Disinfection By-Product Removal by Activated Carbon-using Batch mode

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Abstract:

This research was aimed to study the efficiency of activated carbon to remove Disinfection By-Products (DBPs) from drinking water. This work studies the main compounds of DBPs Trichloromethane (TCM) and Trichloroacetic acid (TCA) at the effect of Temperature (25–35 °C), pH (4−9), adsorbate initial concentration (4–124 mg/l) for TCM, (4–100 mg/l) for TCA and adsorbent weight (15−20 g) of activated carbon. The results show that the adsorption capacity decreases with temperature and pH increasing, and increases with initial adsorbate concentration and adsorbent weight increasing. The kinetics of the adsorption was studies and the results showed that it followed the pseudo-first-order kine tics, also the thermodynamic parameters were determined for adsorption process where the results showed that the adsorption of TCM and TCA on activated carbon was spontaneously and exothermic. The Langmuir and Freundlich isotherms constants were determined for TCM and TCA, at the end of this work eight tap water samples from Baghdad University tap water were tested to determine TCM and TCA concentrations then treated with activated carbon where the removal efficiency was (98.1% − 99.37 %).

Keywords: Disinfection By-Product; DBPs; Drinking Water; Trihalomethane; THMs; Haloacetic Acid; HAAs; Activated Carbon.

1. Introduction

Water has been treated for thousands of years by a variety of processes, though procedures that produce safe potable water were not developed until the 19th century, when it became clear that many serious epidemics were related to sewage contaminated water. It was discovered that chlorine was effective as a disinfectant in destroying pathogenic (disease causing) organisms, and that maintaining chlorine residual in the distribution system produced safe water and protected against harmful contamination. Many countries use chlorination today. Chlorine and other disinfectants can react with trace organics found in many water sources, their by-products may be objectionable in taste or odor, and some may be harmful[1]. While disinfectants are effective in
controlling many microorganisms, they react with natural organic and inorganic matter in source water and distribution systems to form Disinfection By-Products (DBPs). Results from toxicology studies have shown several DBPs (e.g., chloroform, bromodichloromethane, bromoform, trichloroacetic acid, dichloroacetic acid, and bromate) to be carcinogenic in laboratory animals[2]. Other DBPs (e.g., chlorite and certain haloacetic acids) have also been shown to cause adverse reproductive or developmental effects in laboratory animals. Several epidemiology studies have suggested a weak association between certain cancers (e.g., bladder) or reproductive and developmental effects, and exposure to chlorinated surface water. More than 200 million people consume water that has been disinfected. Because of the large population exposed, health risks associated with DBPs, even if small, need to be taken seriously[3].

The maximum contaminant levels (MCLs) in mg/l for total Trihalomethanes (THMs), Haloacetic Acids (HAAs), chlorite, bromate and some of disinfection by-product depending on World Health Organization (WHO), U.S. Environmental Protection Agency (U.S. EPA), European Union (EU), Egypt, Iraq, Syrian Arab Republic and Sudan drinking water standards is given in table (1)[4].

Table (1) Disinfection By-Product Regulations

| Standards in (mg/l)           | WHO  | U.S.EPA | EU   | Egypt | Syria | Sudan |
|------------------------------|------|---------|------|-------|-------|-------|
| Trihalomethanes(THMs)        | –    | 0.080   | 0.100| 0.100 | –     | –     |
| Haloacetic Acid (HAAs)       | –    | 0.060   | –    | –     | –     | –     |
| Chloroform                   | 0.2  | –       | 0.040| –     | 0.03  | 0.15  |
| Bromate                      | 0.01 | 0.010   | –    | 0.025 | –     | 0.017 |
| Bromodichloromethane         | 0.06 | –       | 0.015| –     | –     | 0.04  |
| Bromoform                    | 0.1  | –       | –    | –     | –     | 0.075 |
| Chlorite                     | 0.7  | 1.0     | –    | 0.2   | –     | 0.15  |
| Dibromochloromethane         | 0.1  | –       | –    | –     | –     | 0.075 |
| Dichloromethane              | 0.02 | –       | 0.02 | –     | –     | 0.014 |

There are various methods to remove HAAs including chemical precipitation, membrane process, ion exchange, liquid extraction and electrodialysis. The adsorption technique is one of the preferred methods for removal of Disinfection By-Products (DBPs) because of its efficiency and low cost[5].

