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# Environmental Evaluation of Surfactant: Case Study in Sediment of Tigris River, Iraq

*Rana R. Al-Ani, Fikrat M. Hassan  
and Abdul Hameed M. Jawad Al-Obaidy*

## Abstract

Many chemical pollutants take their way into different environment ecosystems. One of these pollutants is detergent, which these compounds used widely world-wide. There is less attention to their impact on the Iraqi environment, especially on an aquatic system; most of these compounds discharged into the river directly by non-urban communities, in addition to household uses that it had spent throughout the domestic drainage systems. Tigris river is the primary source of water in Baghdad City, Iraq, and passes throughout Baghdad city north to south of the city. This chapter deal with the qualitative and quantitative of these compounds in the sediment as it's considered the sink of most pollutant compounds. The four sampling sites were chosen along the river for 13 months, starting from Feb 2017 to Feb 2018 and represent as dry and wet seasons. Physicochemical parameters had measured during this study. For the sediment sample, two methods used Photolab and HPLC. The two types of surfactants were extracted from the sediment as follows anionic and nonionic surfactants which they had found at all the study sites, especially in some locations in the midstream. For temporal variation, the dry seasons noticed a high concentration for nonionic surfactant (56.19 and 467.3  $\mu\text{g/g}$ ) by Photolab and HPLC, respectively, and for anionic surfactant (135.74  $\mu\text{g/g}$ ) by HPLC. In contrast, by Photolab, only anionic surfactant was recorded a high concentration in wet seasons (72.05  $\mu\text{g/g}$ ). The lowest frequency of anionic and nonionic was recorded in wet seasons by Photolab and HPLC, respectively (41.83  $\mu\text{g/g}$  and not detectable) unless for NS by HPLC in the dry season (10.80  $\mu\text{g/g}$ ). For spatial variation which according to the cluster diagram, the highest concentration for anionic and nonionic surfactants by Photolab had recorded (57.88 and 34.32  $\mu\text{g/g}$ , respectively) at site1, while for HPLC anionic and nonionic surfactants was recorded highest values (48.37 and 235.79, respectively) at site 4. From this study concluded that sites 1 and 4 are the most pollutant than other sites because the activity of discharge of pollution.

**Keywords:** cluster analysis, lotic system, physicochemical factors, surfactants, water pollution

## 1. Introduction

Many of the detergents that had used worldwide comprised of anionic surfactant about 50–60% and nonionic surfactant 40% [1]. Surface active agents

abbreviated to surfactants, which is one of the significant components of detergents that consisted of one or more hydrocarbon chains (organic compounds) and hydrophobic or hydrophilic characteristics [2]. In addition to the widespread uses of surfactants in washing purposes, besides used in the composition of emulsifiers, pesticide formulations, fibers, wetting agents, cosmetics, and treatment of textiles [3].

According to the charge of the hydrophilic part, the surfactants classify into anionic, cationic, nonionic, and amphoteric, and for this reason, it's applied in various domestic and industrial purposes. Thence, they could be passed into all ecosystem compartments (soil, water, and sediment) in multiple ways, after that subjected to different physicochemical processes in an environment like sorption, degradation, and transformation freely [4–6]. These compounds have a high propensity to adsorb in sediments, which represents an extreme concentration [7, 8]. Often, the solid wastes had thrown into the river from sewage treatment plants. These compounds in the environment are different in their fate, behavior, actions, and interaction with other components [9]. The environmental danger of surfactants is bioaccumulation, which has a detrimental effect on aquatic organisms, such as toxicity and endocrine homeostasis. It also improves the solubility of organic compounds in water, which can contribute to movement and aggregation in various divisions of the environmental [8].

The contamination of sediments is a major environmental problem worldwide. Weak ecological management in the past has contributed to natural bodies and erratic incidents, resulting in deposits being swept away by other pollutants [10, 11]. At low concentrations of surfactants in the environment are considered as safe as organic pollutants, while the toxicities at a high level had taken of great interest [12].

