REMOVAL OF HALOACETIC ACIDS (HAAs) IN WATER SUPPLY BY COAGULATION - FLOCCULATION AND ACTIVATED CARBON ADSORPTION PROCESSES

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บทคัดย่อ

กรดฮาโลอะซิติก (HAAs) เป็นสารกลุ่มที่มีศักยภาพในการก่อมะเร็งซึ่งเกิดขึ้นในกระบวนการฆ่าเชื้อโรคด้วยสารคลอรีนของระบบผลิตน้ำประปา งานวิจัยนี้มีวัตถุประสงค์เพื่อกำจัดสารอินทรีย์ธรรมชาติ (NOMs) ที่เป็นสารตั้งต้นของการเกิด HAAs โดยกระบวนการสร้างและรวมตะกอนซึ่งการใช้สารสร้างตะกอน PACl ที่ความเข้มข้น 30 mg/L ร่วมกับสารช่วยสร้างตะกอน Cationic Polymer ที่ความเข้มข้น 0.5 mg/L มีประสิทธิภาพกำจัด NOMs ได้แก่ ความขุ่น และ dissolved organic carbon (DOC) เท่ากับ 96.84% และ 64.42% ตามลำดับ และมีวัตถุประสงค์เพื่อกำจัด HAA_5 โดยการดูดซับด้วยถ่านกัมมันต์แบบเกล็ดชนิด Coconut shell activated carbon (GAC) ซึ่ง HAA_5 ที่เกิดขึ้นเท่ากับ 24.35 µg/L เมื่อมีการเติมสารคลอรีนที่ความเข้มข้น 0.5 mg/L ในน้ำที่ผ่านกระบวนการสร้างและรวมตะกอน ปฏิกิริยาการดูดซับ HAA_5 ของ GAC เกิดขึ้นเพียงชั้นเดียวมีการดูดซับทางเคมีร่วมอยู่ด้วย และพื้นที่ผิวมีจำนวนที่แน่นอน โดยมีค่าความสามารถในการดูดซับ HAA_5 ให้ค่าสูงสุดเท่ากับ 44.05 µg/g และเมื่อกำจัด HAA_5 ด้วยการทดลองแบบคอลัมน์ประสิทธิภาพกำจัด HAAs เกิดขึ้นสูงสุด 100% ซึ่งอัตราเร็วการไหลที่ช้าและชั้นความสูงของ GAC ที่เพิ่มขึ้นมีผลทำให้ประสิทธิภาพการกำจัดสูงขึ้น โดยมีค่าความสามารถในการดูดซับ HAA_5 เท่ากับ 68.38 µg/g

คำสำคัญ: กรดฮาโลอะซิติก (HAAs), กระบวนการสร้างและรวมตะกอน, กระบวนการดูดซับ, น้ำประปา

ABSTRACT

Haloacetic acids (HAAs) is a substance in the group of acids having the potential to cause cancer The acid is found in the process of water disinfection The purpose of this study are 1) to remove natural organic matters (NOMs) which is the initial substance of HAAs from the coagulation-flocculation process. In the process, PACl with the concentration of 30 mg/L mixed with cationic polymer with the concentration of 0.5 mg/L. could remove NOMS which were 96.84% turbidity and 64.42% dissolved organic carbon (DOC), 2) to remove HAAs by using Coconut shell activated carbon (GAC) to absorb. When chlorine substance with the concentration of 0. 5 mg/ L was added in the water in the process of coagulation-flocculation, HAA_5, was 24. 35 µg/ L. The adsorption reaction of HAA_5 and GAC was monolayer together with the chemical adsorption. And specific of surface area. The capacity of the adsorption yielded the highest value which was 44.05 µg/g. When HAA_5 was removed by the column test,

100% HAAs was removed. The slow rate of the flow and the height of GAC which increased resulted in high removal ability. The ability of the adsorption was 68.38 µg/g.

KYEWORDS: Haloacetic acids (HAAs), Coagulation-flocculation process, Adsorption process, Water supply

1. Introduction

Water is important to living things. In the past a few problems could be found in consuming water from natural water resources. On the contrary, at present, natural water has been contaminated. The quality of water is lower. Consequently, the quality of water should be improved by the water irrigation process. Water with the good quality must meet the required standard, clean, not contaminated by toxic substances and diseases so that it can be used and consumed safely.