Several treatment alternatives have been proposed for the removal of DBPs. Granular activated carbon (GAC) has been of a special interest due to its ability to remove a wide range of compounds such as odor and color causing compounds, NOMs, THMs, HAAs and other toxic compounds[6].

Previous researches on the drinking water have showed the occurrence of THMs, HAAs and natural organic matter (NOM) in the chlorinated finished drinking water[7].
Much research on DBPs removal has been focused on NOM (Naturally Occurring Matter) removal only, a few results have been recently reported on the removal of preformed DBPs in controlled experiments[8].

In this research study the efficiency of activated carbon to remove Trichloromethane (TCM) and Trichloroacetic acid (TCA) from prepared water samples at the effect of different temperature, pH value, adsorbate initial concentration and adsorbent weight, using batch adsorption mode, the adsorption isotherms constants and thermodynamic parameters ($\Delta G$, $\Delta H$ and $\Delta S$) for the adsorption process were determined, also the kinetics of the adsorption process was studied and pseudo-first and second-order parameters for the adsorption process were determined.

2. Materials and Methods:
Trichloromethane (CHCl$_3$) with purity of 99.1 % was used to prepare TCM water samples with various concentration 4, 8, 40, 80 and 124 (mg/l) and Trichloroacetic acid (CCl$_3$COOH) crystals with purity of 99.0 % was used to prepare TCA water samples with various concentration 4, 16, 32, 64 and 100 (mg/l), distilled deionized water was used for diluting. Sodium Hydroxide Standard Solution (NaOH) and Hydrochloric Acid Standard Solution (HCl) were used to control pH value of samples.

3. Experimental Procedure:
Prepared water samples with various TCM and TCA concentration were prepared in 500 ml conical flasks with different initial conditions temperature, pH, adsorbate initial concentration and adsorbent weight. A sample of 5 ml was taken every 15 min. for TCM and every 10 min. for TCA and kept in a sample tube then tested with Gas Chromatography (GC) in Ibn Sina State Company. Weighing the TCA and solving it with distilled deionized water to the desired initial concentrations, TCM solution was diluted with distilled deionized water to desired concentrations. To change pH value of samples in the chosen range HCl acid and NaOH base were used in small amounts and pH-meter device was used. A quantity of fresh activated carbon in the range of 15–20 g weight was added to each flask depending on experiment case.

4. Results and Discussions:
In batch adsorption process, adsorbate concentration in water samples changes because of different parameters.

The Effect of Temperature
Because adsorption reactions are usually exothermic, high temperatures would seem to inhibit or slow adsorption, but this is not usually found to be a factor in most systems. An explanation for this may be revealed by considering the rate limiting factor for adsorption again. In carbon, adsorption is limited primarily by the diffusion of solute into the carbon particle. Higher temperatures may impede adsorption at the adsorption site, but they significantly speed up the pace of diffusion, offsetting any negative temperature effect. Small variations in temperature do not tend to alter the adsorption process to a significant extent.

The experiments for TCM initial concentrations 4, 8, 40, 80 and 124 ppm at temperature 293, 298, 303 and 308 K were carried out by water bath with temperature controller to describe the temperature effect on the adsorption of TCM on activated carbon. The results represented in figure (1).
Figure (1) removal efficiency of TCM at different temperature ($C_0=4$–124 mg/l, pH=7, $V=500$ ml, $W=20$ g).

The experiments for TCA initial concentrations 4, 16, 32, 64 and 100 ppm at temperature 293, 298, 303 and 308 K were carried out to describe the temperature effect on the adsorption of TCA on activated carbon. The results represented in figure (2).

