: 440-470 nm). Peaks B and C were assigned to the so called humic acid-like fluorescence [33]. After PAC adsorption, all the intensities of Peaks A-C diminished significantly (Fig. 6(b)) indicating the effectiveness of PAC adsorption as a treatment for the leachate contaminated groundwater. Humic and fulvic-like substance which obtained from FEEM results is more hydrophobic character than non-humic substance. After PAC adsorption, the peaks of fulvic and humic-like substance were disappeared. It can be indicated that the PAC adsorption could reduce HPO character from leachate contaminated groundwater. The results were in a close agreement with the previous section which found that PAC adsorption was efficiently to remove HPO fraction.

4.4.3. THMFP results

Figure 7 shows the THM species present in the leachate contaminated groundwater before PAC adsorption. The THMFP of the leachate contaminated groundwater before PAC adsorption was 1,384 $\mu\text{g/L}$. This indicated that the organic matter in this water could actively form THMs when in contact with chlorine. The untreated leachate contaminated groundwater consisted of four forms of THMFP species: chloroform at 893 $\mu\text{g/L}$, bromodichloromethane at 403 $\mu\text{g/L}$, dibromochloromethane at 40 $\mu\text{g/L}$, and bromoform at 48 $\mu\text{g/L}$. When this untreated groundwater was fractionated into the HPI and HPO fractions, the HPI fraction of the untreated groundwater showed chloroform at 415 $\mu\text{g/L}$, bromodichloromethane at 350 $\mu\text{g/L}$, dibromochloromethane at 56 $\mu\text{g/L}$, and bromoform at 57 $\mu\text{g/L}$, representing a THMFP of 878 $\mu\text{g/L}$. The HPO fraction of the untreated groundwater showed chloroform at 929 $\mu\text{g/L}$, bromodichloromethane at 8 $\mu\text{g/L}$, and bromoform at 39 $\mu\text{g/L}$, representing a THMFP of 976 $\mu\text{g/L}$. It was found that the THMFP of the HPO fraction was higher than that of the HPI fraction even though its DOC concentration was lower. These results are consistent with the results of Rakruam and Wattanachira [18], who found a higher THMFP in the HPO fraction. This indicates that the HPO fraction was highly reactive with chlorine in the forming of THMs. However, a HANFP could not be detected due to its very low concentration. Among the THM species, chloroform exhibited the highest concentration. This result corresponded well with reports by Rakruam [34] and Krutklom [35] of THMFP formation in unpleasant water.

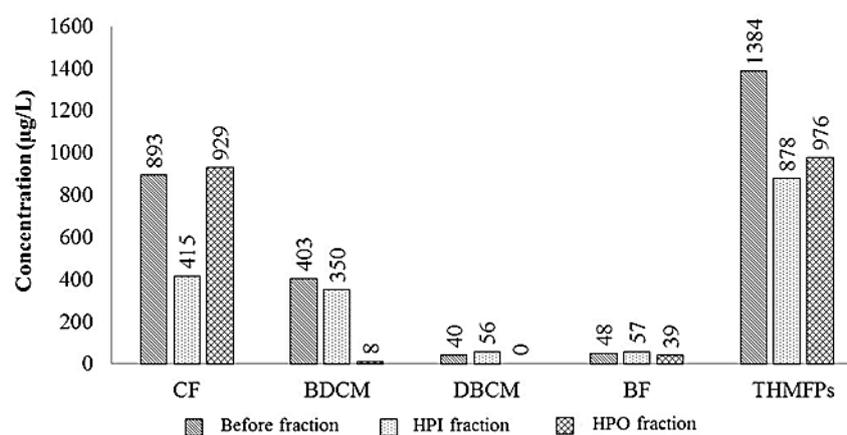


Fig. 7. THM species in the leachate contaminated groundwater before PAC adsorption.