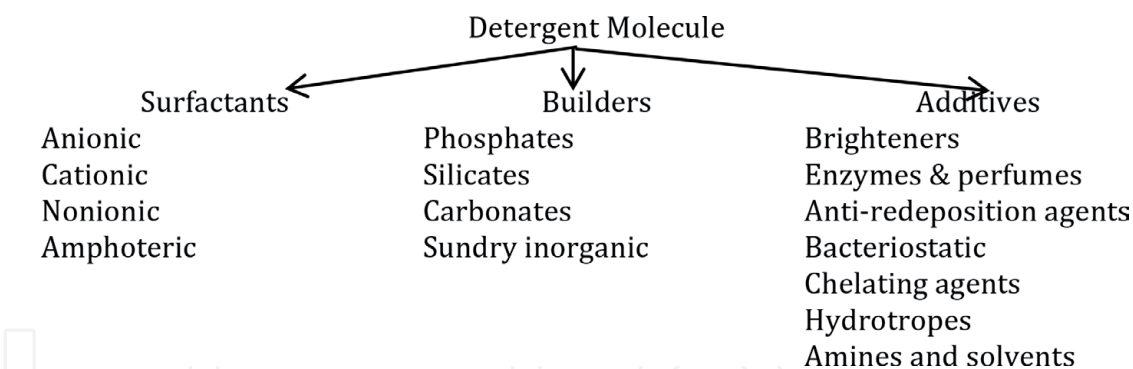
One of the main justifications for this study is that surfactants are very toxic and hazardous substances for aquatic organisms, and their everyday uses in domestic and industrial fields encourage their quantitative and qualitative examination in the Tigris River sediment. There is also a vast knowledge discrepancy that needs to explore concerning a surfactant product on the Tigris River. However, the quantitative and qualitative distribution of these surfactant compounds in river sediment had investigated in this study. Besides, this study also offers quantitative details on the effect of such surfactant classes on some of the river water's physicochemical properties and correlates this evidence with known standards.

## 2. Detergent components

**Figure 1** illustrates the detergent ingredients, which consist of three groups [13].

A detergent is a surfactant that has cleaning characteristics in a dilute solution. Almost the alkylbenzene-sulfonates are usually substances of these compounds, and according to Authors [1, 13] which they mentioned that surfactant has a less ability to link with hard water component ions such as calcium in contrast with soap in hard water because its polar carboxyl. The word detergent in most domestic settings specifically refers traditionally the detergent known as agent of cleaning in restaurants and laundries, also as different home uses.

Detergents are widely present as powders or concentrated solutions. Detergents like soaps work because they are amphiphilic, partly hydrophilic (polar), and somewhat hydrophobic (nonpolar). These properties facilitates the mixture of hydrophobic compounds (such as oil and grease) with water. One of the essential



**Figure 1.**  
 Typical detergents group.

features of detergents is degraded in aquatic systems by microorganisms in the presence of  $O^2$  into more toxic and harmless products ( $CO_2$ ,  $H_2O$ , carbonates, and bicarbonates) [14].

### 3. Surfactants

#### 3.1 Surfactants structure

Surfactants are a component that mainly responsible for the cleaning action of detergents [14].

Surfactants have a unique structure of molecules; one soluble part in polar media (hydrophilic), which is known as the head, while the other part nonpolar media (hydrophobic) is called the tail (**Figure 2**) [13]. They classified according to the head group into anionic, cationic, amphoteric, and nonionic compounds [2]. Anionic and cationic compounds have permanently, negative and positive charges, respectively, that are associated with the C-C chain (**Figure 2**). Anionic compounds have no charge. Instead, they have several atoms that are weakly electropositive and electronegative. That is because of the attraction of electrons to oxygen atoms [15].

The presence of polar and nonpolar groups in a surfactant molecule provides them with specific properties against all media; surfactant tends to absorb various surfaces. At a low concentration in water, the surfactant molecules are found as monomers [8], while at high levels, they exist as micelles (**Figure 3**) [16]. Such micelles are adsorbed at boundary phases in order to eliminate hydrophobic sections from water and the system's free energy [17, 18].

Because of a unique structure of surfactants, they found to use in different anthropogenic activities, including household or industrial products that improve the efficiency of the following processes:

1. Wetting/waterproofing,
2. Foaming,
3. Emulsification,
4. Dispersion or flocculation of vital objects in liquid forms,
5. Dissolving soluble reagents (non-/ in small quantities) in solvents,
6. And the viscosity of solution levels rises or decreases [19].