According to previous studies, water from surface water sources is contaminated by natural organic maters (NOMs) in the range of 1.2-10.6 mg/L per liter [1]. There are both organic and inorganic substances in water. In most water irrigation process, there are steps in removing water color, turbidity, organic and inorganic substances including and suspended solids by coagulation-flocculation process [2]. In order to reduce the contamination of microorganisms, which can affect the consumers' health in water, in the water irrigation process, Chlorine has been added in water to kill diseases. However, the disinfection method caused residues in water which are Halogenated organic by-products. The by-products, Trihalometen acids (THMs) and Haloacetic acids (HAAs), are the substances in the group of substances which tends to cause cancer [3, 4, 5]. HAAs are colorless compounds, vaporize a little, can dissolve in water easily and rather stable. There are 9 types of HAAs but the law controls only 5 types of them in drinking water since they affect human's health. The 5 types are monochloroacetic acid (MCAA) dichloroacetic acid (DCAA) Ttichloroacetic acid (TCAA) monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) [6] US. EPA. has set the standard of the toxic to be not more than 60 µg/L [3]. From the investigation of the water quality in Mahasarakam province, the contamination of HAAs is 39.37 µg/L [7]. Moreover it was found that the contamination of HAAs in Alaskan City, Spain is 50.41 µg/L [8]. There are several methods to remove HAAs in water. For example, 27 - 58% of HAAs can be removed by coagulation-flocculation method [9, 10], 20 - 37 % by ozone [10, 11] or 72.4 – 94% by activated carbon adsorbent [12, 13].

To sum up, the study was conducted to investigate the results of HAAs (MCAA, DCAA, TCAA, MBAA and DBAA) removal in the water supply by coagulation-flocculation method in combination with the use of activated carbon adsorbent to improve water quality. The method in this study can be an alternative in improving the quality of water from the water supply to reduce the risk in taking in the substances which can cause cancer.

2. Materials and methods

2.1 Sample preparation

The sample was synthesized HAA_5 which included MCAA, DCAA, TCAA, MBAA and DBAA with the concentration of 25, 30, 50, 60, 75, 100, 200 and 300 µg/L by US.EPA. Method 552.2. [14,15], after adding 2 ml of concentrated H_2SO_4, 16 g of Na_2SO_4, and the surrogate standard (2,3-dibromopropionic acid), a 40 ml of water sample was extracted with 4 ml of MTBE

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spiked with the internal standard (1,2,3-trichloropropane) manually for 2 min and then 3 ml of extract was methylated by adding 1 ml of 10% H_2SO_4 methanolic solution and kept at 50°C for 2 h. After cleaning with 4 ml of Na_2SO_4 Saturated solution, the extracted was then submitted for GC/MS analysis.

2.2 Adsorbent

To absorb HAA_5, Coconut shell activated carbon (GAC) was used. The characteristics of the GAC is shown in Table 1

Table 1   Characteristics of the GAC

Physical properties	Specification
Particle size distribution (2.36 - 0.60 mm.)	MIN. 90 %
Apparent Density (g/cc)	MIN. 0.53
Moisture (% w/w)	MAX. 8
Ash (% w/w)	MAX. 3.5
Surface Area (m^2/g)	MIN. 1100
Iodine Number (mg/g)	MIN. 1050

Source: Carbokarn Co., Ltd.

2.3 Research Procedure

This study is divided into 2 phases

2.3.1 Batch test

The coagulation-flocculation process was conducted in the experiment to find the appropriate condition in removing HAA_5. 1) Jar test was used to investigate the effect of the coagulation-flocculation process in removing NOMs in water. PACl which is coagulant with the concentration of 10, 20, 30, 40 and 50 mg/L and the concentration of cationic polymer which is coagulant aid was 0.1, 0.2, 0.3, 0.4 and 0.5 mg/L. 2) water with the least amount of NOMs left from the coagulation-flocculation process was added into chlorine with the concentration of 0.5 mg/L to make free chorine left in the range of 0.2 - 0.5 mg/L   and added chlorine with the concentration of 0 - 1.50 mg/L to free chorine left in the range of 0 - 1.50 mg/L   3) 0.05 g. of GAC was used to absorb sample water. $HAA_5$was synthesized at the concentration of 60 μg/L to investigate knetic adsorption. 4) 0.05 g. of GAC was used to absorb sample water. $HAA_5$was synthesized at the concentration of 25, 50, 75, 100, 200 และ 300 μg/L to investigate Isotherm

