Trihalomethane Removal and Formation Mechanism in Water

by

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Introduction

Drinking water is chlorinated to inactivate the bacteria in order to prevent the spread of water borne diseases. However the recent investigations of Rook (1974) and Bellar (1974) indicate that aqueous chlorine reacts with "humic-acid-like" materials, usually referred to as precursors, to form trihalomethanes (THM's). THM's are suspected carcinogens. U.S. EPA (1978) has promulgated that maximum concentration level (MCL) of total trihalomethanes in water should not exceed 100 ug/Q. Hence engineers are required to minimize the concentration of THM's in water, either by removing the precursors before chlorination or by removing the THM's formed by adsorption.

The precursors vary both quantitatively and qualitatively due to hydrological and seasonal changes. For the most part these are difficult to measure.

The objectives of the research were to study the formation kinetics of THM's and their removal using granulated activated carbon (GAC). To avoid the temporal changes the formation studies were made on lyophilized water.
Theory

THM Formation

The aqueous chlorine reacts with a wide variety of organics in water to give rise to haloform reactions and produce THMs. The organics that lead to the formation of haloforms are many such as methyl ketone acetelhydes, ethanol and secondary alcohols. In addition humic acid substances, and algae like material also react with aqueous chlorine to produce THMs., The THM formation also depends on the chemical component of the water especially the presence of Bromine, Iodine because these two will determine the formation of various other halogenated species.

Another source of THMs is due to industrial emissions to the atmosphere. Some volatile organics escape to the atmosphere and halogenated compounds upon combustion generate Cl (also industry discharges large amounts of chlorine to the atmosphere), which reacts to form chlorofom and other trihalomethanes. THM's formed in the atmosphere are washed by

This is a complex reaction mechanism controlled by parameters such as:

- Concentration and type of precursors
- Concentration of chlorine
- Temperature
- pH
- Time
In essence the THM formation process may be described by the following simple equations:

\[
\text{Precursor(s)} + \text{HO}_X \rightarrow \text{CHX}_3
\]

where X may be Cl or Br and CHX₃ may be regarded as a general formula for THM (e.g. chloroform, CHCQ₃).

Precursor is a general term expressing all possible types of chemical species which may react with HOCl, or HOBr to form THMs. Typical reactions for an acetal group as a THM-precursor are shown below:

\[
\begin{align*}
R - C - CH_2^- + HOCl & \rightarrow R - C - CH_2CL + OH^- \\
R - C - CH_2 + HOCl & \rightarrow R - C - CH_2CL + OH^- \\
R - C - CH_3 + H_2O & \rightarrow R - C - OH + CHCL_3
\end{align*}
\]

A SERIES OF HYDROLYSIS AND HALOGENATION REACTIONS

This is a complex reaction mechanism controlled by parameters such as:

- Concentration and type of precursors
- Concentration of chlorine
- Temperature
- pH
- Time
Naturally occurring Bromide reacts with HOCK (see equation 2), to form HOBr, as explained below:

\[
\text{HOCK} + \text{Br} \rightarrow \text{HOBr} + \text{Cl}^-
\]

(6)

HOBr reacts in similar manner as HOCK to form brominated species (CHBr₂U, CHU₂Br, and CHBr₃).

The THM formation continues until either chlorine or precursors are exhausted. The THM formation process is schematically depicted in Figure 1. Smith et al (1980) worked extensively on the variation of THMs in water. The variables such as pH, chlorine concentration and temperature had dramatic effects on the quantities of THM's formed. In our earlier work (Varma et al, 1981) THM formation potential was studied under controlled laboratory conditions. It was observed that kinetic models of THM formation have not been developed because the reaction is rather complex and currently it is not possible to measure the naturally occurring precursors in water. Chlorine is consumed through series and parallel reaction pathways. Hence it was necessary to study the kinetics under well controlled conditions using lyophilized water. The trihalomethane formation potential (THMFP) is used to determine the maximum amount of THMs that can be formed in the system. In essence THMFP is a surrogate way to measure the precursor(s) in water.