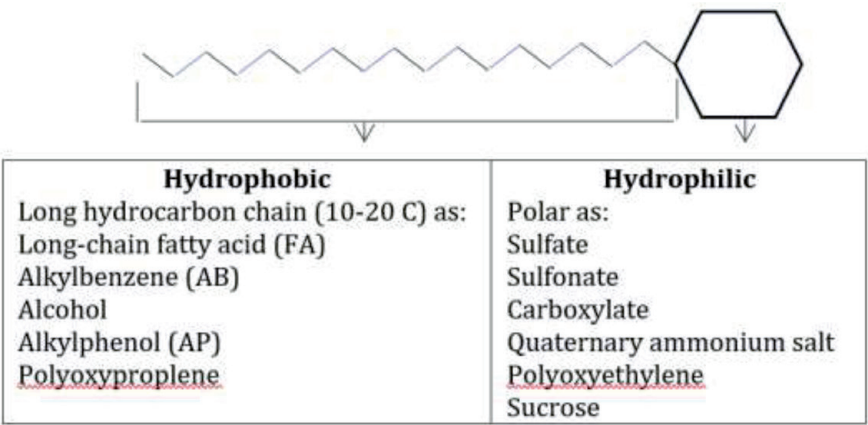


Figure 2.  
Surfactant structure [13].



Figure 3.  
A detergent and soap-micelle in water [16].

3.2 Surfactant applications

Areas of use of surfactants are shown in **Table 1** [6].

3.3 Ecotoxicity of surfactants

Surfactants show a significant impact on biological activities and function, especially AS when bound to proteins, enzymes, and DNA [20]. Quaternary ammonium compounds (QACs) (a type of cationic surfactant) can associate bacterial internal membranes [21]. One of the mixtures of surfactants that can bind to the components of the bacterial membrane is NS. It is found as anti-microbial compounds, as it increases the permeability properties that ultimately cause cell death [22].

Because of the high use of surfactants during everyday life needs to increase the study, the ecotoxicity of these compounds on aquatic life. A significant problem is the concentration of these surfactants in the sewage sludge, which is at high levels. Holt [23] noticed that despite the high concentrations of these surfactants found to degraded in wastewater treatment plants (WWTP), some of them remain in surface water, soil, or sediments [23]. The accumulation of these surfactants at high concentrations inhibits or prevents the sludge of microorganisms from the decomposition of pollutants in WWTP. Different types of surfactants exist in various environmental sections such as surface waters, sewage effluents, etc. Significant risks to the water surface ecosystem as a result of the extensive use and disposal of these surfactants [24]. Therefore, Croatian has identified specific criteria for their presence in the water body in **Table 2** [25]. Numerous studies have examined the toxicity of surfactants on bacteria, algae, invertebrates, and fish in the aquatic environment [26].



Cationic	Anionic	Nonionic	Amphoteric
i. Disinfectants & antiseptic agents.	i. Household detergents & surface cleaners.	i. Household & industrial detergents.	i. Shampoos.
ii. Ingredient of cosmetics, medicine, laundry detergents.	ii. Shampoos.	ii. Emulsifiers, wetting & dispersing agents.	
iii. Fabric softeners.	iii. Hand dishwashing liquids.	iii. Cleaning products.	
iv. Antistatic agents.	iv. Laundry detergents.	iv. Cosmetics.	
v. Corrosion inhibitors.	v. Personal care products.	v. Paints.	
vi. Flotation agents.	vi. Optical brighteners.	vi. Preservative coatings.	
	vii. Dyes.	vii. Ingredient of petroleum products.	
	viii. Dispersant, wetting, & suspending agents.	viii. Ingredient of pesticides.	
	ix. Ingredients of pesticides & pharmaceutical products.	ix. In textile, pulp, & paper industry.	