The THM species in the leachate contaminated groundwater after PAC adsorption are also illustrated in Fig. 8. Chloroform showed the highest reduction of 91% after PAC adsorption, followed by bromodichloromethane at 54% reduction, respectively, whereas the amounts of dibromochloromethane and bromoform did not change. After PAC adsorption, the THMFP of the treated leachate contaminated groundwater was reduced, as shown in Table 2. After the leachate contaminated groundwater was treated

by PAC adsorption, the THMFP value clearly decreased. The THMFP values of the un-fractionated sample, HPI fraction, and HPO fraction in the untreated water were 1,384, 878, and 976 $\mu\text{g/L}$, respectively. The THMFP values of the un-fractionated sample, HPI fraction, and HPO fraction in the treated water were 367, 418, and 132 $\mu\text{g/L}$, respectively. Those results provided reductions of 73%, 52%, and 86%, respectively. It has been explained that a removal of DBP precursors (e.g., DOC) could lead to a lower THMFP [36]. Furthermore, the HPO fraction showed a higher reduction percentage of the THMFP compared to the HPI fraction. As mentioned earlier, HPO fraction was found to react better to chlorine to form THMs with respect to HPI fraction. Hence, the high reduction of HPO fraction resulted in high reduction of THMs.

Table 2. Reduction of the THMFP by PAC adsorption.

Leachate contaminated groundwater	THMFP ($\mu\text{g/L}$)			DOC (mg/L)			DON (mg/L)
	Un-fractionated	HPI	HPO	Un-fractionated	HPI	HPO	Un-fractionated
Untreated water	1,384	878	976	7.5	4.1	2.3	0.60
Treated water	367	418	132	3.4	2.8	0.3	0.26
% Reduction	73%	52%	86%	55%	31%	87%	57%

The higher ability of DOM in term of HPO fraction to form THMs than HPI fraction was confirmed by specific THMFP study. The specific THMFP is the ratio between the THMFP of each fraction and its DOC concentration which used to determine the reactivity of DOM to form THMs as shown in Table 3. The specific THMFP values of the un-fractionated sample, HPI fraction, and HPO fraction in the untreated water were 184.5, 214.1, and 424.3 $\mu\text{g/L}$, respectively. The specific THMFP values of the un-fractionated sample, HPI fraction, and HPO fraction in the treated water were 107.9, 149.3, and 440.0 $\mu\text{g/L}$, respectively. Those results provided reductions of 42%, 30%, and -4%, respectively. HPO was found to have a high specific THMFP value in the untreated groundwater. This confirmed that the HPO fraction was highly reactive with chlorine in forming THMs. These results correlate with the results of Rakruam and Wattanachira [20], which show that HPO gave a higher specific THMFP. Surprisingly, the specific THMFP value in the HPO fraction of the treated groundwater increased from 424.3 $\mu\text{g/mg}$ to 440.0 $\mu\text{g/mg}$. One reason for this is that chlorine could directly and easily react with the HPO fraction in the groundwater after some competitive organic matters were adsorbed by the PAC.

Table 3. Specific THMFP.

Leachate contaminated groundwater	Specific THMFP ($\mu\text{g/mg}$)		
	Un-fractionated	HPI	HPO
Untreated water	184.5	214.1	424.3
Treated water	107.9	149.3	440.0
% Reduction	42%	30%	-4%

The drinking water standard of THMs in Thailand was set according to the WHO guideline value. It states that chloroform must be lower than 300 $\mu\text{g/L}$, bromodichloromethane lower than 60 $\mu\text{g/L}$, dibromochloromethane lower than 100 $\mu\text{g/L}$, and bromoform lower than 100 $\mu\text{g/L}$, and the sum of the ratios of THMs to their guideline values ($G.V.$) must be lower than 1 [37]. The sum of the ratios was calculated as follows:

$$\frac{C_{\text{Chloroform}}}{GV_{\text{Chloroform}}} + \frac{C_{\text{DBCM}}}{GV_{\text{DBCM}}} + \frac{C_{\text{BDCM}}}{GV_{\text{BDCM}}} + \frac{C_{\text{Bromoform}}}{GV_{\text{Bromoform}}} \leq 1 \quad (6)$$

where C represents the concentration of the THM specie.

The chloroform and bromodichloromethane concentrations in the untreated groundwater were higher than the standard. In addition, the sum of the ratio of the THMs of this water was 12.2, which was higher than the standard value. Therefore, organic matters needed to be removed prior to the chlorine disinfection process. After PAC adsorption, chloroform was reduced until its concentration met the standard; the same was true for dibromochloromethane and bromoform. Unfortunately, the bromodichloromethane concentration was still higher than the standard. Moreover, the sum of the ratio of the THMs of this water was 4.4. Therefore, an additional treatment process must be added to meet the THM standard.

