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Determination of Some Volatile Organic Compounds in the water produced at Al-Ahdab oilfield in the Governorate of Wasit, Iraq using Headspace SPE-GC-FID

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Abstract

The study was conducted over the period of Oct 2018 to Apr 2019 and is aimed for the detection and estimation of four hazardous Volatile Organic Compounds VOC (benzene, toluene, ethylbenzene, and xylene) so-called (BTEX) in samples collected from the produced water in the Al-Ahdab oil field in Iraq also to track their availability in the important natural water sources around the field. These compounds pose a risk to human health as well as environment. To avoid the laborious and tiresome conventional extraction methods, water samples were collected and concentrated using solid-phase extraction technique (SPE) which is a robust and cost-effective method of sample extraction with minimal exposure and handling of solvents and then to be analyzed via a gas chromatograph with a flame ionization detector (GC-FID). All of the collected samples were found contaminated with the BTEX compounds by unacceptable limits exceeding the recommended percentages. BTEX compounds were also found in the aquatic samples outside the field. Standard deviation (SD) was ranging from 0.01-0.73. The purpose of this study was to track and monitor the BTEX concentrations in the water produced by the Al-Ahdab oilfield and compare it with the BTEX levels in the water sources near the oilfield. Which is very important to control the impact of the discharged waters on the environment.

Keywords: *BETX, Al-Ahdab oil field, Al-Dalmaj Marsh, General Downstream Canal (GDC), Main Outfall Drain (MOD)*

Introduction

Most oil fields often yield petroleum from underground reservoirs accompanied by what is called produced water, which is brine or water that necessitates disposal. Treatment of this water is of great importance to make it safe to be discharged to the environment [1,2]. The produced water[3] (PW) usually contains different hazardous materials especially high concentrations of dissolved BTEX organic compounds, i.e. (benzene, toluene, ethylbenzene, and xylene)[4]. BTEX compounds are harmful to plants and toxic for other livings. Direct contact with benzene including inhalation may affect the central nervous system of the human body. However, prolonged exposure to it consequentially leads to alteration in hemopoietin tissue appears as anemia and leukopenia[5–7]. Furthermore, high lipophilicity of BTEX made it possible to leak to the brain and causing brain damage, cardiac depression, dizziness, and nausea. While moderate exposure affects the function of kidney and liver[5,7]. When benzene and other BTEX compounds discharged to the environment they can leak to groundwater toxify it with concentrations much higher than those usually detected in surface water due to evaporation suppression[6]. There are different analytical procedures to measure the availability and concentration of BTEX in water[8–10] and in air[11–13]. However, a pretreatment is often necessary for water specimen to separate the components of interest from sample matrices. Solid Phase Extraction (SPE) become a common technique for the analysis of water samples, as it can retain volatile and semi-volatile compounds from the aqueous medium. It is environmentally benign as it requires minimal volumes of solvents and doesn't require any special or complicated equipment[14]. The General Downstream Canal[15] (GDC) [Appendix-2] or the Main Outfall Drain[16] (MOD), known before the year of 2003 as Saddam River or the Third River. With more than a 565 Km long[17], it is upstreaming from Baghdad

north and downstream into the Shatt Al-Arab in Basrah. It was an old project since the 1950s then re-implemented into the 1990s. It is the main source of water for the marshes in southern Iraq[18]. The Al-Ahdab oilfield is located in the Al-Kut governorate and takes the required quantities of water from the MOD close to wetlands of Al-Dalmaj marsh[19,20]. As well as the Al-Ahdab oilfield discharges the produced water to the MOD. Any contaminations discharged to the MOD will reach and toxifying the natural environment and the aquatic life of the wetlands. Thus, it is very vital to regularly examine the water quality released to MOD [21,22]. The produced water samples were collected directly pipelines and reservoirs from the Al-Ahdab oil field then extracted using SPE cartridges for later analysis with GC-FID for the determination of BTEX toxic compounds those may go with the drainage to reach the water resources affecting the environment. The presence of such harmful compounds in both water produced from the oil fields and water sources close to the fields must be examined and supervised regularly to control it and to prevent any bad consequences on humans and biodiversity around the area.

Experimental

Chemicals and materials:

- Gas chromatograph, Shimadzu GC-2014 (Kyoto, Japan) equipped with a flame ionization detector FID.
- Certified standards of BTEX (benzene, toluene, ethylbenzene, and p-xylene) were purchased from ChemService at a concentration of 2000 µg/mL in methanol (West Chest, PA, USA).
- Intermediate solutions were prepared by diluting the standard mixture at concentrations of 1 and 20µg/ml in methanol, Hydrochloric Acid (HCl) 6N(BDH).
- Solid Phase Extraction Tubes (SPEC-R31930B), SiliaPrep SPE Cartridges CleanENVI (Silicycle inc, Canada).

