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RESEARCH ARTICLE

Removal of trihalomethanes in drinking water by using poly-o-phenylenediamine conducting polymer

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Abstract

Reaction between natural organic matter (NOM) and chlorine during disinfecting drinking water form trihalomethanes (THMs) which are possible carcinogen to human health. Hence engineers are required to minimize the concentration of THMs in water either by adsorption or use an alternate disinfectant. The THMs content determination is based on Gas Chromatography- measurements. Poly o-Phenylenediamine (POPDA) was used to remove THMs by adsorption. The removal efficiency of THMs by using different doses of (POPDA) was calculated and also increases by using POPDA/ carbon nanotubes (CNTs) composite. The measured value of THMs in two plants of Beni-Suef governorate namely, American plant 1 and American plant 2 was found to be 64.09 and 43.51 µg/l respectively. The application of (0.32 mg/L) doses of POPDA and POPDA/ (CNTs) composite on sample of American plant 1 for one hour give high removal efficiency reach to 93.64 and 95.58% respectively. The method validation, uncertainty, recovery and linearity of measurement were determined. The adsorption data of THMs on the POPDA and POPDA/CNTs composite was found to fit well with Langmuir and Freundlish isotherm equations.

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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 investigations of (Rook, (1974)) and (Bellar, (1974)) indicate that aqueous chlorine reacts with naturally occurring organic compounds "humic-acid-like" materials usually referred to as precursors, to form trihalomethanes (THMs). Precursors mean natural organic compounds found in all surface and ground water. 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 acetaldehydes, ethanol and secondary alcohols (McGuire, 2004). In addition humic acid substances, algae, leaves and bark material also react with aqueous chlorine to produce THMs. Generally, the THMs formation also depends on the chemical component of the water especially the presence of bromine and iodine because these two will determine the formation of various other halogenated species. Chlorinated organic solvents are found in many raw water because of industrial contamination also source of the THMs formation. The production of THMs can generally be shown as represented in the following equation (Christman, (1966)):

$$\underset{\text{Chlorine}}{\text{Free}} + \underset{\text{(Precursors)}}{\text{Natural Organic}} + \text{Bromide} \rightarrow \text{THM} + \underset{\text{products}}{\text{Other}} \quad (1)$$

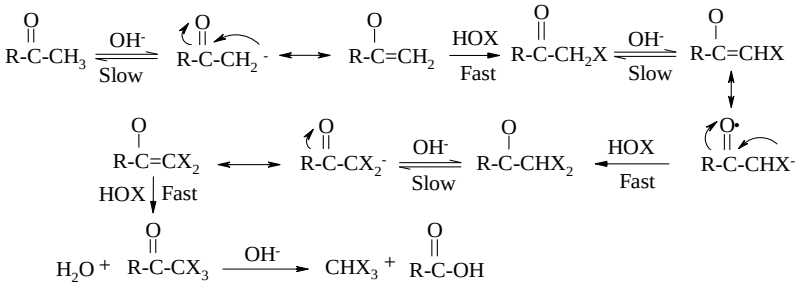
The chlorine usually added in water treatment as chlorine gas (Cl_2) which is rapidly and completely converts to hypochlorous acid (HOCl).

$$Cl_2 + HCO_3 \leftrightarrow HOCl + CO_2 + Cl^- \quad (2)$$

The hypochlorous acid dissociated into hydrogen ions (H^+) and hypochlorite ions (OCl^-) in reversible reaction:

$$HOCl \leftrightarrow H^+ + OCl^- \quad (3)$$

The haloform reaction consists of alternate hydrolysis and halogenations steps (Morris, (1977)); (Rook, (1976)) and (El-Dib, (1995)).



Several studies were made on the possible health effects of THMs in general and chloroform as THMs in particular. Toxicological studies suggest that chloroform caused cancer in experimental animals (rats and mice) and suspected of causing cancer in humans. Chloroform may be absorbed into the body through ingestion, inhalation, and through the skin. The largest source of human exposure to THMs in the U.S. is from the consumption of chlorinated drinking water (Jorgenson, (1985)) ; (Pereira, (1985)).

Evidence of chloroform's acute (Short-Term) effects on humans has been obtained primarily during its past use as an inhalation anesthetic. In addition to central nervous system effects, chloroform anesthesia was associated with cardiac arrhythmias and abnormalities of the liver and kidneys. Chronic (Long-Term) oral exposure of humans to chloroform at high doses results in adverse effects on the central nervous system, liver, kidney and heart (Chu, (1982)); (Borzelleca JF, (1982)); (Jorgenson TA, (1980)) and (Pereira, (1994)).

Long term exposure to high doses of bromodichloromethane (BDCM) and dibromochloromethane (DBCM) cause damage to liver and kidney. BDCM has classified as carcinogens, from Group 2B which possibly carcinogenic to humans.BDCM gave positive results in a variety of in vitro and in vivo genotoxicity assays. In a National Toxicology Program (NTP-USA) bioassay, BDCM induced renal adenomas and adenocarcinomas in both sexes of rats and male mice, rare tumours of the large intestine. Exposure to BDCM has also been linked to a possible increase in reproductive effects such as increased risk for spontaneous abortion or stillbirth (Chu, (1980)); (Borzelleca JF, (1982)); (Ruddick JA, (1983)); (Theiss, (1977)) and (Tobe, (1982)).

In an NTP bioassay, DBCM induced hepatic tumours in female and possibly in male mice but not in rats. International Agency for Research on Cancer (IARC) has classified DBCM in group 3 which not classified as carcinogenicity to humans (Chu, (1980)); (Borzelleca JF, (1982)); (Ruddick JA, (1983)); (Theiss, (1977)) and (Tobe, (1982)).

Bromoform is well absorbed from the gastrointestinal tract. In an experimental, long term exposure to high doses of bromoform cause damage to liver and kidney. In an NTP bioassay, bromoform induced a small increase in relatively rare tumours of the large intestine in rats of both sexes but did not induce tumours in mice. Data from a variety of assays on the genotoxicity of bromoform are equivocal. IRAC has classified bromoform in Group 3 which not classified as carcinogenicity to humans (Chu, (1980)); (Borzelleca JF, (1982)); (Ruddick JA, (1983)); (Theiss, (1977)) and (Tobe, (1982)).

On February 28, 1983, the U.S EPA published in the federal register (page 8406) that maximum contamination level (MCL) of total trihalomethanes (TTHMs) is 0.1 mg/L which the sum of chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) (McGuire, 2004). Consequently, total trihalomethanes are being regulated in potable waters. The four trihalomethanes (THMs) are show as following structure:

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

(a) Treatment to remove trihalomethanes after formation.

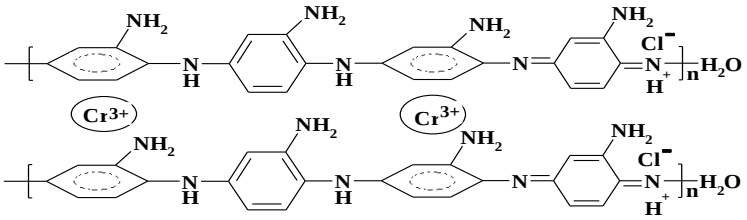
(b) Treatment to remove trihalomethanes precursor(s).

(c) To use an alternate disinfectant.

This investigation deals with the removal of THMs by adsorption on polymer for determination of the removal efficiency of polymer and its application of the investigated polymer on chlorinated potable water containing THMs.