However in large water supply systems the delivery time for water can be very high. For example in metropolitan Washington suburban area it is estimated that the distribution time is about 75 hours. Since chlorine contact time is critical in THM formation, some water authorities are studying the feasibility to reduce the contact time, while others are controlling the THM formation by using chloramines.
NATURAL ORGANIC MATERIAL IN WATER (PRECURSORS)

+HOCl

COMPLEX REACTION PATHWAY

CHLORINATED ORGANIC INTERMEDIATES

HOCl

CHLOROFORM (CHCl₃)

NATURAL BROMIDE IN WATER (Br⁻)

+HOCl

COMPLEX REACTION PATHWAY

Br₂ (BROMINE) + Cl⁻ (CHLORIDE)

DICHLOROBROMOMETHANE (CHCl₂ Br)

DIBROMOCHLOROMETHANE (CH Br₂ Cl)

BROMOFORM (CHBr₃)

FIGURE 1: TRIHALOMETHANE FORMATION PATHWAY
THM Removal

To meet the requirements of THM concentration laid down by U.S. EPA, water authorities can formulate their own strategy. The alternatives are:

(a) treatment to remove trihalomethanes after formation
(b) treatment to remove trihalomethane precursor(s)
(c) to use an alternate disinfectant.

This investigation deals with the removal of THM's by adsorption on GAC, hence no reference will be made to the other methods.

To determine the degree of removal of TTHMs by adsorption, an isotherm test is usually applied. The isotherm is a relationship between the amount of the pollutant adsorbed and its concentration in the aqueous solution at equilibrium. One can screen the potential adsorbents for the removal of the THMs, and compare their effectiveness under varied conditions. Thus the adsorption isotherm can be used as a screening tool in determining the effectiveness of columnar method.

Freundlich equation is employed to test the model. The mathematical equation is

\[
x/M = k \cdot c^{1/n}
\]

where \( x \) = amount of substance adsorbed calculated from original and equilibrium concentrations \( C_0 \) and \( C_t \)

\( M \) = weight of GAC

\( k \) and \( n \) are constants. \( K \) is the intercept at \( C_t = 1 \) (log \( C_t = 0 \)).

\( 1/n \) is the slope of the \( x/M \) vs \( C_t \) plot on a log-log paper. Stationary beds of GAC are used to remove THMs from drinking water. The aqueous solution flows downward through the adsorbent. The adsorbed contaminants accumulate
on the surface of the bed until the amount reaches the maximum level. The maximum amount of the contaminants that can be adsorbed on GAC occurs when the adsorbed concentration is in equilibrium with the concentration of the contaminant in the surrounding aqueous solution. Thus the capacity of the carbon at equilibrium can be determined from the isotherm study. The effluent concentration from the column remains low until the exhausted zone of GAC reaches the bottom of the column and then it starts increasing dramatically to the influent concentrations. At this stage the entire column is saturated and the influence concentration is equal to the effluent concentration.

Blanck (1979) showed that 80 percent breakthrough of TTHM occurred on or before 14 weeks of operation. DeMarco and Wood (1979) demonstrated that strongly adsorbed bromine containing trihalomethanes have smaller critical bed depth, that is, a thinner mass transfer zone. Stevens (1975) also reported the removal of humic-like-matter by a GAC column. Wood and DeMarco (1980) indicated that minimum adsorbed bed depth is 19 cm (7.5 in) to remove the THMFP to 200 ug/l and 32 cm (12.5 in) to 100 ug/l from an average influent concentration of 434 ug/l. It is apparent that more in-depth investigation is needed if GAC or other synthetic resins have to be used for removing THM's formed on the chlorination of drinking water supplies.
Methodology

The research project was divided into two parts (a) formation kinetics and (b) removal mechanism. The removal mechanism was studied both by batch test and columnar method. As a general precaution, all glassware was thoroughly cleaned in hot water with detergent and was rinsed with super Q water. These glasswares were baked in an oven for at least 2 hours at 150° 170°C to get rid of all the organics present. It is advisable not to touch the glasswares with hands. Gloves were used to avoid contamination. Granular activated carbon (GAC) of 200 mesh size supplied by Fisher Scientific Co. was used for all the experimental studies. GAC was washed with super Q water many times till all the fine particles disappeared. GAC was transferred to a drying tray and placed in an oven at 100°C for drying overnight. This washed carbon after drying is ready for use in organic adsorption experiments.