**Table 1.**  
*The areas of surfactants application [6].*

Class of surfactants	MAC/mgL <sup>-1</sup>	
	Surface waters	Sewage system
Anionic surfactants	1.0	10.0
Nonionic surfactants	1.0	10.0
Cationic surfactants	0.2	2.0

**Table 2.**  
*The maximum allowed concentrations (MAC) of surfactants in wastewater effluent, which can release in a natural aquatic recipient and sewage system in Croatia [25].*

3.4 Emission of surfactants into the environment

Because of the particular structure of surfactant molecules, its use in different fields for human life activities. After the use of surfactants or their decomposition products, they will dispose of the WWTP. In case of the absence of WWTP, it will drop into surface water directly and impact aquatic ecosystems such as in the rural area. At the same time, sorption and biodegradation in the WWTP had observed to decompose all surfactants [8, 27].

After treatment processes in WWTP (second stage) for chemical compounds of surfactants, these compounds degraded under optimal conditions about 90–95% of initial surfactant concentration presented in inflowing streams can remove which depending on the efficiency of WWTP [28]. A large part of pollutants extracted as sewage sludge with a percentage ranging from 15% to more than 90%, while it notices that alkylphenol ethoxylates (APE) turned into more toxic when it decomposition [29, 30].

After all processes in WWTP effluents and sewage sludge, different types of surfactants and their degradation (several µg/L or g/Kg) can be existed [28, 31]. As a result of the toxic effects of surfactants through their concentration in different environmental departments, literary studies have increased significantly.

3.5 Fate of surfactants

In the water ecosystem, the surfactants are undergoing sorption and aerobic/ anaerobic degradation processes. As a result of these processes, they lead to the elimination of pollutants and their transport to water systems.

Absorption and adsorption are considered a single process. While the sorption process prevents chemical compounds from degradation and hence their bioavailability can be decreased. Sorption processes are affected by some of the environmental parameters such as temperature, pH, salinity, carbon, or clay content of the particulate phase [8, 32]. Many researchers had observed that there is a relationship between higher salinity of water samples and higher sorption percentages for linear alkylbenzene sulfonate (LAS) on suspended solids such as calcium and magnesium [33]. Some surfactants have turned into more toxic decomposition products (e.g., for alkylphenol ethoxylates (APE) products). The researcher recorded a high concentration of the polar compounds in the dissolved form [33, 34], such as C<sub>10</sub> LAS, short-chain SPC (carboxylic sulfo-phenyl acids), and NPEC (nonyl-phenoxy-monocarboxylates).

The sorption process is associated with the hydrophobic nature of compounds such as:

- i. more polar AS were noticed in the dissolved phases;
- ii. less polar CS (cationic surfactant) and NS notified in the particulate phases where their transport is associated with suspended solids [35].

Through WWTP, the primary degradation of surfactants occurs by the activity of microorganisms to decrease toxic effects on living organisms. Microbes can use surfactants as their energy source and growth requirements during degradation processes. The efficiency of biodegradation of surfactant compounds in the environment is affected by many factors such as the chemical composition of analytes and physic-chemical parameters such as temperature, light, presence of oxygen, and salinity. On the other hand, some of the compounds (e.g., LAS, ditallow dimethyl ammonium chloride (DTDMAC)) may be persistent under anaerobic conditions [8, 35, 36]. Quiroga et al. [37] discovered that salinity adversely affects sodium dodecyl sulphate (SDS) degradation, while temperature increases the degradation process. Also, sediment enhances the biodegradation rate by gathering both surfactants and bacteria together. Cserhati et al. [20] reported that the adsorption of surfactants on sediment leads to stimulate the bacteria to attach them and cause biodegradation of these compounds. Manzano et al. [38] noticed that APE degradation was increased by temperature; at 7°C, about 68% of surfactant degraded while 96% at 25°C. While the degradation of APEs was slow down with light [36].

The presence of surfactants in the water networks leads to their natural decomposition (half-life time of hours to a few days) according to their characteristics and environmental parameters. These surfactants can also be subjected to either adhesion to suspended solids or accumulation in sediments. In environments with a shortage of oxygen (starting at a depth of a few cms), only anaerobic pathways can degrade surfactants. Although processes in the anaerobic state are slower or not detected (e.g., DTDMAC), and pollutants in the sediment are stay longer time [8, 35]. In experimental studies, researchers found that the acceptable degradation percent of LAS with the use of anoxic marine sediments (up to 79% in 165 days) [34, 35].