Experimental

The suggested structure of poly o-pheylenediamine as mentioned by (Sayyah, (2014)) is as shown in scheme (1).



Scheme (1): Poly o-pheylenediamine (POPDA).

2.1- Materials:

O-phenylenediamine provided by Aldrich chemical Co., (Germany). Concentrated hydrochloric acid pure grade product provided by El-Nasr pharmaceutical chemical Co., Egypt. Potassium dichromate provided by Sigma-Aldrich chemical Co., (Germany). N-Hexane provided by Aldrich chemical Co. Methanol HPLC provided by Merk chemical Co., (Germany). The certified mixture analytical standard of trihalomethanes provided by Suplco chemical Co. (USA). Chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) individual standards provided by Suplco chemical Co. (USA).

2.2- Poly- o-phenylenediamine / Carbon nano tube nanocomposite preparation:

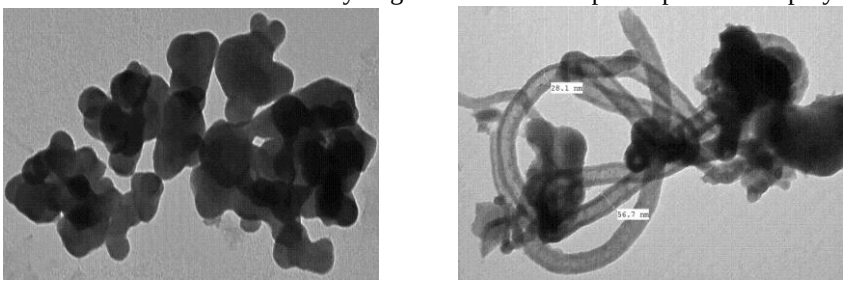
The multi-walled carbon nano-tubes was prepared as published by (Bahgat, (2011)).The MWCNTs /(POPDA) composite was prepared by drop wise chemical polymerization method with HCl as acid medium and $K_2Cr_2O_7$ as the oxidant. The amount of multi-walled carbon nano-tubes was first mixed with 0.3M $K_2Cr_2O_7$ as oxidant by continuous stirring. The monomer amount of o-pheylenediamine was mixed with 0.2 M HCl solution. The weight ratio of o-pheylenediamine: CNTs was 1:1 .The monomer solution was added drop wise carbon nano-tubes mixture under ultrasonication and vigorous stirring. The reaction mixture was subsequently kept under stirring for 2 hrs in an ultrasonic water bath. The precipitate was filtered, and washed thoroughly with deionized water. Finally, the precipitate (composite) was dried in vacuum at 60 ºC.

2.3- Transmission electron microscopy (TEM):

The inner cavity, wall thickness and the tubes length of MWCNTs/POPDA composite were investigated using transmission electron microscopy (TEM) JEOL JEM-1200 EX Π (Japan).

Figure (1-a) show TEM image of poly o-pheylenediamine which spherical or ellipsoidal particles with approximate diameter 60-120 nm either separated or linked with each other.

Figure (1-b) show the transmission electron microscopy images of carbon nano tube /(POPDA) nanocomposite. The nanotubes are accompanied by (POPDA) material, including nanoparticles. The multiwalled tubes range in length from a 30-60 nanometer. The end-caps of the tubes are sometimes symmetrical in shape, but more often asymmetric. The surface of carbon nano tubes are covered by large amount of amorphous particles of poly o-pheylenediamine.



(1-a) (1-b)

Figure (1): The transmission electron microscope of (POPDA) (1-a) and (POPDA) / MWCNTs composite (1-b).

2.4-Prepration of standard (THM) solution:

The stock solution of THMs standard was prepared by transferring the total amount (10µl) of THMs (2000 µg/ml) contained in vial into volumetric flak 5 ml (Class A certified) and making up the volume with methanol. The vial was rinsed with methanol several times and the methanol was transferred into the volumetric flask to ensure the complete transfer. A series of intermediate standard were prepared by mixing appropriate quantities of the stock solution with hexane.

2.5-Sampling:

The samples were collected in 25 ml vial equipped with a screw cap and TFE-faced silicone septum. The vials washed with detergent, rinsed with tap and distilled water, and dry at 105 ^{0}C for one hour before use in an area free of organic vapors. The samples are collected in duplicate without passing air bubbles through the samples and

register the score time, date of collection and temperature. The samples should be analyzed within 10 days of collection.

2.6-Gas chromatography:

The quantitative measurements for all the samples were carried out with a Model Agilent Gas Chromatograph fitted with a Micro- electron capture detector. The install a 30m x 0.32 mm x 0.25 µm methyl silicon (HP-1) column into inlet and µECD detector.

The operating data of the Gas Chromatograph is provided below:

Column : 30m x 0.32 mm ID x 0.25 µm
Carrier : Nitrogen 99.999%
Oven temperature program:
30 ^{0}C for 9 min
35-40 ^{0}C at 10^0 /min
40 ^{0}C for 3 min
40-150 ^{0}C at 6 min
Injector :Split/Splitless

Injection Volume 1.0 µl, 250 ^{0}C
Inlet temperature: 250 ^{0}C, 24.89 pi
Total flow 146 ml/min
Detector :Micro Electron Capture Detector (µECD)
Detector Temperature: 300°C
Nitrogen make up gas at 60 ml/min

2.7-Validation and uncertainty measurement:

2.7.1-Method validation:

The quantification of THMs was based on a five- point calibration graph obtained by plotting the detector response against concentration of the calibration. Limit of detection (LOD) is calculated by visual evolution. The visual determination of LOD is performed by preparing THMs samples with known concentrations and establishing the level at which the THMs can be reliably detect. Also, limit of detection (LOD) is calculated by standard deviation- slope ratio method. This approach is based on the residual standard deviation of the calibration curve (σ) and the slope of registration curve as represented in the following equation:

$$LOD = 3.3\ x\ \frac{\sigma}{slope} \quad (1)$$

The limit of quantification (LOQ) is calculated by standard deviation- slope ratio method (σ/slope) using the following equation:

$$LOQ = 10\ x\ \frac{\sigma}{slope} \quad (2)$$

The total response result then converts into concentration (µg/ml).

2.7.2-Sample preparation:

Let samples and standards reach the room temperature. Open each sample vial and take 25 ml of sample. By using a clean volumetric pipette transfer 5 ml hexane and add to the sample vial. Vigorously shake by hand for 2 min or use a rotary platform shaker set at 60 to 100 rpm. Let phases separate for at least 5 min. where emulsions do not separate on standing, centrifuge or transfer entire emulsion to separate vial. Use a disposable buster glass pipette, transfer at least 1 ml of upper hexane extract to autsampler vial with open screw –top cap and TFE septa.