Stock solutions of T HM's were prepared gravimetrically by determining the weight of the chloroform in a known volume of methanol. The concentration of the stock solution is reported in µg/l (microgram per liter). The stock solution was diluted in 1:10 ratio with methanol to an intermediate solution. This intermediate solution was further diluted with super Q water via progressive dilutions to analytical requirements to a known concentration before each experiment was conducted. Subsequently, the gravimetric technique of determining concentration of stock solution was checked by the analytical technique i.e., the gas chromatogram, and it was found to be nearly close. A sample calculation for determining stock solution concentration is shown in Appendix A.
It was necessary to concentrate the water sample. Several methods for concentration are available, namely, vacuum distillation, synthetic resins (XAD-8 or XAD 2) adsorption and subsequent elution, reverse osmosis, and lyophilization. Each method has its own strengths and weaknesses; however, considering the simplicity, ease and minimal loss of volatile matter during the procedure, lyophilization was selected for concentrating the sample.

Twenty (20) gallons of water were lyophilized; the water was evaporated under low vacuum and dried solids were collected in a glass bottle and kept in a refrigerator until its use. The solids were re suspended in Super "Q" water and pH adjusted to 8.00.

To this water, chlorine was added to obtain predetermined concentration. A separate study showed that an initial concentration of 5 mg/Z of chlorine resulted in 1 mg/z free chlorine in the aqueous solution after 100 hours of reaction time. This chlorine dose was consistent with the normal chlorine dose added by the Washington Suburban Sanitary Commission (WSSC), and most other municipalities.

The chlorine solution was prepared by bubbling chlorine gas through super "Q" water. A known amount of this solution was added to achieve the desired concentration.

The reaction flask (brown glass bottle), was carefully washed and baked. It was placed in a constant temperature bath* set at a predetermined temperature (21°). The actual temperature of the bath was within ± 0.5° of the set reaction temperature.

* Blue M Company, Blue Island, Illinois
At various time intervals, two samples of approximately 100cc each were withdrawn from the reaction vessel for analysis. In one sample, the pH was measured and excess chlorine was then neutralized with sodium thiosulfate solution.

The chlorine in the other sample was measured by a Specific Ion electrode** fitted with a residual chlorine electrode. This was standardized against the DPD method. Subsequently, this sample was analyzed for THM. These data were collected at various time intervals.

**Batch Method:** For small scale experimental studies, batch test is the most ideally suitable method. The reason being, it is simple, needs very few equipments and it is cheaper.

In the laboratory batch test were conducted by taking four 2000 ml volumetric flasks with stoppers. Washed GAC of varying amounts were weighed and placed in volumetric flasks. A known concentration of chlorophorm (CHC\textsubscript{3}) was prepared from the stock solution. A 20 ml sample of flask contents at time t=0 was collected in glass vials. and screwed tightly and stored in the refrigerator. CHC\textsubscript{3} solution was added to the volumetric flask noting the day and time at the start of the experiment. The solutions were vigorously shaken for thorough mixing of CHC\textsubscript{3} and GAC. Samples were taken every two hours and filtered through 0.45 u filter, labelled and stored in glass vials for the further analysis of CHC\textsubscript{3}. The tests were conducted for 8 to 10 days.

** Orion Specific Ion Meter. Orion Research Inc. - Cambridge, Mass.**
Another set of batch tests involved using a separate flask for each sample. This was done to keep the volume and concentration constant throughout the experiment.

In these experiments 0.5 gm of GAC was placed in nine (9) - 250 ml volumetric flasks. The flasks were filled with the same concentration of THM solution. The flasks were placed in dark environment and shaken several times, manually. At the end of each day, for nine days, one flask was taken from the batch. A known volume of solution was filled, and analyzed for THM's, as explained later.