### 3.6 Surfactants in sediment

The adsorption of surfactants on sediments depends on their charge, which is a significant factor. The CA can undergo sorption in deposit much faster. In contrast to AS like sodium dodecylbenzene sulfonate (SDBS) [39]. Factors that increase the ability of CS to adsorb on sediment particles are pH, organic carbon contents,

charge of its head, and surface sediment charge. So SDBS shows lower sorption than the CS due to the negative charge of SDBS as compared to CS that have a positive charge [39]. Thus the adsorption of surfactant types in sediment can be put in the order as Cationic > Nonionic > Anionic. Marcomini et al. [40] showed a significant temporal difference in LAS concentration and nonyl-phenol ethoxylates (NPEOs) in Lake Venice. They have explained high temperature that affects biodegradation. Temporal variation had for some surfactants in Glatt River (Switzerland) [30]. The surfactants are nonyl-phenol, lipophilic nonylphenol monoethoxylate and nonyl-phenol diethoxylate.

## **4. Materials**

### **4.1 Equipments and instruments**

The types of equipment and instruments used in the current study as below (Table 3)

### **4.2 Chemicals materials**

See Table 4.

## **5. Methods**

### **5.1 Study area**

This research was done along the Tigris River within Baghdad city in Iraq for four specific locations for the period from February 2017 to February 2018. Samples (water and sediment) had collected per month for five months of the wet season and eight months of the dry season. The collection of samples had done between 8.30 am to 2.30 pm hours. Four sites had chosen to cover from north to south of Baghdad city. Sample locations are; Al-Muthanna bridge (Site 1-upstream), Al-Sarrafia Bridge (Site 2-midstream), Al-Shuhada Bridge in the north of Baghdad city (Site 3-midstream) and Al-Dora Bridge in the south of Baghdad city (site 4-downstream); (Figure 4). Global Positioning System (GPS) (Table 5), locations of the research sites were determined.

### **5.2 Water sampling and analysis**

Duplicate water samples (1 liter) had collected from the surface layer (depth 20–30) in stopper fitted clean polyethylene bottles pre-washed with distilled water. The polyethylene bottles were rinsed several times before filling with water samples from the river. The physical and chemical properties for water samples were measured directly after collection. Air temperature (AT), electrical conductivity (EC), turbidity (Tur.), water flow (WF), water temperature (WT), pH were all measured in the field. At the same time, other parameters were analyzed directly in the Environmental Research Center at the University of Technology, Iraq. Such as salinity (S‰), total dissolved solids (TDS), total suspended solids (TSS), nitrite (NO<sub>2</sub>), nitrate (NO<sub>3</sub>), phosphate (PO<sub>4</sub>), biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), organic matter percent (OM%), and total organic carbon percent (TOC%). All tests had done by the standard methods [41].