2.7.3-Detrimination of uncertainty:

Although, there can be several potential source of uncertainties arising from individual preparation and measurement steps. Combined uncertainty in estimation was determined for THMs measurements as per the statistical procedure of the EURACHEM/ CITAC Guide CG 4 (EURACHEM 2000). Four individual sources of uncertainties were taken into account; standard preparation (U_1), curve linearity (U_2), sample preparation (U_3) and recovery (U_4) as described below (Sanyal, (2011)):

Uncertainty for purity of analytical standard (SU): The uncertainty of standard purity declared in the supplier's certificate was given without any confidence level, rectangular distribution was assumed for calculating standard uncertainty (Eq. 3).

$$\mathrm{SU} = \frac{U_{(x)}}{\sqrt{3}} \quad (3)$$

Where $U_{(x)}$ represents the uncertainty value give in the certificate for purity of standard. Also, uncertainty of Micro-pipettes and volumetric flasks were obtained from the calibration certificate of micro pipette and volumetric flasks which calculated as equation (3).
The reputability calculation was calculated as following equation:

$$U = \frac{s}{\sqrt{n}} \quad (4)$$

Where (s) is the standard deviation of measurement and n is number of measurements.
The uncertainty due to differences of temperature between certificate temperature and laboratory temperature was calculated as equation:

$$U = \frac{V \times t \times \Delta T}{\sqrt{3}} \quad (5)$$

Where V is volume of flask or pipette, t is the differences of laboratory temperature and ΔT temperature coefficient.
Non-linearity of calibration curve can be also considered as another source of uncertainty. Uncertainty associated with the calibration curve was calculated according to following equation:

$$U = \sqrt{(\frac{s}{b_1})((\frac{1}{p}) + (\frac{1}{n}) + \frac{(C_0 - C')^2}{s_{xx}})} \quad (6)$$

Where(s) is the standard deviation of the residuals of the calibration curve, b_1 is the slope of the calibration curve; p is the number of measurements of the unknown, n is the number of points used to form the calibration curve, C_0 is the calculated concentration of the analyte from the calibration curve, C' is the arithmetic mean of the concentrations of the standards used to make the calibration curve and s_{xx} is calculated as given in Eq. (7)

$$s_{xx} = \sum(cj - c')^2 \quad (7)$$

Where j = 1, 2,..., n. cj is the concentration of each calibration standard used to build up the calibration curve.
In the present study, the random errors of extraction, clean up, and GC analyses steps were approximated by standard deviations which were calculated from repeated determinations of analytes expressed as repeatabilities. The precision was calculated according to the Eq. 6.

$$U = \frac{s}{\sqrt{n} \times x} \quad (6)$$

Where(s) is the standard deviation of the results obtained from the recovery study, n is the number of assays and x is the mean value of the concentration recovered.
The combined uncertainty (U) was calculated as $U = [(U_1^2 + U_2^2 + U_3^2 + U_4^2)^{1/2}]$ and reported as expanded uncertainty (2U) which is twice the value of the combined uncertainty at95% confidence level.

3. Result and Discussion:

3.1-Validation of the method:

Linearity of calibration curve, LOD and LOQ

The linearity of each THMs was established by plotting GC-μECD response (peak area) versus concentration as shown in figure (2). The data sets show excellent linearity in each concentration range, with correlation coefficients (R^2) nearly≥ 0.99 for each THMs in the matrix. The limit of detection (LOD) which represents the lowest amount of THMs can be reliably detected was calculated by visual evaluation and standard – slope ratio method is represented in Table (1). The data of LOD obtained from visual evaluation and standard – slope ratio (σ/slope) method are in good agreement and confirmed each other. The data of LOQ is represented in Table (1) which represents the lowest concentration of THMs that can be determined with an acceptable level of precision and accuracy.

Table (1): The data of LOD and LOQ for individuals of THMs.

Method	Chloroform	BDCM	DBCM	Bromoform
LOD (visual evolution)	3.00	0.2215	0.3125	0.8254
LOD (σ/slope)	2.9011	0.1401	0.1916	0.7462
LOQ	8.7871	0.4243	0.5806	2.2614

Accuracy and Precision

The accuracy which means the closeness of agreements between the measured THMs value and the true THMs value is calculated using the following equation:

$$\text{Accuarcy} = \frac{X_0}{\mu} \text{ x } 100 \quad (9)$$

Where X_0 is measured value and μ is true value.

Table (2) shows the three run of known standard mixture of THMs 80μg/L and the accuracy value was found in the range 97.88-103.67%.

The precision parameters calculated using ANOVA single factor calculations. From the data in table (2), value of variance within –laboratory standard deviation (S_r) is 0.098319208 and variance between –laboratory standard deviation (S_L) is 0.020999506. The repeatability limit (r) and the reducibility limit (S_R) was found to be 0.278243359 and 0.284519113respectively. These data insure that, closeness of agreement between measured values obtained by replicate measurements under specified conditions.

3.2-Measurment of uncertainties:

Table 3 show the individual and companied uncertainties result of THMs measurements. The total uncertainty was evaluated taking four main sources arising from standard preparation (U_1), curve linearity (U_2), sample preparation (U_3) and recovery (U_4). Figure (3) shows the contribution of individual uncertainties to total uncertainty value. The uncertainty due to calibration (45.14%) represents the most important source of the total uncertainty. This followed by uncertainty due to recovery (24.26 %) and standard preparation (22.07 %). The uncertainty associated with sample preparation provides an insignificant component (8.53%) of total uncertainty. The combined uncertainty (U) was found to be 0.036μg/L and reported as expanded uncertainty (2U) for each measurement was found to be ± 0.072 μg/L.