2.3.2 Column test with adsorbent

One fixed bed column with 5 cm. in diameter and 30 cm. in height is shown in Figure 1. The study investigated the results of the 0.6 and 1.0 L/h flowing rate of through the adsorbent with the GAC height of 10, 15 and 20 cm.   What was found from the test was used to study a breakthrough curve in order to find the ability of HAA_5 treatment in the column test.
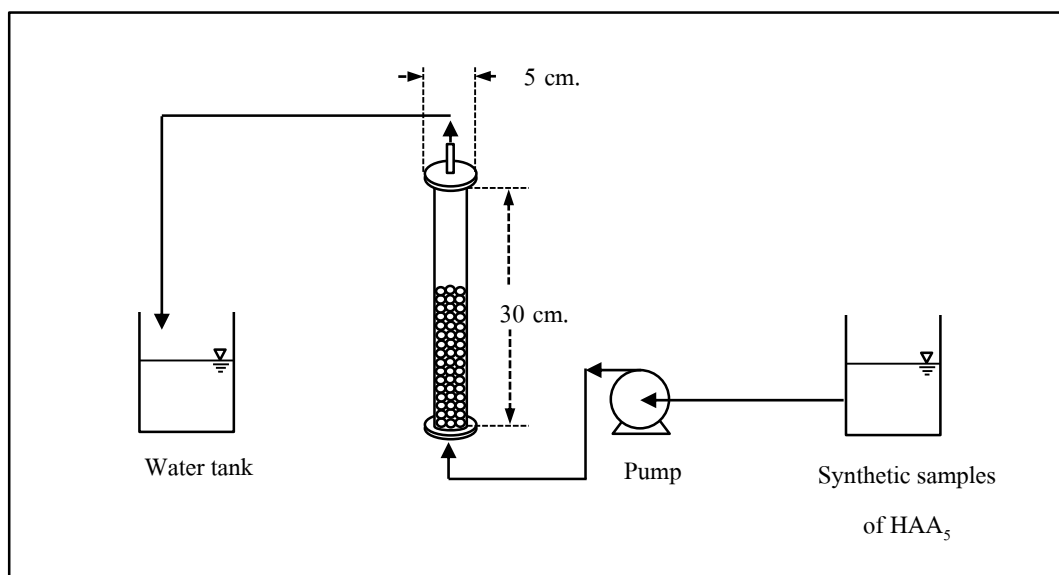
Figure 1   Column test

