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Removal of Chloroform ($CHCl_3$) from Tehran Drinking Water by GAC and Air Stripping Columns

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ABSTRACT

The harmful substances, defined as trihalomethanes (THMs), were found to be formed during the disinfection of drinking water when chlorine was used as the disinfectant. In this research, the effectiveness of granular activated carbon (GAC) and air stripping (AS) packed column for the removal of chloroform ($CHCl_3$) (as THMs basic indicator compound in many resources) in range of 50 to300µg/L, from drinking water was studied. Pilots of GAC and air stripping columns were designed and set up. The study was carried out for the two cases of deionized and chlorinated Tehran tap water. Also the effects of flow rate, chloroform and TDS concentrations were considered in both treatment systems. Gas chromatography (GC) with electron capture detector (ECD) was used for determination of chloroform concentration in inlet and outlet samples. The obtained data were analyzed by SPSS and non-parametric Kruskal–Wallis method. Results showed a positive correlation between the flow rate and chloroform concentration, and removal efficiencies. The average of variations of removal efficiencies for AS and GAC columns with deionized water samples were, 89.9%, 71.2% and for chlorinated Tehran tap water were 91.2% and 76.4%, respectively. The removal of feed residual chlorine in these columns with 0.5, 0.8 ppm was 100%, respectively and re-chlorination for finishing water was recommended. Results showed AS to be considered more effective in chloroform removal for conventional water treatment plants as a finishing process.

Keywords: *Drinking water, THMs removal, Chloroform, Air stripping, GAC column*

INTRODUCTION

Chlorine, the most commonly used disinfectant in the most water treatment plants, reacts with natural or man-made organic matter in water and forms disinfection by products (DBPs), including trihalomethanes (THMs) (WHO, 1998 and Marawski, 2000). The THM compounds and mainly chloroform ($CHCl_3$) are toxic or carcinogenic and thus represent a direct health risk such as liver and kidney cancer, nervous system and reproductive effects (Odom, 1999; King, 2000; Yang, 2000).

The current regulation of U.S Environmental Protection Agency (USEPA) in drinking water is 80 µg/L (EPA, 1999). The Commission of the European Communities proposed a council directive with parametric values of 40 and 15µg/L for chloroform and bromodichloromethane, respectively (Marawski, 2000; Yoon, 2003).The recommended value by WHO for chloroform is 30 µg/L (WHO, 1998). The Islamic Republic of Iran regulation of THMs for chloroform, bromoform, bromodichloromethane and dibromo- chloromethane is 200, 100, 60 and 100 µg/L, respectively (ISIRI, 1997). Several treatment alternatives have been proposed for the removal of THMs and its

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precursors. Removal can be performed with adsorption on activated carbon, oxidation, stripping and biological treatment. USEPA has proposed utilizing these processes to eliminate or reduce potentially carcinogenic organic substances in public supplies (Ducom, 1999;Yang, 2000). But these processes present several drawbacks such as toxic by-products formation, transfer of pollutants to the air or to a solid phase, difficulties in adapting to variations of concentrations and feed flow with time (King, 2000; Marawski, 2000). The best option in water resources management is to protect water quality in dam reservoirs and rivers in order to minimize the concentration of THMs precursors. The second alternative is THMs precursors' removal with the aim of THMs formation minimization. But in the situations in which the up-mentioned options are not applicable (because of high level of water pollution and technical constraints in water treatment plant), THMs removal should be highly considered in order to protect the human health (WHO, 1998; Marawski, 2000; Wietlik, 2002). Application of granular activated carbon (GAC) and air stripping columns have been of special interest due to their potential for removal of a wide range of compounds such as natural organic matters (NOMs), THMs, odor and color and other organic toxic compounds (Ducom, 1999 ;Odom, 1999 ; Mahmud, 2002). The main objective of this research was to investigate the performance and efficiency of GAC and AS columns for THMs removal from drinking water (deionized & Tehran tap water) and to compare the results under different operational conditions. The specific objectives were as follows:

Study the performance of GAC column under different operational conditions of flow rate, $CHCl_3$ &TDS concentrations.

Study the performance of air stripping column under various operational conditions of flow rate, $CHCl_3$ and TDS concentrations.

MATERIALS AND METHODS

The schematic flow diagram for the GAC column is shown in Fig. 1.

GAC was washed with deionized water to remove all carbon fine particles, dried at 105ºC for 2 days and cooled in a desiccator. A plexcy glass column with internal diameter (ID) of 25 cm and height of 90 cm was filled with GAC. The AS pilot was similar as GAS column and was filled with packing material spiral PVC pieces with length of 1.5 cm and thickness of 0.5 mm. The schematic flow diagram for the Air stripping column is shown in Fig. 2.