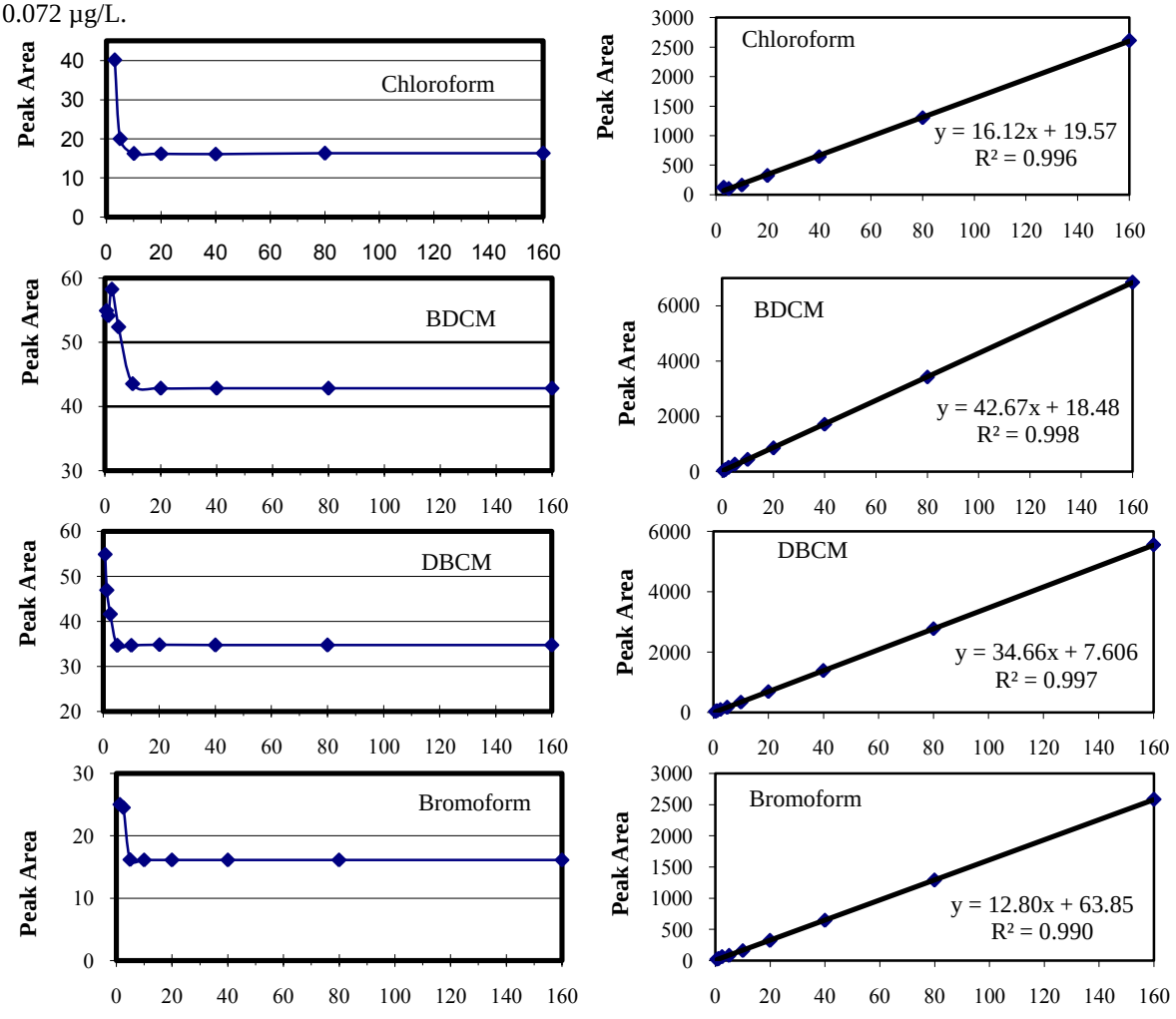


Figure (2): The relation between GC-μECD response and different concentrations of individual THMs.

Table (2): The measured value of different injections of known standard 80µg/L of THMs.

No	Run_1	Run_2	Run_3	Accuracy		
1	82.52	81.65	80.21	103.07	101.99	100.19
2	78.62	79.8	83.001	98.20	99.68	103.67
3	80.29	80.31	79.254	100.29	100.31	98.99
4	78.65	78.36	80.25	98.24	97.88	100.24
5	80.65	80.98	78.69	100.74	101.15	98.29
6	81.46	79.25	80.21	101.75	98.99	100.19
7	79.32	78.65	79.68	99.08	98.24	99.53
8	80.21	79.36	80.67	100.19	99.13	100.76
9	78.58	80.24	78.489	98.15	100.22	98.04
10	79.86	82.35	80.24	99.75	102.86	100.22
Average = 80.06				Max %	103.67	
				Min %	97.88	

Table (3): The individual and companied uncertainties result of THMs measurements.

No	Standard preparation (U_1)	Linearity (U_2)	Sample preparation (U_3)	Recovery (U_4)	Companied uncertainty(U)	Expanded uncertainty (2U)
1	0.01412	0.02887	0.00545	0.01552	0.036102967	0.07220593

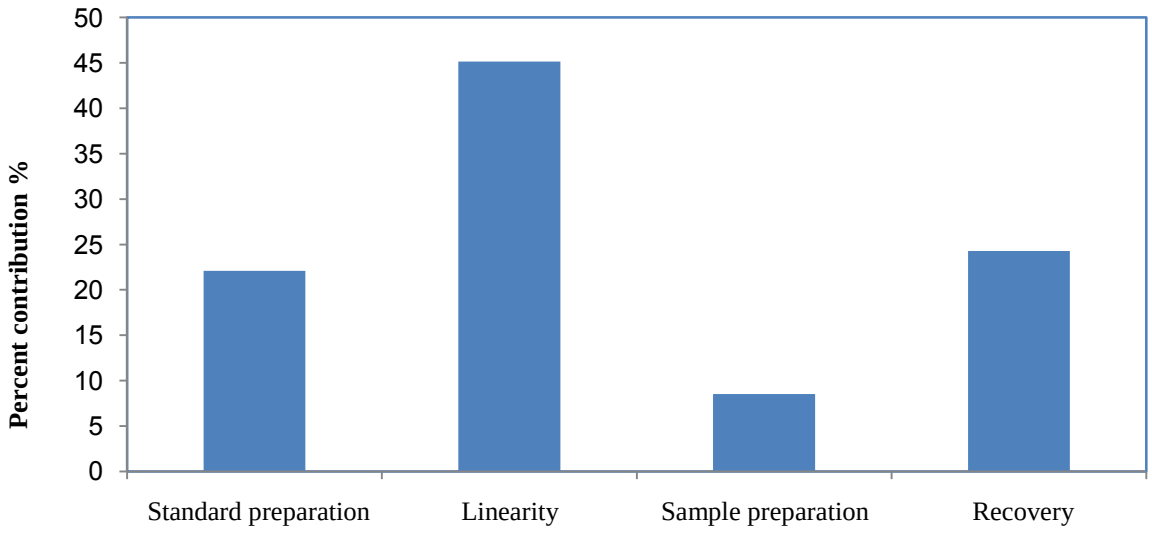


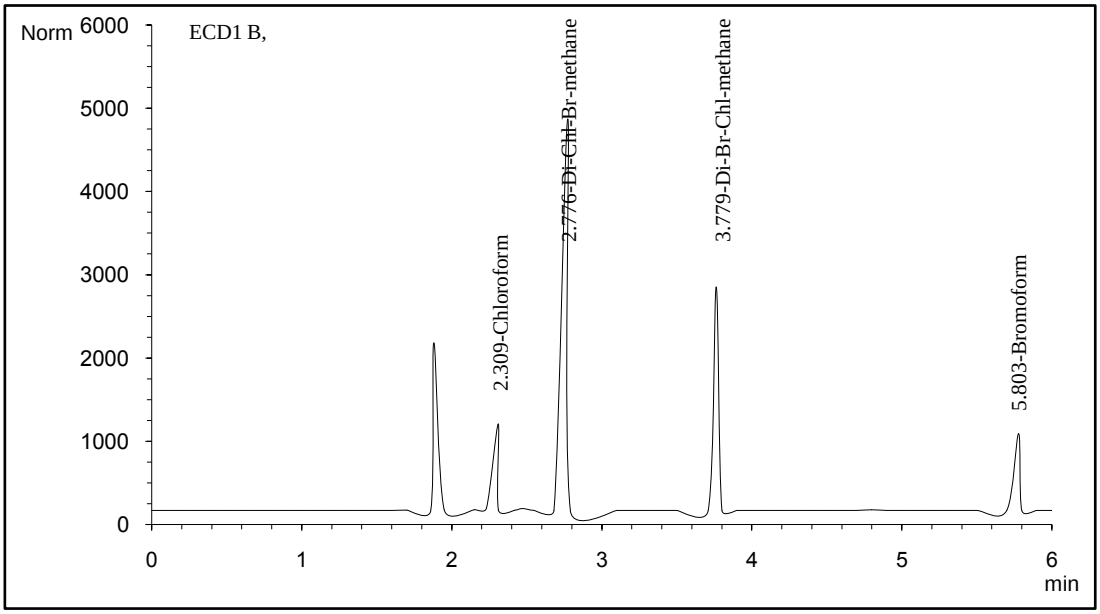
Figure (3): The contribution of individual uncertainties to the total uncertainty values.

3.3- The removal efficiency of THMs using POPDA and CNTs/ POPDA composites:

Several methods are available for measurement of THMs in drinking water (AGENCY., (1980)); (MIEURE, (1977)) and (REDING, (1978)). Method 6232B Standard method (Lenore, (1998)) is a simple liquid-liquid extraction gas chromatographic method that is highly sensitive and very precise for these compounds and certain other chlorinated solvents. This method is applicable for determination of THMs component in drinking water, intermediate stages of treatment, surface and ground water.