Figure (2) removal efficiency of TCA at different temperature ($C_0=4$–100 mg/l, pH=7, $V=500$ ml, $W=20$ g).
The results show that the removal efficiency of TCM and TCA increases with decrease in temperature, this is due to the fact that the adsorption reactions are exothermic, then the increase temperatures would inhibit or slow the adsorption.

**Effect of pH**

pH strongly influences the adsorption as hydrogen and hydroxide ions are adsorbed and the charge of the other ions are influenced by pH of the solution. Change of pH value in adsorption system could lead to the transformation of chemical characteristics on the surface of activated carbon and the form of the adsorbate, thus it plays an important role in the adsorption performance. Acidic or alkali species may change the surface chemistry of the adsorbent by reacting with the surface groups. These effects may lead to significant alterations in the adsorption equilibrium depending on the pH[9].

The experiments for TCM initial concentrations 4, 8, 40, 80 and 124 ppm at pH value of 4, 7, and 9 were carried out to describe the effect of pH on the adsorption process. The results represented in figure (3).

![Figure (3) TCM removal efficiency at different pH value (C₀=4–124 mg/l, Temp. =298 K, V=500 ml, W=20 g).](image)

The experiments for TCA initial concentrations 4, 16, 32, 64 and 100 ppm at pH value of 4, 7, and 9 were carried out to describe the effect of pH on the adsorption process. The results represented in figure (4).
Figure (4) TCA removal efficiency at different pH value (C_o=4−100 mg/l, Temp. =298 K, V=500 ml, W=20 g).

It can be seen that the total amount of TCM and TCA removed from solution at equilibrium at different pH value increases with decreasing pH value. This can be explained on the basic of formation of a positively charged surface on adsorbent. A low pH value quite probably results in a lowering of the decrease of the negative charge on the adsorbent, thus changing the adsorption of the negatively charged adsorbate.

Effect of TCM and TCA initial Concentrations

The initial concentration is inversely related to adsorption equilibrium time. This may be explained by the fact that since the rate of diffusion is controlled by the concentration gradient, it takes a longer contact time to reach adsorption equilibrium for the case of low values initial solute concentration.

Because adsorption rate is limited by diffusion, variables that influence diffusion have a significant effect on adsorption rate. For example, a higher concentration gradient across the surface of the adsorbent particle will increase the rate of adsorption[10]. The experiments were carried out at different TCM initial concentrations 40, 80 and 124 ppm to describe the effect of TCM initial concentration on adsorption process. The samples were taken at different time period 15, 30, 45 and 60 minute, the results were represented in figure (5).
Figure (5) TCM adsorption capacity at different TCM initial concentration ($C_0 = 40$, 80 and 124 mg/l, Temp. = 298 K, pH=7, V=500 ml, W=20 g).

The experiments were carried out at different TCA initial concentrations 32, 64 and 100 ppm to describe the effect of TCA initial concentration on adsorption process. The samples were taken at different time period 10, 20, 30 and 40 minute, the results were represented in figure (6).

Figure (6) TCA adsorption capacity at different TCA initial concentration ($C_0 = 32$, 64 and 100 mg/l, Temp. = 298 K, pH=7, V=500 ml, W=20 g).

These results show that the adsorption quantity at any period of time increases with the initial TCM concentration increasing. This is due to the fact that the increase in the initial concentration expands the difference between the bulk concentration and that on the surface of
the adsorbent and leads to the increasing driving force and consequently increases the adsorption rate and then increases the capacity.

Effect of Adsorbent Weight

The adsorbent weight is an important factor determining the capacity of adsorbent in a batch adsorption. It followed the predicted pattern of increasing adsorption capacity as the dosage was increased. The experiments were carried out to describe the effect of activated carbon weight 15, 18 and 20 g on the TCM and TCA adsorption process. The effect of Adsorbent Weight on adsorption of TCM and TCA were represented in figure (7) and (8) respectively.

![Figure (7) TCM adsorption capacity with different activated carbon weight (C_o=124 mg/l, Temp. =298 K, pH=7, V=500 ml).]
Figure (8) TCA adsorption capacity with different activated carbon weight (C₀=100 mg/l, Temp. =298 K, pH=7, V=500 ml).