THMs measurements

THMs (chloroform) measurements in samples were performed by Shimatzu GC-17A gas chromatograph equipped with an electron capture detector (ECD).The used column was with 0.32 mm diameter packed by DB-5. Samples were measured by method No. 6232 B (Liquid-Liquid extraction gas chromatography) from (Odom, 1999). To increase the reliability of the results, samples were measured and studied for at least three times (AWWA, 1994).

GAC column

The sample water was pumped to the column in up-flow mode with a Lowara Ind. Model peristaltic pump through Teflon tubing. Experimental steps for determination of removal efficiencies for GAC column were as follows:

Adjustment of feed temperature at 17±0.5 ºC, flow rate at 1 L/min and preparation of chloroform samples with deionized water in concentration range of 50 to 300 µg/L in order to study the effect of THMs concentration on R% (R% is the chloroform removal percentage). Preparation of THMs samples with deionized water and with a concentration of 100 µg/L of chloroform , temperature of 17±

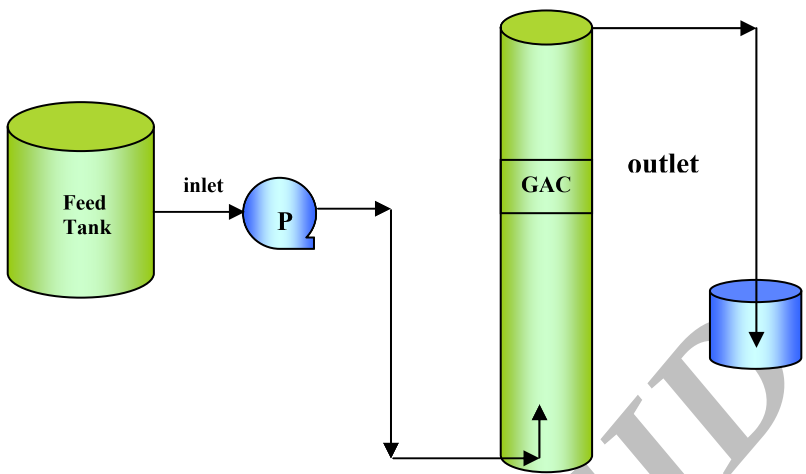
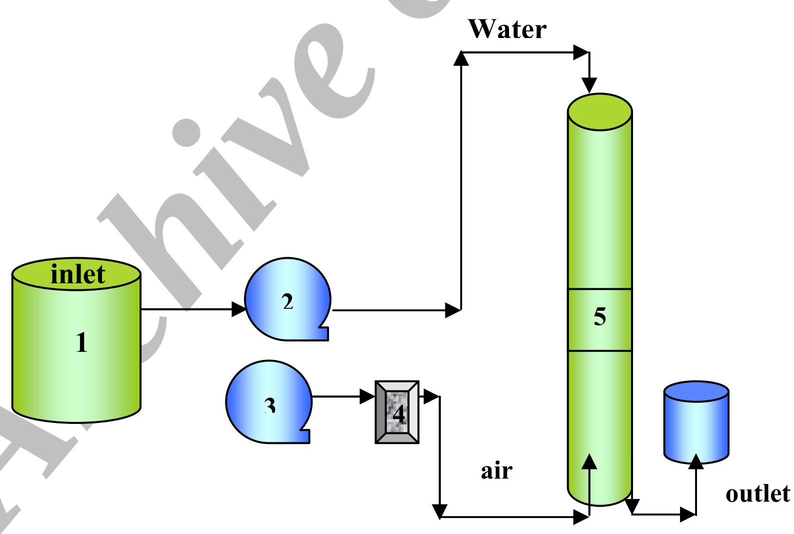


Fig. 1: Schematic flow diagram for GAC pilot



1. Feed tank
2. Feed pump
3. Air compressor
4. Flow meter
5. Air stripping column

Fig. 2: Schematic flow diagram for air stripping pilot

0.5 ºC and inlet flow rates of 0.5 to 3 L/min in order to study the effect of flow rate on R%. Preparation of THMs samples as above mentioned to study the effect of TDS concentration on R% of chloroform with different concentrations of 250, 500, 750 and 1000 mg/L. Conducting the up-mentioned steps with Tehran tap water and in upwards conditions.