To check instrument quality of measurement, known standard 480 µg/l (120 µg/l from each ($CHCl_3$), ($CHBr_3$), ($CHBrCl_2$) and ($CHBr_2Cl$) is prepared as given in section 2.3 and the potable water sample was collected as in section 2.4.

Figure (4) shows the chromatogram of THMs for 480µg/l known standard. The retention time (RT) of each ($CHCl_3$), ($CHBr_3$), ($CHBrCl_2$) and ($CHBr_2Cl$) are 2.307, 2.765, 3.760 and 5.772 minute respectively. Figure (5, 6) shows the chromatogram of THMs for water samples collected from Beni-Suef governorate plants namely, American plant 1(AP_1) and American plant 2(AP_2). From figure (5) of (AP_1) it is observed that, the individual THMs concentration ($CHCl_3$), ($CHCl_2Br$) and ($CHBr_2Cl$) are 46.64, 12.38 and 5.06 µg/L respectively, however bromoform ($CHBr_3$) not detectable due to lower concentration of bromine in River Nile water. The chloroform is the most common compound nearly 72% of THMs compounds. From figure (6) of (AP_2) it is observed that, the individual THMs concentration ($CHCl_3$), ($CHCl_2Br$) and ($CHBr_2Cl$) are 31.37, 8.67 and 3.476 µg/L respectively, however bromoform ($CHBr_3$)was not detectable. Also, the chloroform is the most common compound nearly 72% of THMs compounds. The two plants are located on the River Nile and in the same site but the total THMs of (AP_2) is lower than (AP_1) due to moving the point of chlorination in (AP_2) to the clarified water before filtration stage.



External Standard Report

Sorted By : Signal

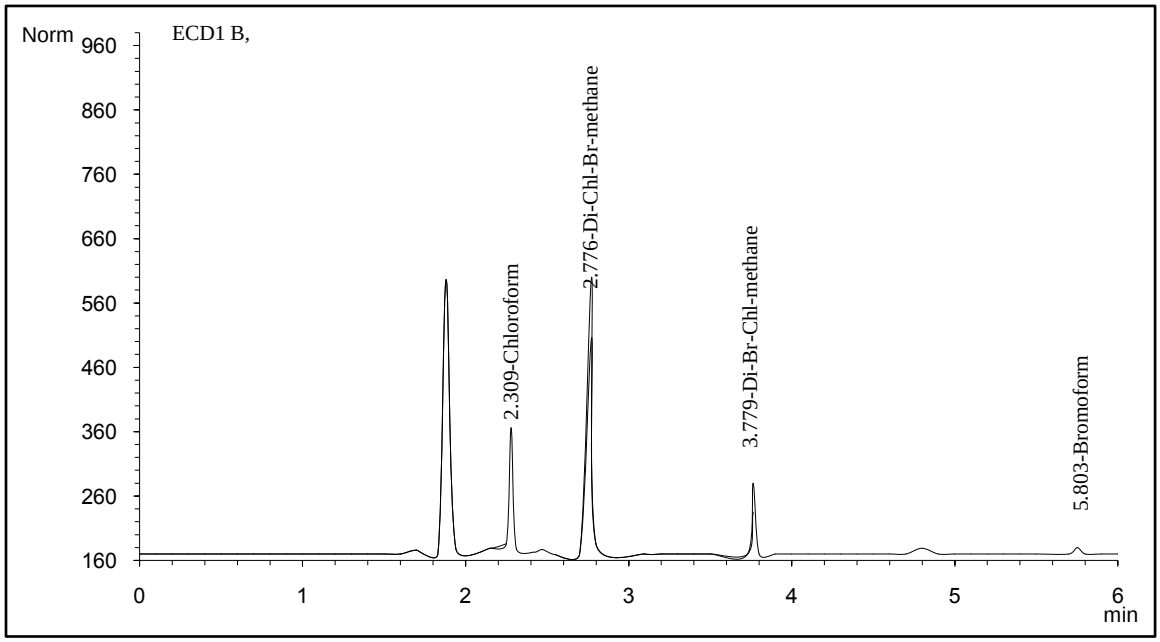
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor With ISTDs

Signal 1 : ECD1 B,

Ret Time [min]	Type	Area [Hz*s]	Amt/Area	Amount [µg/L]	Name
2.309	**VV**	**1660.30554**	**0.0656819**	**109.0520224**	**Chloroform**
2.776	**VB**	**5994.30908**	**0.0207385**	**124.3129789**	**BDCM**
3.779	**BB**	**4930.06494**	**0.0260268**	**128.3138142**	**DBCM**
5.803	**BB**	**2101.03076**	**0.0580934**	**122.0560204**	**Bromoform**
Totals :				**483.73484**	

Figure (4): The chromatogram of THMs for known standard using GC micro- electron capture detector products.

By adding different doses of POPDA and POPDA /CNTs composite to known standard containing 483.73 µg/L THMs, sample of (AP_1) containing 64.09 µg/L THMs and sample of (AP_2) containing 43.51 µg/L THMs for 30 min with stirring. Let solution for 2 min to stand and add to each vial 5 ml hexane, shake using rotary platform shaker set at 80 rpm. A liquid of upper organic phase was removed carefully using buster pipette and transfer to micro vials. The micro vials were arranged in sequence on the rack of GC for analysis. The extract is injected into GC equipped with a linearized micro electron capture detector (µECD) for separation and analysis. The instrument automatically injects one sample after another, and the data are printed. The area on the graph was integrated for determination of the concentration of samples in µg/L using Chemstation 32 program. The relations between the removal efficiency as a function of POPDA and POPDA /CNTs composite dose are represented in figures (7, 8). The removal efficiency increase with increasing dose of POPDA, POPDA /CNTs composite and the removal effect reaches at critical concentration after which tends to achieve steady state values. This means that, the adsorption of THMs on the POPDA or POPDA /CNTs composite surface reaches equilibrium. Table (4) represents the applying (0.32 g/L) dose of POPDA, POPDA /CNTs composite on the Beni-Suef (AP_1) for different time intervals. From the listed data it is observed that, the removal efficiency increase by increasing contact time and early 90% of THMs removed after one hour.