3.   Results and discussion

3.1   Batch studies

3.1.1 Effects of coagulation-flocculation process

The sample of raw water from Sura Pond at Suranaree University of Technology was used in the experiment. It was found that PAC with the concentration of 10, 20, 30, 40 and 50 mg/L in combination with cationic polymer with the concentration of 0.5, 0.3, 0.5, 0.4 and 0.3 mg/L could remove 88.62 98.06 96.84 92.72 and 19.06% of turbidity in the water respectively and could remove 43.28 59.17 64.42 61.65 and 28.9% of DOC respectively. When PACl and cationic polymer concentration increased, the efficiency to remove turbidity tended to decrease since the greater availability of cationic polymer could destroy the stability of floc. Adding PACl increased turbidity and decreased the efficiency of the removal [16]. Using PACl, a coagulant, with the concentration of 30 mg/L in combination with cationic polymer with the concentration of 0.5 mg/L could best remove turbidity and DOC in water. AS a result, turbidity of raw water used to produce water supply decreased 14.47 NTU from the initial value to 0.46 NTU and caused DOC of raw water decreased from the initial value 5.08 mg/L to 1.81 mg/L since PACl has the mechanism in destroying the electricity stability, absorbing [17, 18] as shown in Figure 2
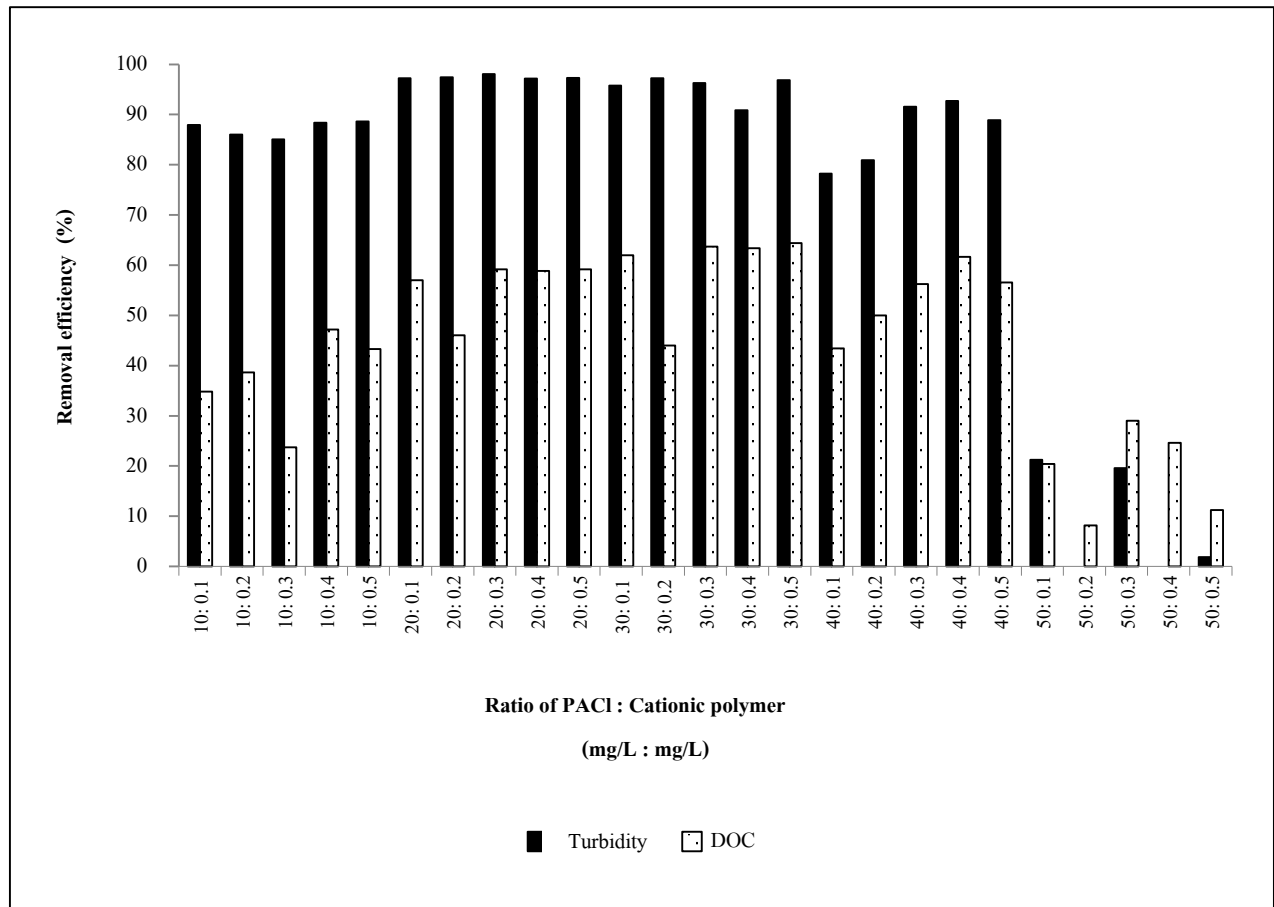
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Figure 2   Efficiency of turbidity and DOC removal in raw water for producing water supply by coagulation-flocculation process.