Air stripping column

The sample water was pumped to the column in down -flow mode with a Lowara Ind. Model peristaltic pump through Teflon tubing. The air-to-water ratio was 20:1 and supplied by a Sibata compressor. The design of air-stripping packed-column for steady–state mass transfer was based on the following relationships (Viessman, 1993 and Hammer, 1996):

Z= (HTU) (NTU) **(1)**

Z= depth of packing,m
HTU=height of a transfer unit, m
NTU=number of transfer units (dimensionless)

HTU= L / ρ_L k_L a **(2)**

L= water mass loading rate, kg/m^2.s
ρ_L =water density, kg/m^3
L/ ρ_L = volumetric loading rate, m^3/m^2.s
K_La = overall mass transfer coefficient, s^{-1}

NTU= (S/S-1) Ln (C_{in}/C_{out}) (S-1) +1 / S **(3)**

S= stripping factor, mol/mol (dimensionless)
C_{in}= chloroform concentration in influent, kg/m^3
C_{out} = chloroform concentration in effluent, kg/m^3

S=H (Q_A/Q_W) **(4)**

H= Henry's law constant (dimensionless)
Q_A = volumetric airflow rate, m^3/s
Q_W= volumetric water loading rate, m^3/s

Experimental steps for determination of chloroform removal efficiencies for air stripping column were as follows:

- Adjustment of feed temperature at 17±0.5 ºC,water flow rate at 1 L/min, air flow at 40 L/min and preparation of chloroform samples with deionized water in concentration range of 50 to 300 µg/L of CHCl3 in order to study the effect of THMs concentration on R% (R% is the chloroform removal percentage).
- Preparation of THMs samples with deionized water and with a concentration of 100 µg/L of chloroform, temperature of 17± 0.5 ºC, air flow rate at 40 L/min and inlet water flow rates of 0.5 to 3 L/min in order to study the effect of flow rate on R%.
- Preparation of THMs samples as above mentioned to study the effect of TDS concentration on R% of chloroform with different concentrations of 250, 500, 750 and 1000 mg/L $CaCO_3$.
- Performing the up-mentioned steps with Tehran tap water and in upwards conditions.

RESULTS

GAC adsorption column performance

The correlation between $CHCl_3$ removal percentage from deionized water with variation of flow rate and chloroform concentrations is shown in Tables 1 and 2, respectively. The best removal efficiency was obtained with flow rate of 0.5 L/min and CHCl3 concentration of 100µg/L (R%=86.6).The change of flow rate was from 0.5 to 3 L/min, resulted to the decrease of R% to 69.1%. Also the amount of R% varied from 87.4 % to55.1 % with increasing $CHCl_3$ concentration from 50 to 300 µg/L (about 32% decrease).

Air stripping column performance

The variations of removal efficiency with $CHCl_3$ concentrations and flow rates are shown in Table3 and 4, respectively. Also Fig.3 shows the comparison between performances of GAC column and air stripping pilot on $CHCl_3$ removal with TDS concentration variations in feed deionized water.

The maximum efficiency for this pilot was 97.6% with water flow rate =1 L/min, air flow rate = 40 L/min, 50 µg/L $CHCl_3$ and 17ºC. In this pilot, R% varied from 82.3% to 97.6% with increasing $CHCl_3$ concentration from 50 to 300 µg/L and 83.2% to 97.2% with variation of feed flow rate from 0.5 to 3 L/min.

Chlorinated Tehran tap water

Tehran tap water was used as the feed for all of the up-mentioned experiments. Comparisons between performances of GAC column and air stripping column in chloroform removal of Tehran tap water are shown in Table 5. Best results were obtained from air stripping pilot (91.2%), making it an efficient process to remove THMs from drinking water but decreasing of $CHCl_3$ rejection performance with the increase of feed flow rate may be considerable (24% decrease of performance with flow rate increasing from 0.5 to 3 L/min).

Table 1: Percent of chloroform removal from deionized water in GAC column pilot versus flow rate variations

Flow rate (L/min)	C_{in} (µg/L)	C_{out} (µg/L)	$CHCl_3$ rejection (%)	Sd. Dev.
0.5	100	2.8	97.2	0.31
1	100	3.3	96.7	0.74
1.5	100	11.4	88.8	0.25
2	100	12.5	87.4	0.97
2.5	100	15.4	84.6	0.42
3	100	17	83.2	0.12

Table 2: Percent of chloroform removal from deionized water in GAC column pilot versus $CHCl_3$ concentration variations

C_{in} (µg/L)	C_{out} (µg/L)	$CHCl_3$ rejection (%)	Sd. Dev
50	1.2	97.6	0.95
100	4.2	95.8	1.24
150	7.2	95.2	0.71
200	15.1	92.5	0.29
250	33	86.8	0.64
300	53.3	82.3	0.92

Table 3: Percent of chloroform removal from deionized water in air stripping pilot versus flow rate variations

Flow rate (L/min)	C_{in} (µg/L)	C_{out} (µg/L)	$CHCl_3$ rejection (%)	Sd. Dev
0.5	100	13.3	86.6	1.27
1	100	18.9	81.2	2.21
1.5	100	19	80.9	0.63
2	100	22.5	77.3	1.05
2.5	100	27.5	72.8	0.54
3	100	31	69.1	0.39

Table 4: Percent of chloroform removal from deionized water in air stripping pilot versus CHCl3 concentration variations