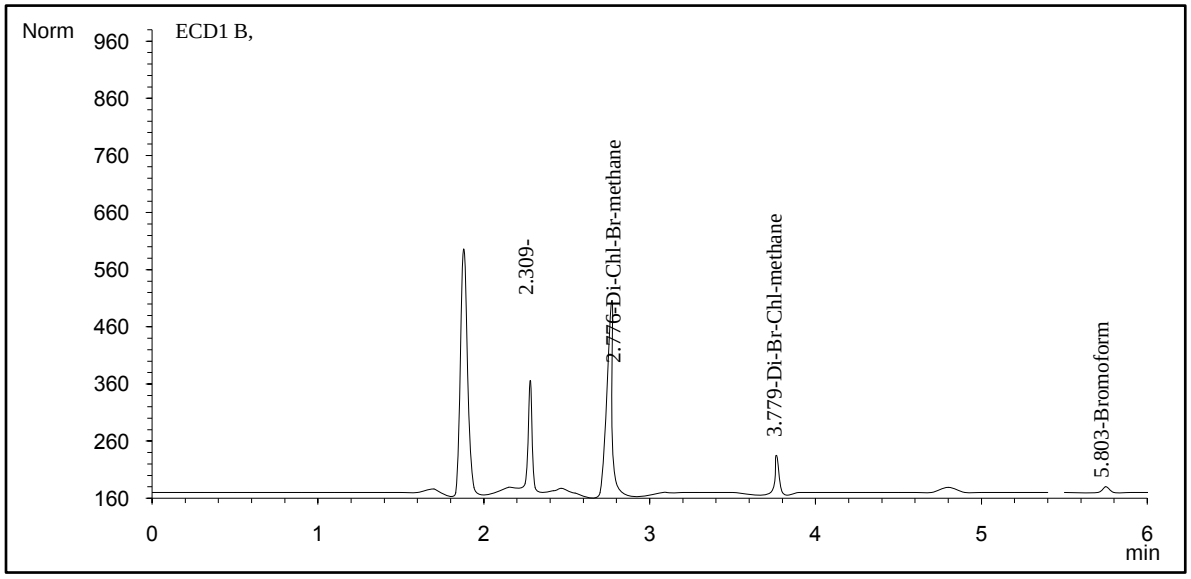


External Standard Report

Sorted By : Signal
Multiplier : 1.0000
Use Multiplier & Dilution Factor With ISTDs

Ret Time [min]	Type	Area [Hz*s]	Amt/Area	Amount [µg/L]	Name
2.309	**VV**	**1275.35487**	**0.0365738**	**46.64457394**	**Chloroform**
2.776	**VB**	**1838.30908**	**0.0067385**	**12.38744574**	**BDCM**
3.779	**BB**	**617.35470**	**0.0082073**	**5.066815229**	**DBCM**
5.803	**BB**	**0.0000000**	**0.0000000**	**……..**	**Bromoform**
Totals :				**64.09883**	

Figure (5): The chromatogram of THMs for potable water of American plant1 (AP_1).

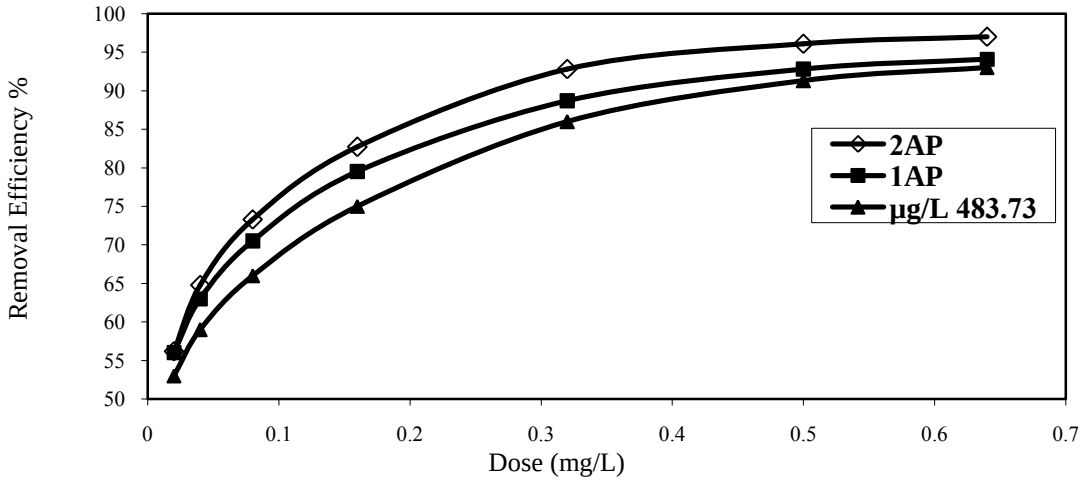


External Standard Report

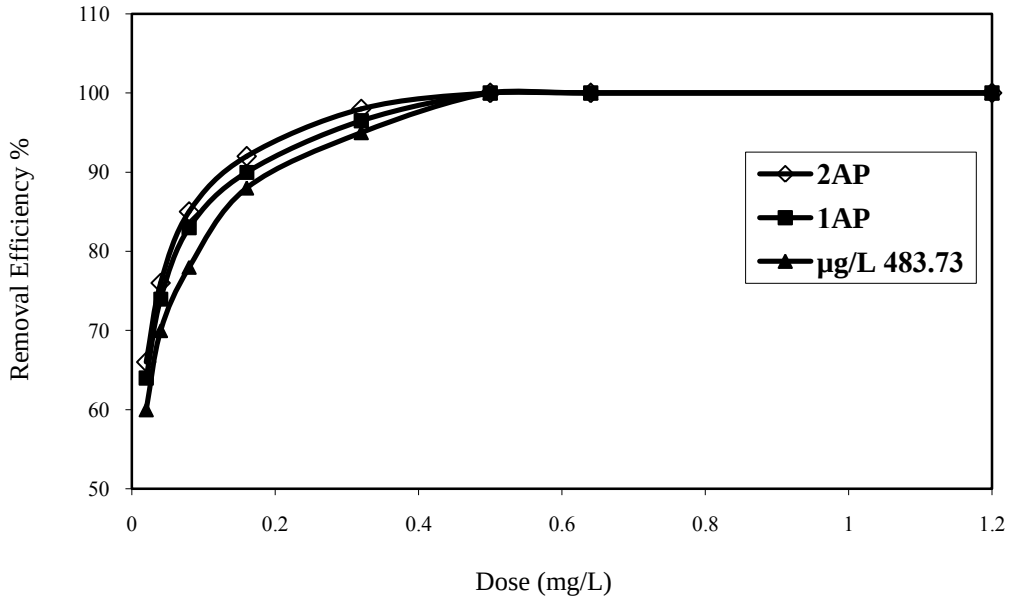
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor With ISTDs
Signal 1 : ECD1 B,

Ret Time [min]	Type	Area [Hz*s]	Amt/Area	Amount [µg/L]	Name
2.309	**VV**	**1023.65891**	**0.0306537**	**31.37893313**	**Chloroform**
2.776	**VB**	**1622.87413**	**0.0053425**	**8.67020504**	**BDCM**
3.779	**BB**	**498.96857**	**0.0069547**	**3.470176714**	**DBCM**
5.803	**BB**	**0.0000000**	**0.0000000**	**……..**	**Bromoform**
Totals :				**43.51931**	

Figure (6): The chromatogram of THMs for potable water of American plant2 (AP_2).



Figure(7): The relation between the POPDA dose and the removal efficiency of THMs in water treatment plants of Beni-Suef governorate and known standard 483.73 µg/L THMs for 30 min.



Figure(8): The relation between the POPDA/MWCNTs composite dose and the removal efficiency of THMs in water treatment plants of Beni-Suef governorate and known standard 483.73 µg/L THMs for 30 min.

Table (4): Effect of interval time on the removal of THMs by applying (0.32 µg/L) dose on Beni-Suef (AP_1) containing 64.09 µg/L.