Locations of the collection of PW samples:

PW water samples were collected in 1-liter bottles from three sites within the Al-Ahdab oilfield and five sites on the Main Drain river outside the field in Wasit province, Iraq. The sample bottles were sealed with Teflon then transported on the same day to the laboratory under refrigerated conditions.

In the laboratory, samples were preserved at a temperature of 4° C, and then were filtered through a 0.45µm Millipore filter and diluted for the analysis of BTEX. Figure (1) showing the location of the Ahdab oilfields in Iraq. The Al-Ahdab oilfields campus dimensions are about 10 Km long by 3 Km. The oilfield area is located among three Secondary Surface Drain canals (SSD) and a Main Surface Drain canal (MSD) those dispense directly into the MOD which flows toward the southern marshes. While table (1) specifies the spatial coordinates of the sample collection sites.

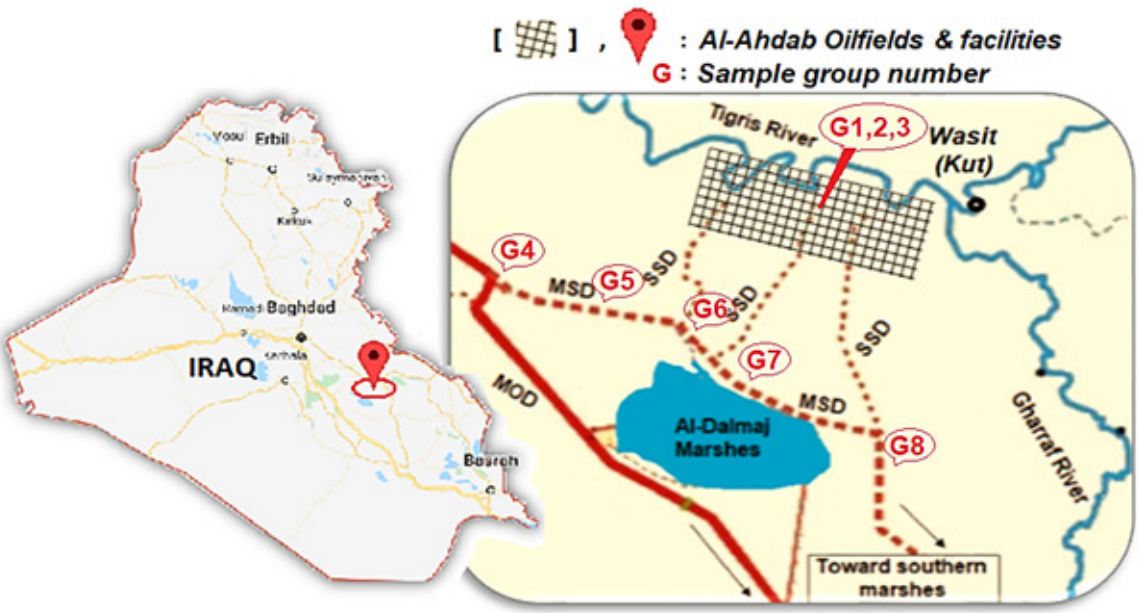

Figure 1. The location of the Al-Ahdab oil fields mediated among SSD(s) and MSD those discharge directly into the MOD[23].

Table.1: Spatial coordinates of the produced water samples classified as per their stage of process and site of collection

Sample Group	Description	PW treatment stage	Coordinates	
			Latitude	Longitude
1	Water produced within the Al-Ahdab oil field	PW before treatment	32º49´ 14.65 N	45º 69´ 26.63 E
2		PW after treatment	32º49´ 22.46 N	45º 68´ 26.72 E
3		PW surplus in evaporation ponds	32º48´ 82.77 N	45º 66´ 98.91 E
4	Water collected outside the oil field from MOD	Just before Al-Ahdab Injection water supply line from MOD	32º44´ 96.28 N	45º 10´ 43.37 E
5		Al-Ahdab Injection water supply line from MOD	32º40´ 41.36N	45º 20´ 81.96 E
6		After Al-Ahdab Injection water supply line from MOD	32º40´ 26.10 N	45º 20´ 75.40 E
7		From Al-Ahdab Injection water supply ponds	32º39´ 94.95 N	45º 21´ 29.45 E
8		After Al-Ahdab Injection water supply ponds	32º38´ 90.78 N	45º 21´ 05.43 E

Sample injection parameters GC/FID conditions:

A cold trap (cry focus) cooled with a flow of liquid nitrogen (LN2), mounted prior to the separating column RTX-624,20m,0.18mm,1µm for the purpose of re-concentration of the VOCs.