The second set of experiments was performed to determine the adsorptive capacity of GAC. As several doses of carbon ranging from 0.05 to 0.5 gm were placed in 250 ml volumetric flasks. The flasks were filled with a known concentration of THM solution placed in dark environment, and shaken manually. All experiments were continued for 10 days, the time to reach the contents in equilibrium state. The time was evaluated from the first set of experiments. The time varied from 7 to 8 days; hence 10 days was selected. At the end of the prescribed period, a known volume of solutions was filtered from each flask, and analyzed for THM's.

**Columnar Method:** The laboratory set up for continuous column consists of a tank to store THM solution, continuous glass column, and a vacuum pump, as shown in Figure 1a.

A known quantity of GAC was weighed and placed in the glass column. A known concentration of THM solution was added to the storage tank which has an opening at the bottom through which a narrow tube is connected to the inlet of a glass column. The
Figure 1a: Schematic Diagram of the Columnar Method for THM Adsorption
flow of solution is controlled by the pump. To start the experiment the sample at time $t=0$ was collected, which denotes the initial concentration. The pump was started and the time noted. Maximum care was taken to maintain a constant head, i.e., to maintain constant inflow and outflow from glass column. In the experiments conducted the flow varied from 160-500 ml/hr but a constant flow rate was maintained for each experiment. Samples were collected every 15 minutes from the effluent and stored in glass vials, properly labelled and refrigerated. The tests were conducted for 2 to 3 hours depending on the concentration of the THM solution and quantity of carbon used. The collected samples were analyzed for determination of THM's by the method described in the analysis section.

**THM Analysis:**

The analysis for THM's was performed by the liquid-liquid extraction technique. 10 ml of the sample were taken in a screw capped test tube to which 1 ml of pentane was added. The tube was capped tightly, and shaken vigorously for one minute. It was allowed to stand until the separation of phases was clearly visible. A liquid of the upper organic phase was removed carefully with disposable pipette and transferred to micro vials before it was sealed. These micro vials were arranged in sequence on the rack for the G.C. analysis. The instrument automatically injects one sample after another, and the results are printed. The area on the graph was integrated for determination of the concentration of the sample in micrograms per liter ($\mu g/l$).

The quantitative measurements for all the samples were carried out with a Hewlett-Packard Model 5830 Gas Chromatograph fitted with a Ni $^{63}$
electron capture detector. The glass volume was 1" x 4', packed with 10 percent FFAP on gas-chrom Q. The operating data of the GC is provided below:

- Column: 6.4mm x 1.22m(* x 4') Glass
- Packing: 10% FFAP on Gas-Chrom Q
- Carrier Gas: Argon-Methane 95%/5%
- Carrier Gas Flow Rate: 50 ml/min
- Oven Temperature: 90°C
- Injection Temperature: 250°C
- Detector: Ni - Electron Capture
- Detector Temperature: 300°C

Liquid-Liquid Extraction Method using pentane has been investigated in detail by many researchers (Richard and Junk, 1977; Mieure, 1977; Varma et al, 1979). These researchers found that pentane has the advantages of low solubility in water, good distribution coefficients and favorable polarity and volatility for effective separation from the THM's.

This technique has the advantages of being fast (about 5 minutes per sample), has minimal interferences from other commonly occurring organics in water and requires-very little equipments besides an electron-capture GC detector.

Typical chromatograms are included in Appendix B.
Results and Discussion

I. THM Formation Kinetics

Several sets of experiments were performed. The effect of varying chlorine dose on the THM formation with respect to time was studied at fixed precursor concentration. Similarly in another set of experiments, the solid concentration was varied keeping the chlorine dose, pH, and temperature constant. These sets of experiments were conducted for time frames: 100, 6 and 1 hours.

The last time frame was investigated primarily to evaluate the reaction kinetics, while the 100 hour time frame was investigated to simulate large distribution systems, typical of large metropolitan areas.