No	Time (min)	Removal Efficiency (%) of POPDA	Removal Efficiency (%) of POPDA/CNTs
1	5	28.23	36.28
2	10	37.59	47.19
3	15	59.43	77.11
4	20	78.16	86.27
5	25	81.28	91.54
6	30	89.08	93.65
7	60	93.64	95.58
8	120	95.42	98.17
9	240	94.76	100
10	One day	95.07	100

3.4-Adsorption isotherms

3.4.1-Langmuir isotherm

In 1916, Irving Langmuir published an isotherm which retained his name which one of the simplest model. Langmuir isotherm is based on these assumptions. The surface of the adsorbent is uniform; all the adsorption sites

are equal; there is no interaction between the ions; all adsorption occurs through the same mechanism. At the maximum adsorption, only a monolayer is formed and; molecules of adsorbate do not deposit on other. Langmuir isotherm can be defined according to the following formulas (SevilVeli. J, (2007)):

$$q_e = \frac{V_m\, KC_e}{1 + \mathrm{K}VC_e} \tag{11}$$

Where q_e is the amount of adsorbed per unit adsorbent mass (µg/mg), V_m is the monolayer capacity, k is the equilibrium constant and C_e is the equilibrium concentration of the solution (µg /L).

When the initial concentration rises, adsorption increases while the binding sites are not saturated. The linearized Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants equation can be written in the following linear form:

$$\frac{1}{q_e} = \frac{1}{V_m} + \frac{1}{V_m K} \cdot \frac{1}{C_e} \tag{12}$$

The experimental data obtained was found to fit well with Langmuir isotherm. Figures (9, 10) represent curves fitting of (POPDA) and (POPDA) / MWCNTs respectively. From the linear plots of 1/ $q_e$vs 1/ C_e; the linear form of Langmuir equation for (POPDA) and (POPDA) / MWCNTs adsorption was given by the following expressions:

$1/ q_e = 0.0043 + 4.9699\ 1/ C_e$ $\quad r^2 = 0.96$ POPDA (13)

$1/ q_e = 0.0033 + 246.68\ 1/ C_e$ $\quad r^2 = 0.94$ (POPDA) / CNTs (14)

From these regression equations and the linear plots, the values of the Langmuir constants were calculated as shown on table (5).

3.5.2. Freundlich isotherm

Freundlich isotherm (Igweand, (2007))is used for modeling the adsorption on heterogeneous surfaces; to estimate the adsorption intensity of the adsorbent towards the adsorbate.

This isotherm can be explained by the following equation:

$$q_e = K_f C_e^{(1/n)} \tag{15}$$

Where C_e is the equilibrium concentration (µg /L), q_e is the amount adsorbed (µg/mg) and K_f and n are constants incorporating all parameters affecting the adsorption process, such as adsorption capacity and intensity respectively.
The linearized form of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as [28].

$$\log q_e = \log K_f + 1/n\ \log C_e \tag{16}$$

K_f and n were calculated from the slopes of the Freundlich plots log q_e vs. logC_e.

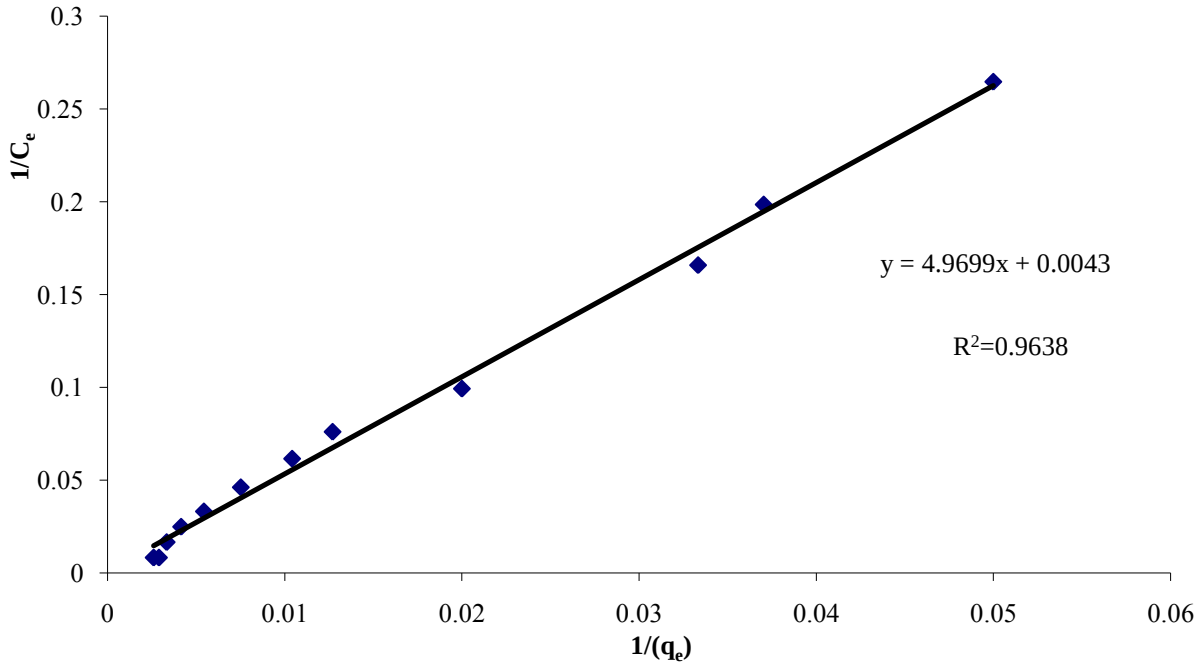


Figure (9): Langmuir adsorption isotherm of (POPDA).

Figures (11, 12) shows the dependence of log q_e from logC_e for POPDA) and (POPDA)/ MWCNTs composite.Table (6) shows the values of Freundlich adsorption isotherm constant. The values of (n) according to Kadirvelu and Namasivayam (2000 between 1 -10 represent beneficial adsorption (Ahalya, (2005))

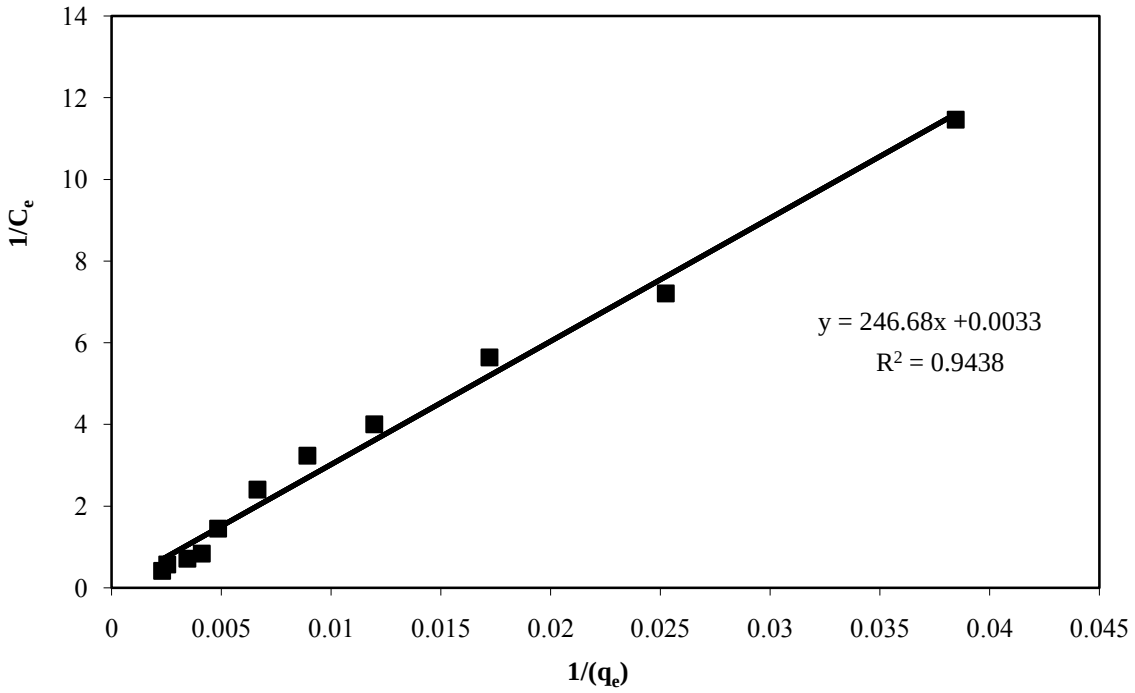


Figure (10): Langmuir adsorption isotherm of (POPDA/MWCNTs) composite.