3.1.2 Effects of HAA_5 concentration

In the experiment, raw water from the coagulation-flocculation process in which PACl with the concentration of 30 mg/L left in the small amount was used in combination with cationic polymer with the concentration of 0.5 mg/L since there was NOMs, Initial HAA_5 was left in the least in raw water [19]. The addition of chorine with the concentration of 0.5 mg/L yielded 0.3 mg/L free chlorine residual which was HAA_5 with the concentration of 24.35 µg/L which included TCAA with the concentration of 24.35 µg/L 24.35 µg/L. Moreover, the addition of chorine with the concentration of 1.5 mg/L have yielded 0.71 mg/L free chlorine residual. The residual caused HAA_5 with the concentration of 35.24 µg/L. HAA_5 included DBAA, TCAA and DBAA with the concentration of 0.45, 32.12 and 2.68 µg/L respectively. The increase of free chorine residual caused the concentration of the residue higher [20] as shown in Figure 3 and 4.
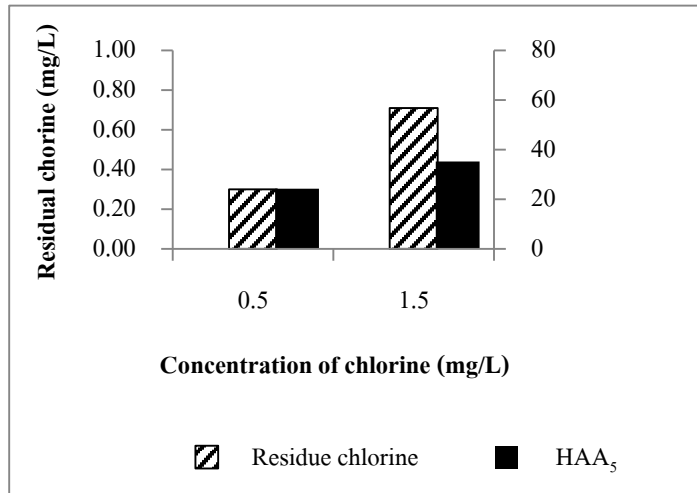
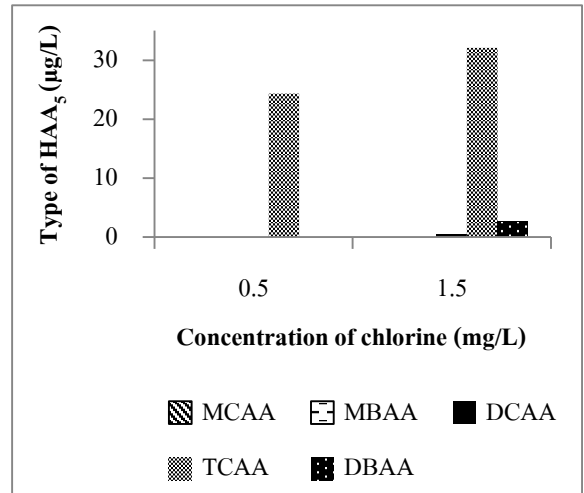**Figure 3** Residue caused of Haloacetic acid compare with residual chlorine.

Figure 4 Residue caused types of Haloacetic acid compare with residual chlorine.

3.1.3 Effect of adsorption kinetic

The adsorption kinetic was analyzed by pseudo- equation as indicated in the first equation and pseudo-second order equation as indicated in the second equation. From the first equation k1 was 0.2607 h^{-1} and from the second equation k_2 was 0.0121 g/µg* h. The findings indicated that GAC of adsorption Kinetic HAA$_5$ similar to pseudo-second order equation according to R^2 which was approaching 1 as shown in and the finding was related to the findings from most research studies [21] as shown in Figure 5 and Figure 6

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (1)$$

When q_t is referred to the HAA$_5$ and GAC adsorption capacity at equilibrium (µg/L), k_1 is referred to constant flow rate of pseudo-first order (h^{-1}) and t is referred to the adsorption time (h)

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

When k_2 is referred to constant flow rate of pseudo-second order (g/µg*h)

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$$y = -0.1132x + 1.6241$$
$$R^2 = 0.9376$$