TTHMFP as well as CHU$_3$ formation potential at different time intervals are given in Figure 2. It indicates that CHU$_3$ predominates. Consequently, in reporting the results, CHC$_2$H$_3$ is the species frequently referred to, though the other species were also measured. Formation rate of THM decreases with time. At the end of the experiment the residual chlorine was 1.2 mg/L. The solids concentration in Potomac water supplied by WSSC is usually in the neighborhood of 110 mg/L.

A plot of CHU$_3$ formation potential at two different chlorine dosages of 5 and 11.2 mg/L is given in Figure 3. A similar plot for 1 hour at various chlorine doses is depicted in Figure 4. These figures indicate that TTHMFP increased with increasing chlorine however the increase was not linearly proportional to the chlorine dose.

At a constant chlorine dose and fixed temperature, the chloroform formation was plotted against time, for three different solid concentrations.
SOLIDS CONC = 115 mg/l
CHLORINE DOSE = 2 mg/l

FIGURE 2  THI FORMATION AS A FUNCTION OF T
SOLIDS CONC = 114.3 mg/l

FIGURE 3: CHCL₃ FORMATION AS A FUNCTION OF TIME
FIGURE 4  TTHM FORMATION WITH TIME AS A FUNCTION OF CHLORINE DOSE
on a log-log graph as shown in Figure 5. The resulting plots are linear.
The plot at solid concentration of 15 mg/l does not indicate a significant increase in CHU₃ formation potential at 100 hours; probably the precursors were depleted in a short time. However, when the solids were increased (109 and 150 mg/R₃), the CHU₃ formation increased.
Essentially the slopes for these plots are the same suggesting that qualitatively the mechanism of THM formation remains unaltered.
Figures 6 through 8 show formation of chloroform for various chlorine doses, for 100 hour, 6 hour and 1 hour time durations. In these experiments the concentration of precursor was kept constant, and any increase in CHU₃ was caused by a corresponding change in chlorine dose. The family of curves obtained shows that the slopes are about the same on a log-log plot indicating that there is no significant shift in the mechanism of reaction.

The role of chlorine in the formation of trihalomethane in water is not well understood. Investigators appear to differ, and the comparative analysis of limited published data on this subject cannot be done precisely because information on precursor concentration and chlorine consumed is not readily available.

A semi-empirical model is needed which would be source dependent to account for the variation in the precursor type and concentration. The simplest model to describe this situation is expressed below:

\[
d \text{THM}/dt = K[\text{precursor}]^a [\text{Chlorine}]^b
\]
CHLORINE DOSE = 5.0 mg/L

SOLIDS CONC. (mg/L)

CHLORINATION CONC. (mg/L)

TIME (HOURS)

FIGURE 5: CHLORINATION CONC. AS A FUNCTION OF SOLIDS CONC.
SOLIDS CONC. = 109 mg/L

CHLORINE DOSE (mg/L)

TIME (HOURS)

FIGURE 6: CHL$_2$ CONC WITH TIME AS A FUNCTION OF CHLORINE DOSE
SOLIDS CONC = 115 mg/L

FIGURE 7: TTHM CONC WITH TIME AS A FUNCTION OF CHLORINE DOSE
SOLIDS CONC = 115 mg/L

CHLORINE DOSE (mg/L)

FIGURE 8: THM CONC WITH TIME AS A FUNCTION OF CHLORINE DOSE
This model was examined at high precursor concentration for various chlorine doses and the rates at time, t=0 were found by extrapolation of 1 hour tests. The results are shown in Figure 9. A log-log plot of rate at zero time vs. initial concentration of chlorine (Figure 10) gives a slope of 0.3 for Potomac water. It should be emphasized that since the parameters in this model are strongly dependent on the water source, caution is needed in extrapolating these results to other sources of water or drastically different conditions of the same water. However with extensive data very accurate local semi-empirical models can be developed for various bulk concentrations of solids in water. These models can then be used to predict the THM formation potential in water and control it before it becomes history.
SOLIDS CONC. = 115 mg/L

CHLORINE CONC. (mg/L)

TIME (MINUTES)

0 10 20 30 40 50 60

0.16 0.33 0.50 0.67 0.83 1.00

(HOURS)

RATE OF TTHF FORMATION WITH TIME AS A FUNCTION OF CHLORINE DOSE
\[ \log r = \log k + n \log c \]

SLOPE, \( n = 0.30 \)

**Figure 10**: Initial rate of THM formation as a function of chlorine concentration.
II. THM Removal

(a) Batch Tests

Physical adsorption is a nonspecific phenomena and is caused by the weak forces of attraction between the molecules. The adsorbed material from the aqueous solution deposits in multilayers on the surface of the solid matter. It is generally believed that the quantity of the adsorbed substance by a given sample of an adsorbent depends upon the nature of the material and its concentration. Temperature is also a factor, however it was practically constant.