The aqueous samples were extracted and concentrated (5ml)then placed into 20ml headspace vials. The injected volume was set to 1 ml (the split ratio was 5:1 and the linear velocity was set to 45 cm/sec. The GC oven temperature started from 50 °C for 1min, gradient temperature, ramping 35 °C/min up to 280 °C. The water samples were purged with helium (99.995% purity) at a flow rate of 40 ml/min for 11 min at 26 °C. The volatiles was thermally desorbed and transferred to the GC which attached to a Flame Ionization Detector (FID) via a heated transfer line. After desorption, the trap was cleaned by heating it up to 200 °C for 8 min.

The analysis was adapted according to the EPA method 624 for the measurement of VOCs in water[24,25]. The analysis of the water samples was accomplished using headspace technique with a cold trap (cry focus). The usage of an (Elite 624 capillary column 30m x 0.25mm, 1.40µm) as a separating phase with such narrow bore column enables the reduction of the analysis time(fast GC) nonetheless maintaining the chromatographic resolution successfully.

The vaporized samples were injected from the headspace to the column quite slowly as per the normally small split ratio (5:1) implemented in favor of sensitivity. However, the application of fast GC approach in combination with the slow headspace sampling has compensated the lateness in analysis duration.

Results and Discussion

One liter of each PW aqueous sample was extracted and retained on SPE cartridges then retrieved by desorption from the sorbent bed of the SPE cartridge by 1 ml of dichloromethane. Which increased the limit of detection and sensitivity of the method by concentrating the samples 1000 times. The resultant extract has been placed in a 10 ml headspace vial (5 replicate vials for each sample). Direct injection in headspace HS mode was performed at the temperature of 280 ºC in programmed temperature vaporization (PTV) injector for a GC-FID.

The BETX levels in water samples were expressed in the unit of µg/ml. The limit of detection (LOD) for benzene has turned out to be 0.001 µg/ml. Figure (2) exhibited a GC-FID chromatogram of a standard mixture of BTEX at the concentration of (1 µg/ml) of each component. The total chromatographic runtime was less than 8 minutes. While table (2) listed common chromatographic values for the analysis of (1 µg/ml) standard BTEX samples.

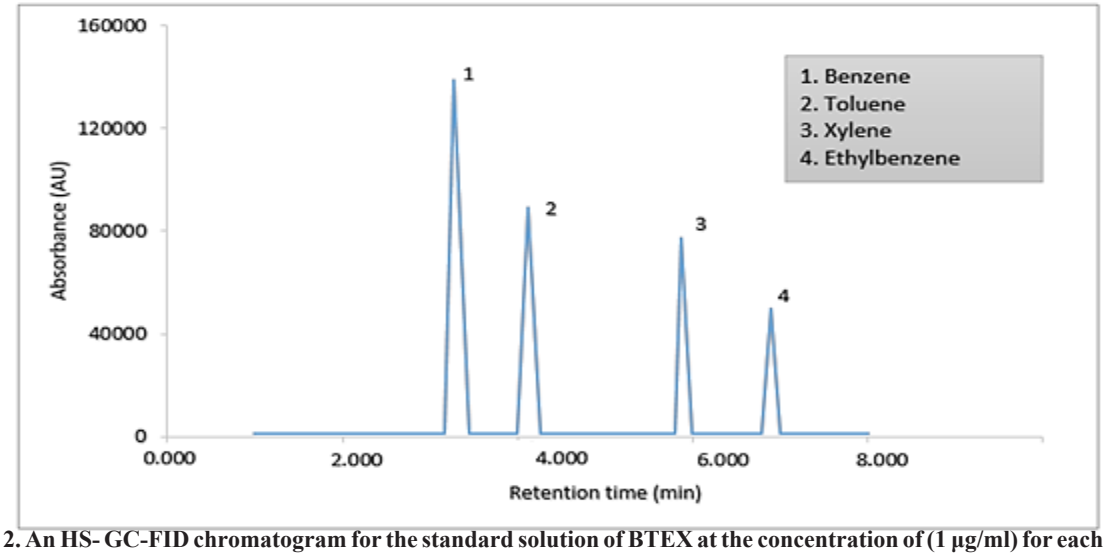

Figure 2. An HS- GC-FID chromatogram for the standard solution of BTEX at the concentration of (1 µg/ml) for each component.

Table 2.Tabulation of the chromatographic values worked out for the analysis of standard BTEX samples in the concentration of (1 µg/ml) for each component where; retention time in minutes, (K') Capacity factor, (α) Separation factor, (Rs) Resolution, and (N) the Number of Theoretical Plates.