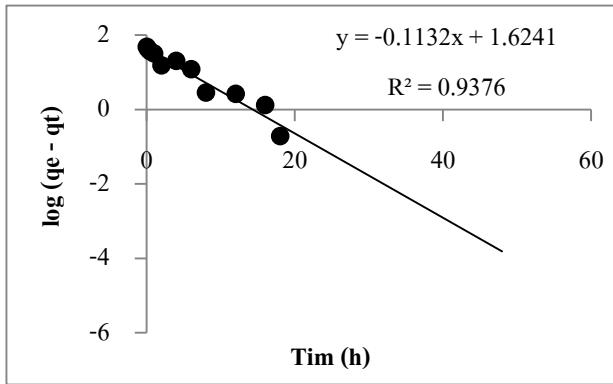**Figure 5**   pseudo-first order

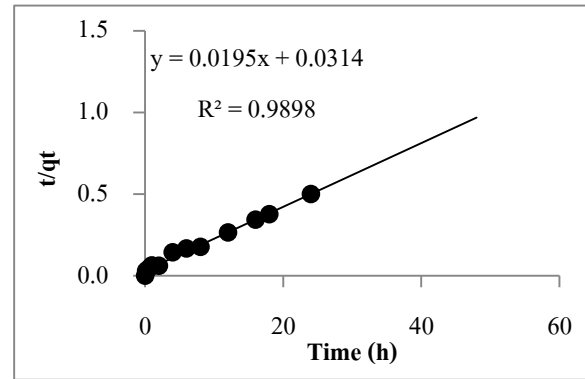
$$y = 0.0195x + 0.0314$$
$$R^2 = 0.9898$$

Figure 6   pseudo-second order

3.1.4 Effect of Isotherm Adsorption

According to the analysis by the equation of Langmuir Isotherm adsorption as shown in Equation 3 and by GAC had R^2 value higher than Freundlich isotherm adsorption. Langmuir isotherm adsorption is the equation that shows the adsorption of HAA_5 moleguls at the certain sites on GAC surface area. The values of the adsorption were the same in all areas. The HAA_5 adsorption capacity by GAC yields the highest value at 44.05 µg/L as shown in Figure 7 and 8

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m \times K_L} \tag{3}$$

Where q_m is the highest adsorption capacity which occurred as one layer (µg/L). Langmuir isotherm adsorption (µg/g) or K_L was constant.

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \tag{4}$$

Where Freundlich isotherm adsorption or K_F is constant

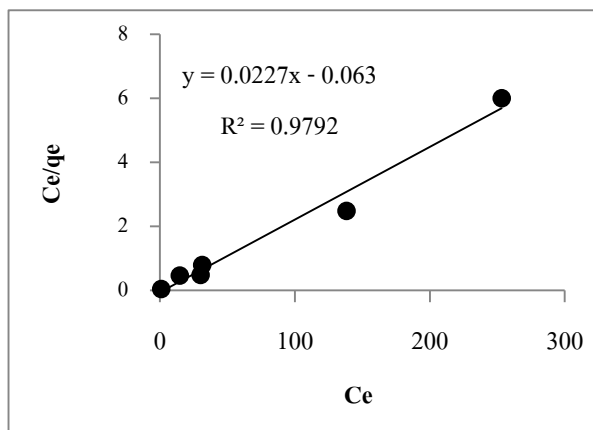$$y = 0.0227x - 0.063$$
$$R^2 = 0.9792$$

Figure 7   Isotherm Langmuir adsorption

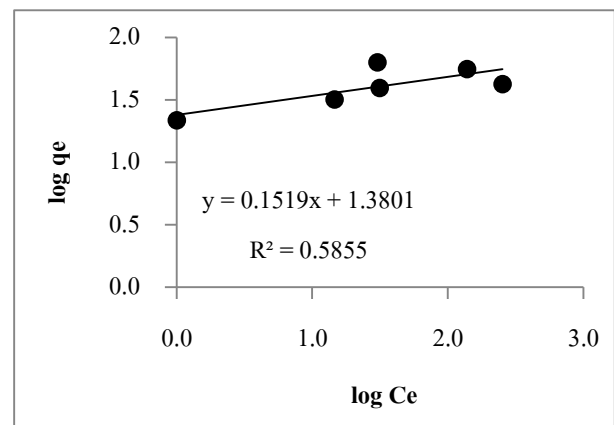$$y = 0.1519x + 1.3801$$
$$R^2 = 0.5855$$