Figures 11-13 represent the typical plots of residual total trihalomethanes (TTHM's) versus time. It is evident that the equilibrium concentration was achieved between 7 to 8 days on the basis of these experiments. A 10 day period was selected to measure the adsorbability of different THM's on GAC. Initial concentrations of about 350 ug/l were used with 0.5 g of GAC in batch tests. The maximum concentration level permissible (100 vg/t) reached in about two days. During this time 250 ug/l was removed. After about two days, the rate of removal of THM decreased dramatically until a plateau was attained in 6-8 days. The equilibrium concentrations ranged from 10-50 ug/l indicating a removal of 86-97%. These results show that GAC is capable of reducing the effluent concentration of THM to about 10 ug/l. Some health authorities contend that 100 ug/l MCL is high and poses significant public health threat.

A batch test for lower concentration of 100 ug/l (Figure 14) of CHU₃ gave a 90% removal in less than a day.
Carbon Dose = 0.5 cm
Initial TTHM Concentration = 353.4 μg/L

Figure 11  Contact Time Versus TTHM Remaining
Figure 12 Contact Time Versus TTHM Remaining

Contact Time (days)

Carbon Dose = 0.5 gm
Initial TTHM Conc. = 362.5 µg/L
Figure 13: Contact Time Versus TTHM Remaining

Carbon Dose = 0.5 g/m
Initial TTHM Conc. = 358.5 μg/l
Figure 14: Contact Time vs. CHCl₃ Remaining

Carbon = 0.5 g
Initial CHCl₃ Concentration = 100 µg/l

Contact Time (days)
A plateau was reached in about two days and the equilibrium concentration was 3 ug/l indicating a 97% reduction.

As earlier expressed, Freundlich equation is often expressed in a logarithmic form:

\[ \log \frac{X}{M} = \log k + \frac{1}{n} \log C_t. \]

Adsorption data, when plotted as \( \frac{X}{M} \) vs \( C_t \) on a log-log plot according to the above equation will yield straight lines.

Tables 1 and 2 summarize the initial carbon doses used and residual chloroform or total trihalomethanes remaining in the solution after treatment with GAC. The columns in the tables are self explanatory. Values of \( \frac{X}{M} \) (mg of TTHM or chloroform/ g carbon) were plotted functions of equilibrium concentrations in Figures 15 and 16. The resulting plots are straight lines verifying the Freundlich Isotherm hypothesis.

The parameters \( k \) and \( \frac{1}{n} \) were obtained from these plots. The resulting equations for the removal of TTHM and CHCl_3 are plotted as:

- **TTHM**:
  \[ \log \frac{X}{M} = 0.795 + 0.560 \log C_t \]

- **CHCl_3**:
  \[ \log \frac{X}{M} = 1.449 + 0.918 \log C_t \]

and 9

where \( X \) and \( M \) are in mg-and \( C_t \) is in mg/t. A higher \( \frac{1}{n} \) value for CHU_3 indicates that the breakpoint will occur more abruptly for CHCL_3 used singularly than in mixed substrate conditions. From the THM formation kinetics results presented earlier in Figure 2, it is evident that the chloroform formation is about 90% of the TTHM's. Therefore in the removal mechanism chloroform will appear earlier in the effluent than the other three species which will be adsorbed for a longer period of time. Therefore the emphasis should be given to CHU_3 concentration in the effluent more heavily than the arithmetic
Table 1: Freundlich Isotherm Data for Total Trihalomethanes