Kinetics study

In this study adsorption data are applied to the pseudo-first order, pseudo-second order kinetic models to find the rate constants of adsorption.

The results show that the adsorption process of TCM and TCA on activated carbon take pseudo-first order kinetic because the degree of fit for the pseudo-first-order model is larger than the degree of fit for pseudo-second-order model. Pseudo-first and second order obtained parameters for TCM and TCA adsorption on activated carbon were summarized in table (2) and table (3) respectively.

Table (2) pseudo-first and second-order parameters for TCM adsorption on activated carbon (C₀=124 mg/l, pH=7, Temp. =298 K, V=500 ml, W=20 g).

| Temp. | Qₑ (mg/g) | Qₑ (mg/g) | K₁ | R² | Qₑ (mg/g) | K₂ | R² |
|-------|-----------|-----------|----|----|-----------|----|----|
| 298 K | 3.093     | 3.8       | 4.84×10⁻² | 0.9417 | 25.2       | 8.8×10⁻⁵ | 0.0461 |

Table (3) pseudo-first and second order parameters for TCA adsorption on activated carbon (C₀=100 mg/l, pH=7, Temp. =298 K, V=500 ml, W=20 g).

| Temp. | Qₑ (mg/g) | Qₑ (mg/g) | K₁ | R² | Qₑ (mg/g) | K₂ | R² |
|-------|-----------|-----------|----|----|-----------|----|----|
| 298 K | 2.496     | 2.93      | 7.73×10⁻² | 0.9595 | 4.27       | 7.53×10⁻³ | 0.9411 |

Adsorption Isotherms

The applicability of adsorption isotherms to study the adsorption behavior has also been analyzed by Langmuir and Freundlich isotherm models were used to illustrate the experimental
isotherms and isotherm's constants. Langmuir and Freundlich isotherms for TCM adsorption on activated carbon represented in figure (9) and (10) respectively.

Figure (9) Langmuir adsorption isotherms for TCM on activated carbon ($C_e = 4–124 \text{ mg/l}$, pH=7, Temp. =298 K, V=500 ml, W=20 g).

Figure (10) Freundlich adsorption isotherms for TCM on activated carbon ($C_e = 4–124 \text{ mg/l}$, pH=7, Temp. =298 K, V=500 ml, W=20 g).

The results show that the adsorption of TCM on activated carbon follows Freundlich adsorption isotherm because the value of correlation factor ($R^2=0.9921$) is closed to 1 more than for Langmuir isotherm, also Langmuir model involves an assumption that the energy of adsorption is the same for all surface sites and not dependent on degree of coverage. The
Freundlich assumes that the energy of adsorption vary on surface sites such in reality because real surfaces are heterogeneous.

The obtained Langmuir and Freundlich isotherms constants for TCM adsorption on activated carbon were summarized in table (4).

**Table (4) TCM Langmuir and Freundlich isotherms constants (C_o=4−124 mg/l, pH=7, Temp. =298 K, V=500 ml, W=20 g).**

| Temp. | Langmuir isotherm constants | Freundlich isotherm constants |
|-------|-----------------------------|-------------------------------|
|       | K_L(l/mg)                   | Q_o(mg/l)                     | R^2 | K_F | n_f=1/n | R^2 |
| 298 K | 10.615                      | 4.078                         | 0.9733 | 8.847 | 0.701 | 0.9921 |

For TCA the Langmuir and Freundlich isotherms represented in figure (11) and (12) respectively.

**Figure (11) Langmuir adsorption isotherm for TCA on activated carbon (C_o=4−100 mg/l, pH=7, Temp. =298 K, V=500 ml, W=20 g).**
Figure (12) Freundlich adsorption isotherm for TCA on activated carbon (C_0 = 4–100 mg/l, pH = 7, Temp. = 298 K, V = 500 ml, W = 20 g).

The results show that the adsorption of TCA on activated carbon follows Freundlich adsorption isotherm because the value of correlation factor (R^2 = 0.9996) is closer to 1 more than for Langmuir isotherm.