Figure 8   Isotherm Freundlich adsorption

3.2   Column studies

3.2.1 Effect of HAA$_5$ flow rate through based-fix column

The HAA$_5$ removal at the flowing rate 0.6 and 1.0 L/h passing through the column of GAC which was 10 cm. high. By using synthesized HAA$_5$ water with the concentration of 30 μg/L and pH was controlled at 7. It was found that the flow rate of 0.6 L/h was 96.63% efficient in removing HAA$_5$ from the beginning to the second hour of the experiment and from the second hour to the end of the experiment at the twelfth hour. It was found that at the flow rate of 0.6, HAA$_5$ removal efficiency decreased continuously to 81.44% at the flow rate of 1.0 L/h. The efficiency of HAA$_5$ removal was more than 89.52% since the beginning of the experiment from the beginning to the sixth hour of the experiment and from the sixth hour to the end of the experiment at the twelfth hour. The efficiency of HAA$_5$ removal occurring continuously decreased to 71.60%. The average flowing rate efficiency at 0.6 litr per hour (85.34%) could remove HAA$_5$ could remove HAA$_5$ better than the average flowing rate efficiency at 1.0 litr per hour The increasing flow rate caused incomplete adsorption leading to decreasing removal efficiency.
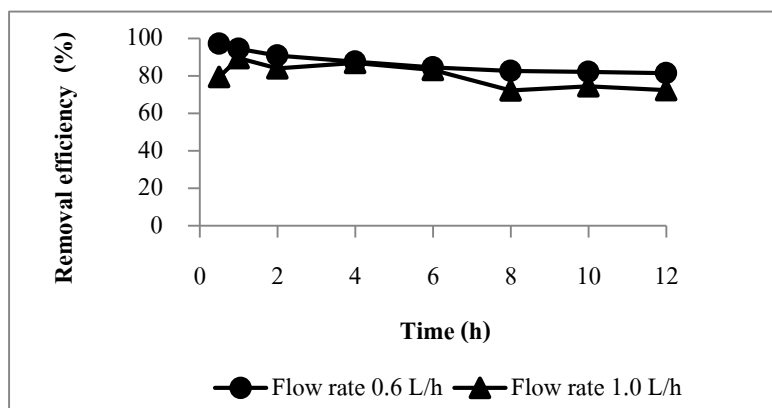

Figure 9   HAA$_5$ removal efficiency at different time with different flow rates**.**

3.2.2   Effects of adsorbent bed height

Different bed height and weight which were 100 cm. 15 cm. and 20 cm. with the weight of 115.21 g, 169.60 g. and 215.25 g respectively of GAC were used to remove HAA$_5$. Synthesized HAA$_5$ with the concentration of 30 μg/L was used to control pH at 7. It was found that GAC with 10 cm. height had 96.75 % maximum efficiency in removing HAA$_5$. From the second hour to the end of the experiment at the twelfth hour. the efficiency of HAA$_5$ occurred continuously. GAC with the height of 15 cm. and 20 cm. had 100% of efficiency in HAA$_5$ removal from the second hour to the end of the experiment at the twelfth hour as well. It can be seen that the efficiency at the average height of 15 and 20 cm. (100% respectively) could remove more HAA$_5$ that the efficiency was at the average height of 10 centimeter (85.46%). Since the amount of GAC increased, the surface area could absorb more HAA5 as shown in Figure 10.
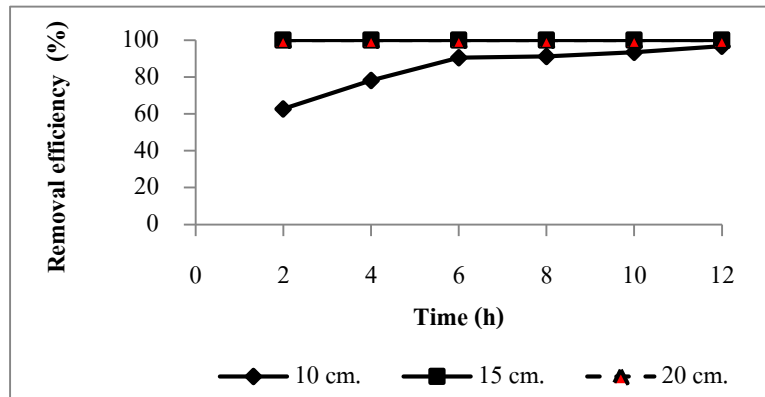
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Figure 10 HAA_5 removal efficiency at different times and different GAC height

3.2.3 Effect of breakthrough curve on HAA_5

The finding from 3 tests which are 1) the effect of HAA5 with the concentration of 24.35 µg/L by synthesized HAA_5 water to the concentration of 30 µg/L. 2) the effect of the flow rate through the fixed-based column at 0.6 L/h and 3) the effect of the 15 cm. height of GAC that was the adsorbent as shown in Figure 11. It was found that the breakthrough time was 12.5 hours. The Break point was 7.6 liter with the concentration of 1.5 µg/L or 5% of HAA5 concentration was sent to the column. The exhaustion point with the concentration of 28.5 µg/L or 95% of HAA5 concentration was sent to the column for 23.8 hours which was the operation period of the system. The total amount of water sent to the column was 14.3 liter.