<table>
<thead>
<tr>
<th>Carbon Dose M (grams)</th>
<th>TTHM Remaining (mg/0 Ct)</th>
<th>TTHM Adsorbed Co - (mg/0 Ct)</th>
<th>TTHM Adsorbed Co - Ct as mg of solute</th>
<th>( \frac{X}{M} ) (mg/gram)</th>
</tr>
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<tr>
<td>0</td>
<td>0.364</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>0.05</td>
<td>0.073</td>
<td>0.291</td>
<td>0.073</td>
<td>1.460</td>
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<td>0.026</td>
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<tr>
<td>0.50</td>
<td>0.002</td>
<td>0.362</td>
<td>0.091</td>
<td>0.182</td>
</tr>
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Freundlich Parameters

\[
\begin{align*}
\log k &= 0.7951 \\
\frac{k}{k} &= 6.24 \\
\frac{1}{n} &= 0.560 \\
\text{Corr. Coeff} &= 0.960
\end{align*}
\]
Table 2: Freundlich Isotherm Data for Chloroform

<table>
<thead>
<tr>
<th>Carbon Dose M (grams)</th>
<th>TTHM Remaining Co - (mg/z) Ct</th>
<th>TTHM Adsorbed Co C = X as mg o solute</th>
<th>TTHM Adsorbed Co - (mg/0 Ct)</th>
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Freundlich Parameters

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<td>Corr. Coeff</td>
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Slope, $1/n = 0.560$
$k (at C_t = 1.0) = 6.24$

Figure 15: Carbon Loading as a function of equilibrium concentration for TTHM
Slope, $1/n = 0.918$

$k (at C_f = 1.0) = 28.09$

Figure 16: Carbon loading as a function of equilibrium concentration for CHC$_3$.
sum of all the four THM species, when evaluating the reaction kinetics of adsorption.

b) **Columnar Tests:**

Continuous adsorption tests were performed in a packed glass column under different conditions of CHU₃ concentrations and carbon. A steady flow rate of 288 ml/hr was maintained. The results are presented in Figures 17 through 20.

The conditions for Figure 17 employed an influent CHCR₃ concentration of 214 ug/l and the quantity of carbon was 2 grams. The greatest adsorption occurred in the first half hour and at that time the effluent concentration had reached from 0 to about 50 ug/l. Thus the removal rate dropped from 100 to 75% in about half hour. Gradually the plateau reached at an effluent concentration of about 65 ug/l indicating that GAC on a continuous basis can provide a system to meet the EPA requirements.

Figure 18 shows a smaller concentration of CHCk₃ (74 ug/l) and a larger amount of carbon (3 grams) than the previous experiment. In this case, plateau was attained earlier = between 15 and 30 minutes at an effluent concentration of 20 ug/l. Figure 19 shows a plot of an experiment where the carbon was reduced to 1 gram and the influent CHCk₃ concentration was also reduced to 53 ug/l. In this case the removal efficiency was about 50 percent. The scatter in the data suggests a possibility of chromatographic effect. Figure 20 shows a plot of further carbon content (0.5 grams) and influent CHCR₃ concentration (36ug/l) reduction. The trend in decrease in removal efficiency continued with decrease in carbon and decreasing influent CHU₃ concentrations.

The practical way to remove THM's from water supplies is by
Figure 17: Concentration vs Time Plots for Continuous Adsorption of THM's

- $X = CHCl_3$
- $O = Total$ THM
- Carbon Dose = 2 gm
- Flow Rate = 288 ml/hr
- Initial Conc. (CHCl₃) = 214 µg
- Initial Conc. (THM) = 220 µg
Figure 18: Concentration vs Time plot for Continuous Adsorption of THM's
Figure 19: Concentration vs Time plot for Continuous Adsorption of THM's
Figure 20: Concentration vs Time plot for Continuous Adsorption of THM's
continuous process. Our results show that GAC can be used to meet the existing EPA-THM standards. In addition it has the reserve capacity of providing an effluent with many time more stringent standards with a judicious choice of conditions such as retention time, flow rate, packing size and regeneration techniques.
Conclusions

(1) The study of THM formation indicates that about 90% of the TTHM formed is CHCR₃.