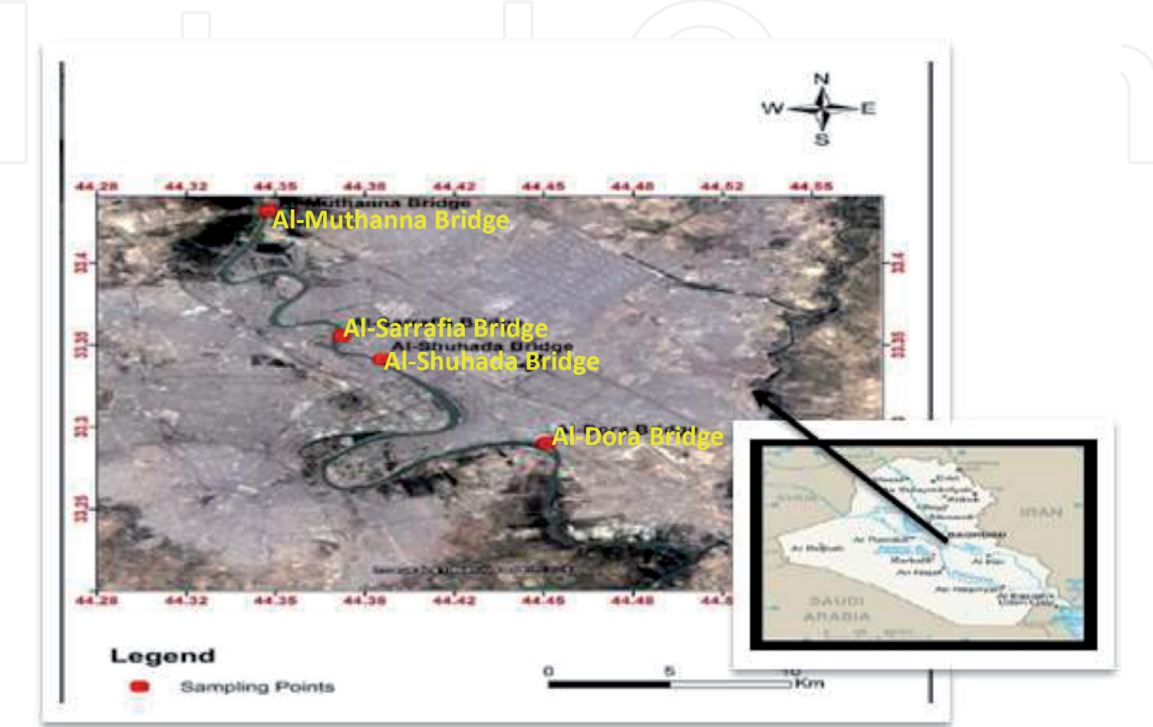
Item	Devices	Company/Origin
1	Temperature, pH, Salinity, EC (portable meter H19811)	WTW/Germany
2	Incubator	Memmer/Germany
3	High-Performance Liquid Chromatography-Tandem Spectrometry (HPLC 8040)	SyknmS1122/Germany
4	COD Meter	Lovibond/Germany
5	Distillation device	Waterpia/Korea
6	Multiparameter photometer/C99	Hanna/Romania
7	Multiparameter photometer/HI83200	Hanna/Romania
8	Turbidity meter	Lovibond/Germany
9	Oven	Memmer/Germany
10	Sensitive balance	Phoenix/Korea
11	Vacuum pump	China
12	Ekman Grape Sampler	BDH/Germany
13	Photolab S12 (PHD)	WTW/Germany
14	Filter paper 0.45 µm	Whittman/UK
15	Ultrasonic Bath	ISOLAB/Germany
16	GPS device	GPS Map 78 s Germin/Tiwan

**Table 3.**  
*List of equipments and instruments in this study.*

Item	Material	Company/Origin
1	MnSO <sub>4</sub> .H <sub>2</sub> O	Fluka/Germany
2	KOH	Fluka/Germany
3	KI	Sigma-Aldrich/Germany
4	NaN <sub>3</sub>	Fluka/Germany
5	NaOH	Fluka/Germany
6	Na <sub>2</sub> , NO <sub>3</sub> , PO <sub>4</sub> Kit	Hanna/Romania
7	COD	Lovibond/Germany
8	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Fluka/Germany
9	Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> .6H <sub>2</sub> O	Fluka/Germany
10	H <sub>2</sub> SO <sub>4</sub>	Fluka/Germany
11	H <sub>3</sub> PO <sub>4</sub>	Fluka/Germany
12	NaF	Fluka/Germany
13	HCL	Fluka/Germany
14	Formaldehyde 37–40%	Romil/UK
15	Methanol	Romil/UK
16	Ethylacetate	Fluka/Germany
17	Dichloromethane	Romil/UK
18	Acetic acid	Fluka/Germany
19	Acetonitrile	Fluka/Germany
20	Anionic surfactant Kit	WTW/Germany
21	Nonionic surfactant	WTW/Germany

Item	Material	Company/Origin
22	4-dodecylbenzene sulfonic acid mixture of isomersm $\geq 95\%$	Sigma-Adrich/Germany
23	4-nonylphenyl-polyethylene glycol non-ionic	Sigma-Adrich/Germany
24	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	Fluka/Germany

**Table 4.**  
*List of chemical materials in this study.*



**Figure 4.**  
*The study sites in the Tigris River, Baghdad city-Iraq.*

**5.3 Sediment sampling, extraction, and analysis**

Sediment samples had collected using an Ekman Grab ( $n = 3$ ) for each site to 5 cm depth from the river. Excess water drained and added an adequate 10% formalin volume to submerge the sediment for storage as glass jars and transported to the laboratory. Aluminum foil cleaned with methanol was put over the pot's mouth and then put into the cap to avoid sample contamination. Laboratory sediment samples had reserved at approximately 4°C before surfactant analysis [42].