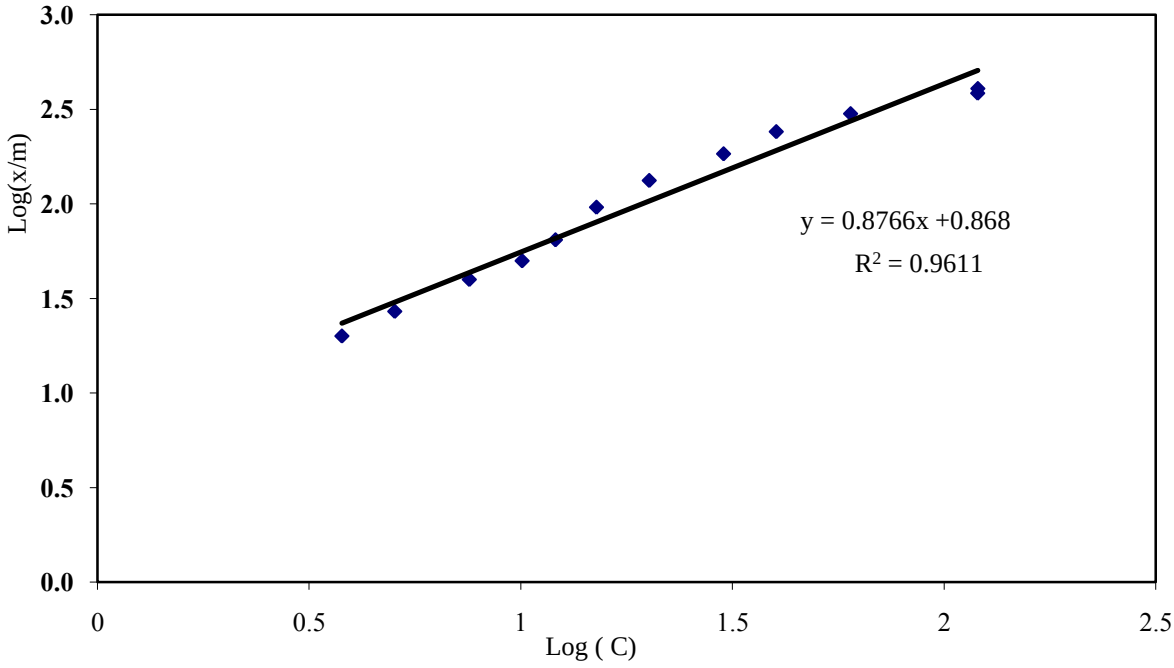


Figure (11): Freundlich adsorption model for interactions of THMs on (POPDA).

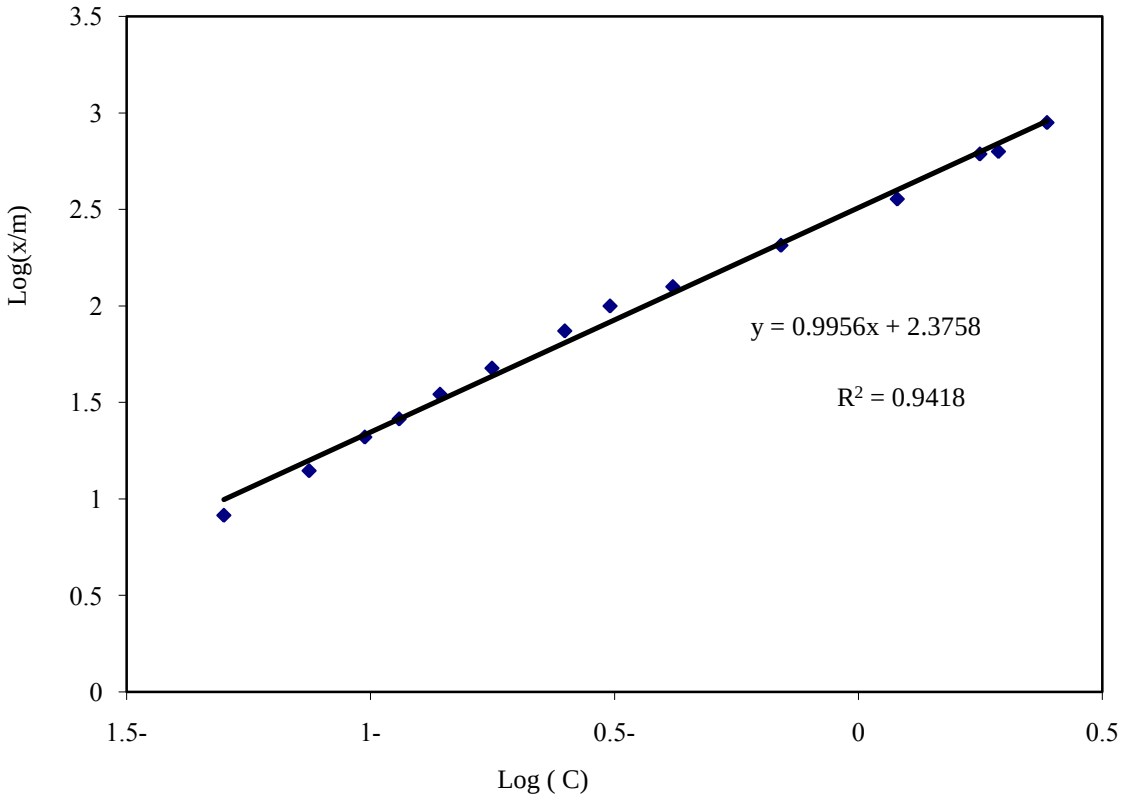


Figure (12): Freundlich adsorption model for interactions of THMs on (POPDA)/ MWCNTs composite.

Table (5):Langmuir isotherm parameters.

Adsorbent	r^2	K x 10^{-3}	V_m
POPDA	0.96	0.8	232.56
POPDA/MWCNTs	0.94	0.013	303.03

Table (6): Freundlich isotherm parameters.

Freundlich isotherm parameters			
Adsorbent	**R^2**	**n**	**K_f**
POPDA	0.9611	1.141	7.68
POPDA/MWCNTs	0.9956	1.005	237.75

Conclusion

- **The chloroform is the most common compound of THMs present in potable water of Bani-Seuf governorate.**
- **The POPDA and POPDA/CNTs composite are highly active in removing THMs from drinking water.**
- **The removal efficiency of POPDA/CNTs composite increase with increasing contact time and nearly 90 % of THMs removed after one hour.**
- **The experimental data obtained was found fit well with Langmuir and Freundlich isotherms.**

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