Based on these results, it should be mentioned that the water treatment process used should be satisfactory to reduce the HPO fraction prior to the chlorine disinfection process, as the HPO fraction in this study was present at a low concentration in terms of its DOC in the leachate contaminated groundwater. This is because of its high potential for forming THMs. From the results, it was concluded that the formation of THMs did not only depend on the concentration of a precursor (i.e., DOC or DON) but also the DOM fractions.

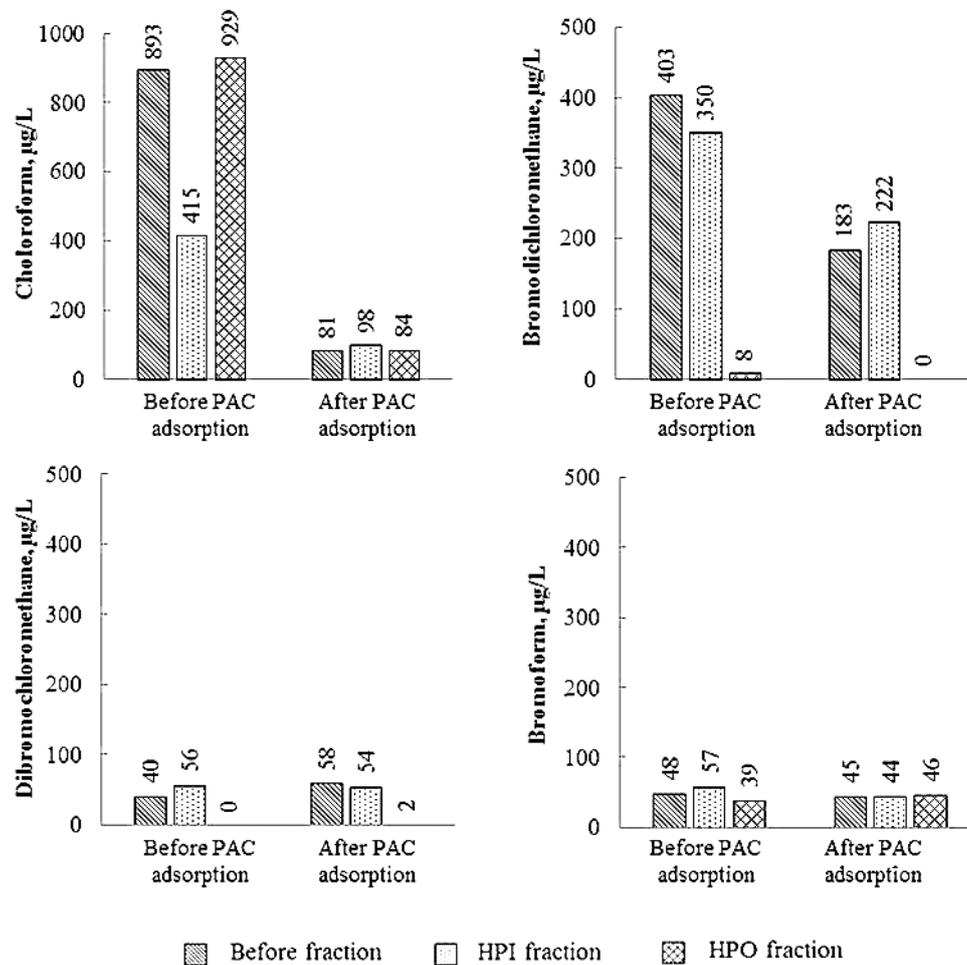


Fig. 8. THM species before and after PAC adsorption.

5. Conclusion

In this investigation, PAC adsorption was able to moderately improve the leachate contaminated groundwater. DOC, DON, and THMFP could be reduced by 55%, 57%, and 73%, respectively. The HPO fraction showed a higher THMFP compared to the hydrophilic fraction (HPI), and HPO fraction was identified as high reactivity toward THMFP. Although the HPO fraction could be successfully reduced by 87% after PAC adsorption, its specific THMFP remained high. The formation of THMs did not only depend on the concentration of a precursor but also the DOM fractions that were fractionated. Although

the HPO fraction was treated efficiently, the specific THMFP of the HPO fraction remained high, requiring the use of an additional water treatment prior to the chlorine disinfection process.

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