Equation 5 was used to calculate for HAA_5 adsorption capacity. It was found that HAA_5 adsorption capacity in the column study was 68.38 µg/L. When HAA_5 adsorption capacity of the column test was compared with that of the batch test by the calculation at 30 µg/L concentration by Langmuir isotherm adsorption at the 48.54 µg/L adsorption capacity. It was found that HAA_5 adsorption capacity of the column test was higher than that of the batch test due to the difference of the 2 experiments. The GAC amount used in the column test was higher. The contact time in adsorption was continuous till the saturation point was reached. It was possible that another mechanism could occur in the column test such as filtration causing higher removal value.

$$\text{Absorption capacity} = \frac{\sum_{n=1}^{T}(C_e - C_{ei})dV_i}{Weight(media)} \tag{5}$$

Where C_e was HAA_5 concentration at exhaustion piot (95 % of the initial concentration), C_{ei} was HAA_5 concentration in the system at volume i and V_i was the volume at time i

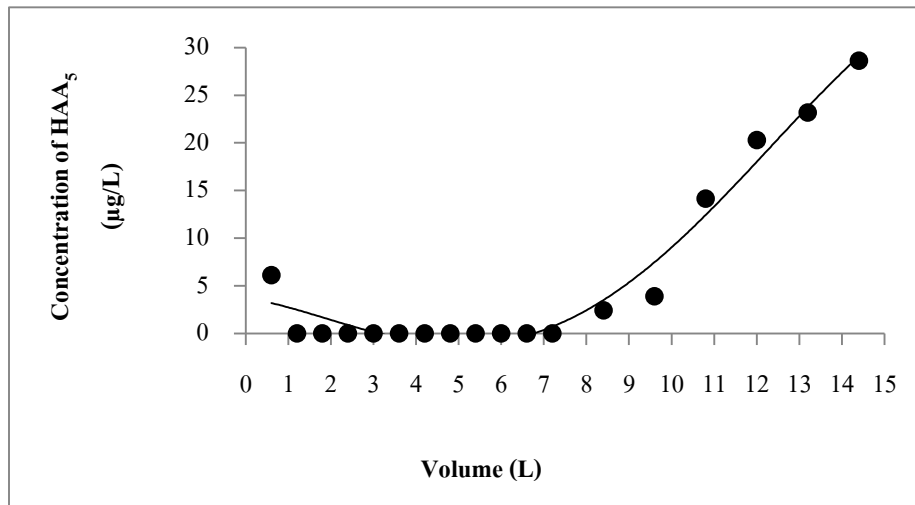Phongthon Saengchut[1*], Prapat Pentamwa[2] and Sudjit Karuchit[1]

Figure 11   Breakthrough curve

4.   Conclusions

Removing NOMs which is the initial substance of HAAs by the coagulation-flocculation process using PACl, a coagulant, with the concentration of 30 mg/L in combination with cationic polymer, a coagulant aid, with the concentration of 0.5 mg/L could best remove turbidity and DOC. The efficiency in removing turbidity was 96.84% and DOC was 64.42%. When chorine with the concentration of 0.5 and 1.5 mg/L was added, the addition caused 24.35 and 35.24 µg/L HAA_5. Increasing concentration of chorine caused HAA_5 to have higher concentration as well. Besides, in testing HAAs reaction, it was found that GAC had pseudo-second order reaction. The adsorption was one layer. It is possible that the chemical adsorption also occurred. The type of the adsorption was Langmuir Isotherm. It can be seen that HAA_5 molecular provide equal adsorption in all areas at all sites. The maximum HAA_5 adsorption was 44.05 µg/g

The flow rate through the fixed-base column at 0.6 L/h flow rate efficiency could remove HAA_5 better than at 1.0 L/h flow rate efficiency because the long contact between HAA_5 and GAC height at 15 and 20 cm. could remove HAA_5 better than the height at 10 cm. In other words, higher amount of GAC resulted in more areas for absorbing HAA_5. In conclusion, the flow rate which was slow resulted in better removal efficiency. GAC height resulted in removal efficiency. The efficiency depended on the increasing height. In the column test, HAA_5 adsorption was 68.38 µg/g due to another mechanism which also occurred.

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