The obtained Langmuir and Freundlich isotherms constants for TCA adsorption on activated carbon were summarized in table (5).

Table (5) TCA Langmuir and Freundlich isotherms constants (C_0 = 4–100 mg/l, pH = 7, Temp. = 298 K, V = 500 ml, W = 20 g).

| Temp.   | Langmuir isotherm constants | Freundlich isotherm constants |
|---------|-----------------------------|--------------------------------|
|         | K_l (l/mg)                  | Q_o (mg/l)                     | R^2  | K_f | n_f = 1/n | R^2  |
| 298 K   | 16.159                      | 3.223                          | 0.9067 | 8.096 | 0.6425 | 0.9996 |

Calculation of Thermodynamic Parameters for Adsorption Process

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. These parameters such as the change in Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) were determined using VantHoff equation[11]. The results show that the adsorption process of TCM and TCA was spontaneous and exothermic, the
obtained thermodynamic parameters for TCM and TCA adsorption on activated carbon at Temp. =298 K were summarized in table (6) and (7) respectively.

Table (6) thermodynamic parameters for TCM adsorption on activated carbon (C_o=124 mg/l, pH=7, V=500 ml, W=20 g).

| Temp. (K) | ΔG (KJ/mol) | ΔH (KJ/mol) | ΔS (KJ/mol. K) |
|-----------|-------------|-------------|---------------|
| 298       | -14.86      | -89.25      | -0.2496       |

Table (7) thermodynamic parameters for TCA adsorption on activated carbon (C_o=100 mg/l, pH=7, V=500 ml, W=20 g).

| Temp. (K) | ΔG (KJ/mol.) | ΔH (KJ/mol.) | ΔS (KJ/mol. K) |
|-----------|--------------|--------------|---------------|
| 298       | -15.92       | -44.09       | -0.0945       |

Removing TCM and TCA from random tap water samples

Tap water samples were taken at different days from tap water and tested for TCM and TCA concentrations.

The pH value of samples was pH≈7.0 and the flasks put in the water bath and collected to ambient temperature of T=298 K then 20 g of activated carbon was added to every sample with shaking and lift to reach final concentrations.

TCM and TCA removal efficiencies were calculated and summarized in table (10).

Table (8) removal efficiency of TCM and TCA from tap water (pH=7, Temp. =298 K, V=500 ml, W=20 g).

| Sample no. | TCM removal efficiency % |
|------------|--------------------------|
| 1          | 98.7 %                   |
| 2          | 98.5 %                   |
| 3          | 98.5 %                   |
| 4          | 98.1 %                   |
The results show the removal efficiency of TCA from tap water was greater than to TCM, this difference represented in figure (4-33).

![Figure (13) TCM and TCA removal efficiency from tap water (pH=7, Temp. =298 K, V=500 ml, W=20 g)](image)

This can be explained by the difference between compounds in ability to adsorb, because it different in molecular weight, molecular structure and solubility in water. The water solubility of organic compounds within a particular chemical class decreases with increasing chain length, because the compound becomes more hydrocarbon-like as the number of carbon atoms becomes greater.

5. Conclusions:

The following points can be concluded from this work:
1. Adsorption by activated carbon was an effective process for removal of Trichloromethane (TCM) and Trichloroacetic acid (TCA) from water samples.
2. The capacity of adsorption increases with:
   a. The increase in adsorbate initial concentration.
   b. The increase in adsorbent weight (W).
   c. The decrease in temperature.
   d. The decrease in pH value.
3. In tap water samples the efficiency of activated carbon to remove TCA was greater than to remove TCM.
4. The removal efficiency of TCM and TCA from prepared water samples is greater than from tap water samples.
5. The degree of fit of Langmuir isotherm were $R^2=0.9733$ and $R^2=0.9067$ for TCM and TCA respectively, while degree of fit of Freundlich isotherm were $R^2=0.9921$ and $R^2=0.9996$ for TCM and TCA respectively.
6. The adsorption of TCM and TCA on activated carbon was followed pseudo-first-order model kinetics.
7. The adsorption of TCM and TCA on activated carbon was spontaneous and exothermic.

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