Concentration (1 µg/ml)		Peak area	K'	α	Rs	N	Recovery	RSD%
Benzene	3.26	109773	9.867	..	..	3214.397	97.3	0.076%
Toluene	3.94	116824	12.13	1.21	3.24	2425.563	99.2	0.09%
Ethylbenzene	5.95	146627	18.83	1.51	3.65	3211.111	98.8	0.1%
Xylene	6.96	156049	22.2	1.17	3.06	4610.741	100.1	0.05%

The collected samples from inside the field were classified into three main groups; The first group (Group 1) represents the PW aliquot before treatment, (Group 2) represents the PW from the stage after treatment, and (Group 3) representing the PW collected from the evaporation ponds as shown in Table (3).

Table 3. The average concentrations of BTEX found in aquatic samples collected from the site of the Al-Ahdab oil field. Analyses were taken place using HS-SPME-GC-FID

Compound	Sample concentration in (µg/ml)								
	Group 1			Group 2			Group 3		
	Min Max	Mean	SD	Min Max	Mean	SD	Min Max	Mean	SD
Benzene	0.88 - 1.63	1.26	0.26	0.05 - 0.65	0.35	0.21	0.01 - 0.22	0.12	0.07
Toluene	0.23 - 2.31	1.29	0.73	0.12 - 0.55	0.34	0.15	0.31 - 0.11	0.21	0.07
Ethylbenzene	0.14 -1.52	0.83	0.40	0.03 - 0.54	0.29	0.18	0.12 - 0.32	0.22	0.01
Xylene	1.39 -1.85	1.62	0.16	0.81 -0.98	0.89	0.06	0.95 -1.52	1.24	0.16

While those samples collected from outside the oilfield were represented into five main sets (Group 4 to 8); directly from MOD before Injection water supply line, from Al-Ahdab Injection water supply line from MOD, from less than a kilometer next to Al-Ahdab Injection water supply line, from Al-Ahdab Injection water supply ponds, and after it respectively as listed in Table (4) below. The data listed in the table concluded, there was no contamination with BTEX for the water samples taken from Al-Ahdab Injection water supply line from MOD (group 5) and directly from MOD before Injection water supply line (group 4). While the water samples collected from less than a kilometer next to Al-Ahdab Injection water supply line (group 6) as well as those collected from Al-Ahdab Injection water supply ponds and after it (groups 7 and 8) respectively have shown some contamination with BTEX compounds which confirm our suspicions that the oilfield may get rid off some untreated PW directly to the MOD which may pollute to the marshes in the southern area of Iraq those fed from MOD steam and the serious impact on the environment and biology.

Table 4. The average concentrations of BTEX found in aquatic samples collected from MOD. The BTEX levels in samples of the groups (4, and 5) were undetectable. Analyses were taken place using HS-SPME-GC-FID

Compound	Sample concentration in (µg/ml)								
	Group 6			Group 7			Group 8		
	Min Max	Mean	SD	Min Max	Mean	SD	Min Max	Mean	SD
Benzene	u.d- 0.135	0.0675	0.045	u.d-0.102	0.051	0.034	u.d-0.321	0.1605	0.106
Toluene	u.d- 0.109	0.0545	0.036	u.d- 0.201	0.1005	0.067	u.d-0.132	0.066	0.044
Ethylbenzene	u.d- 0.114	0.057	0.038	u.d- 0.322	0.161	0.107	0.121-0.322	0.222	0.047
Xylene	0.232-0.504	0.368	0.064	0.289-0.566	0.428	0.048	0.521-0.948	0.735	0.101

Average concentrations of BTEX were found within the range of µg/ml. These findings point out the are of the same order of magnitude as those reported by other authors, such as in the effluent of produced water from platforms of two different petroleum production units located in the Campos Basin, State of Rio de Janeiro, Brazil (283–1855 mol/ L for benzene, 87.04–2224 mol/L for toluene, 16.77–1220 mol/ L for ethylbenzene and 67.35–5969 mol/ L for xylenes)[26].and in Norway total BTEX of 8000 µg/L was measured[27].

Conclusion

BTEX pollutants were successfully collected from water samples inside and around Al-Ahbad Oilfield using the environmentally friendly technique of SPE. The extracted water samples were accurately quantized by GC-FID. Reliability and performance of the method of determination were validated by working out the detection and quantification limits, precision and accuracy. Concentration levels ranged from 0.21 and 1.62 µg/mL for BTEX in the PW samples collected from inside Al Ahdab oilfield.

Financial Disclosure: There is no financial disclosure.

Conflict of interest: None to declare.

Ethical Clearance: All experimental protocols were approved under the AL-Mustansiriyah University, College of Science, chemistry department and all

experiments were carried out in accordance with approved guidelines.

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