C_{in} (µg/L)	C_{out} (µg/L)	$CHCl_3$ rejection (%)	Sd. Dev
50	6.4	87.4	0.36
100	19.8	80.2	0.82
150	40.9	72.7	0.87
200	62.7	68.8	0.97
250	99.5	60.3	0.24
300	134.4	55.1	0.43

Table 5: Comparison between performances of GAC column (Q=1 L/min, T=17ºC) and air stripping pilot (Q=1 L/min, air flow=40L/min) on Tehran tap water

Parameter	Inlet	GAC Outlet	GAC R%	A.S Outlet	A.S R%
TDS (mg/L)	348	149.9	56.9	329	5.5
TSS (mg/L)	17.6	13.3	24.4	17.3	1.7
Residual chlorine (ppm)	0.2	0.0	100	0.0	100
Conductivity (µS/cm)	317	231.7	26.9	306	3.5
CHCl3 conc. (µg/L)	56	13.2	76.4	4.9	1.2

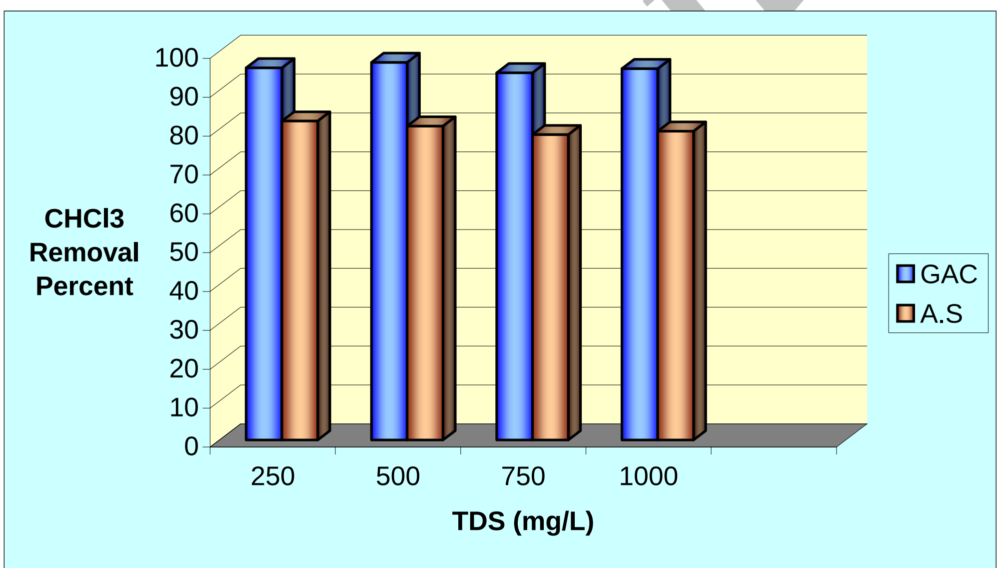


Fig. 3: Comparison between performances of GAC column (Q=1 L/min, T=17ºC) and air stripping pilot (Q=1 L/min, air flow=40L/min) on $CHCl_3$ removal with TDS concentration variations in feed deionized water

DISCUSSION

The obtained data from GAC column were analyzed by SPSS and non – parametric Kruskal- Wallis method. Results showed that there would a linear relationship between flow rate and chloroform concentration with $CHCl_3$, removal percentage (R %) but variations of TDS concentration had no significant effect on R% (R%= 79.5 to 82.5). The potential of GAC column to remove of THMs precursors in Ankara drinking water was previously reported by Capar and Yetis. They reported GAC column to have the capability of effective removal of THMs precursors but they did not determine the effect of TDS on efficiency of this system (Capar and Yetis, 2002).The synthetic carbon spheres derived from phenol resin were used as GAC for water purification from THMs by Morawski and Inagaki. According to their results, it might be possible to change the adsorptive properties of GAC by nitric acid treatment and creating a different complex on its surface that might lead to increase adsorption abilities (Morawski and Inagaki, 1997). Similar with GAC column, results of SPSS statistical analysis showed straight relationship between flow rate and chloroform concentration with $CHCl_3$ R% in air stripping system but variations of TDS concentration had no significant effect on R%. Variation of TDS from 250 to 1000 mg/L CaCO3 can change the R only 1%. Mahmud and Kumar showed volatile organic carbons (VOCs) to be removed by air stripping and good results were obtained. But they did not determine effect of TDS concentration and flow rate variations on VOCs removal efficiency (Mahmud and Kumar, 2000). Research on air stripping for Tehran tap water indicated that the presence of salts and other dissolved compounds did not interfere on THMs (chloroform) removal efficiency both in GAC and air stripping systems. Although both GAC adsorption and air stripping pilots showed acceptable performances for THMs removal from drinking water, but the air stripping system was more efficient, and may be considered for low flow rate and relatively high energy demand in large water treatment plants.

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