(2) Over a wide range of chlorine concentrations (2-15 mg/t) the mechanism of THM formation remains unchanged.

(3) Over a wide range of solids (precursors) concentrations (15-50 mg/k), the mechanism of THM formation remains unchanged.

(4) The THM formation increases with increase in chlorine concentration but the increase is not linear.

(5) The THM formation increases with increase in precursors concentration.

(6) The rate of THM formation decreases with time.

(7) A simple kinetic model for THM formation predicts an order of 0.3 for chlorine concentration.

(8) Adsorption studies for THM removal indicate an equilibrium time of about 6-8 days.

(9) The THM removal by GAC appears to conform to Freundlich Isotherms.

(10) The breakpoint in chloroform removal as compared to TTHM appears more abrupt.

(11) Columnar studies confirmed the batch data that GAC can be effectively used for THM removal on a continuous basis to meet EPA regulations - both current and probable stringent standards in the future.

(12) The removal efficiencies decrease with decrease in carbon content and decrease in influent chloroform concentrations.
Recommendations

(1) Attempts should be made to develop a more rigorous predictive model for THM formation in water.

(2) Studies should be carried out to determine the seasonal effects and incorporate them in the predictive model.

(3) The removal efficiencies of binary and multicomponent systems of THM's should be studied in a continuous manner.

(4) The effects of carbon dose and influent concentrations on the removal efficiencies and carbon life should be quantified.

(5) A predictive model for THM removal by GAC should be developed.
References


2) Blanck, C.A., "Trihalomethane Reduction in Operating Water Treatment Plants", JAWWA, 71, 525-528 (September 1979).


Appendix A

Sample Calculations

weight of 50 ml volumetric flask below mark with methanol and lid = 90.2882 gm
weight of flask and chloroform and methanol and lid = 90.2986 gm

\[
\begin{align*}
90.2986 \text{ gm} & - 90.2882 \text{ gm} \\
\hline
0.0104
\end{align*}
\]

weight of chloroform

concentration of chloroform = 0.0104 gm/50 ml

or 10.4 mg/50 ml

or 10400 ug/50 ml

OR 208 vg/ml - stock solution

Take 10 ml of stock solution and make it to 100 ml with methanol. The concentration would become 20.8 vg/ml - This is the Intermediate Solution.

Take the required amount of Intermediate Solution according to the concentration requirements for each experiment.
Appendix B

GC Analysis

The THM analysis using GC-electron capture detector produces computerized plots of relative peak intensities and peak areas. Typical plots for a few samples are included in this Appendix. The nomenclature for these plots is as follows:

\[
\text{Speci, #1} = \text{CHCR}_2 \text{Br} \\
2 = \text{CHU}_3 \\
3 = \text{CHU Br}_2 \\
4 = \text{CHBr}_3
\]

RT indicates the retention time for each-speci, which identifies the speci. Area is calculated by the integrator in the instrument and relative amounts in ug/l are displayed on the chromatograms. The initial concentration of CHU$_3$ for the sample plots shown was 214 ug/l and the TTHM was 220 ug/l.
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Appendix C

Glassware Used

- Volumetric pipettes: 0.5 ml, 1 ml, 5 ml, 10 ml, and 2.0 ml
- Graduated pipettes: 0.5 ml, 1 ml, 5 ml, 10 ml, and 2.0 ml
- Pi pumps, microliter syringes
- Volumetric flask: 10 ml, 25 ml, 50 ml, 100 ml, 200 ml, 250 ml, 500 ml, 1000 ml, and 2000 ml
- Screw caps and test tubes
- Tweezers, thermometers
- Drying tray, tongs or pair of gloves, test tube rack, scintillation vials, scintillation rack, filtration flask, vacuum pumps
- Filter paper 0.45 μ, beakers all sizes, disposable pipettes, pipette dispenser
- Wash tray, microvial, microcaps, crimper, methanol, CHCk₃ solution
- Granular activated carbon
- Dark bottle for storing GAC
- Oven, refrigerator, continuous column storage tank