For 16 hours at 80°C in the oven, the sediment sample for AS dried. After excluding large stones and grit from the dry sediments, surfactant compounds were then extracted (10 gm) with methanol at 50°C (240 V, 3A, 50 Hz) by Ultrasonic water bath (ISOLAB/Germany). Three 10 min extractions (50 ml and 2 x 40 ml) had been done, and then by centrifugation. It then concentrated the combined extract to 2 ml [42].

For NS, sediment samples were homogenized before extraction by sieving with a 2 mm stainless steel sieve. Also, in the same method above, extraction of surfactant compounds was done with Ultrasonic water bath by using a mixture of methanol-dichloromethane (7:3, v/v). The final elutes evaporated afterward with a gentle stream of nitrogen gas and reconstituted with 1 ml of methanol [33].

The photometer photo lab S12 (PHD) and the High-Performance Liquid Chromatography system configuration (HPLC) (Syknm-S1122- Germany)

Site number	Site name	Coordinates	
		Longitude (E)	Latitude (N)
1	Al-Muthanna Bridge	44°34'55.50"	33°42'83.22"
2	Al-Sarrafa Bridge	44°37'36.01"	33°35'37.53"
3	Al-Shuhada Bridge	44°38'79.03"	33°33'79.59"
4	Al-Dora Bridge	44°45'02.84"	33°28'96.82"

**Table 5.**  
*The geographical positions (GPS) of the study sites.*

measured both AS and NS after extraction. The 4-dodecylbenzene sulfonic acid and 4-nonyl-phenyl-polyethylene glycol were used as standard solutions in this study for AS and NS, respectively.

5.4 Statistical appraisal

Data had exposed to descriptive statistical analysis and one-way variance analysis (ANOVA). Probabilities less than 0.05 ( $P < 0.05$ ) have been used statistically significant. Also, Cluster Analysis (CA) had used the Statistical Release 7 program to classify data, cases, or objects or clusters. The principal component analysis (PCA) was conducted as a series of irrelevant variables to retrieve critical information. Results provided plotting graphs in which the elements of the forecasts groups, along with the loading of the variables. Through the value of Eigenvalue had concluded the essential component or by the proportion of the explained variance [43, 44].

6. Results

6.1 Physicochemical parameters of Tigris River water

The results of the physicochemical parameters of the Tigris River water samples had compared with the Iraqi Maintaining System Law [45] and the Canadian Council of Ministers of the Environment (CCME) [46, 47] guidelines illustrated in Table 6.

Air temperature (AT) had ranged between 12.55–43.73°C. In comparison, the water temperature (WT) showed a noticeable seasonal trend with a minimum value of 10.36°C recorded in the wet season and a maximum value of 30.11°C in the dry season.

An EC in this study had ranged between 580.50 and 1108.75  $\mu\text{S}/\text{cm}$  in dry and wet seasons, respectively, indicated levels higher than the limit standards.

The concentration of salinity (S‰) varied from 0.2 to 0.48‰, respectively, in the dry and wet seasons. The TDS ranged from 362.75 mg/L during the dry season to 711.75 mg/L during the wet season, but these high concentrations for S‰ and TDS are within the limited value.

The lowest value of total suspended solids (TSS) in the dry season was 3.00 mg/L, and the highest level in the dry season was 84.50 mg/L, while turbidity varied from 10.61 to 193.75 NTU in the wet and dry seasons, respectively.

Water flow (WF) had recorded the highest value in the dry season (0.71 m/s) (Table 6).

Parameters	Range		Mean	Standard Deviation	Standard values	
	Minimum	Maximum			Law 25/1967	CCME
Physical Parameters						
Air temperature (AT) (°C)	12.55 (w)	43.73 (d)	26.27	±9.64	—	—
Electrical conductivity (EC) (µs/cm)	580.50 (d)	1108.75 (w)	876.27	±148.05	0.5–1.0	—
Salinity (S) ‰	0.20 (d)	0.48 (w)	0.35	±0.08	—	—
Total dissolved solids (TDS) (mg/L)	362.75 (d)	711.75 (w)	563.87	±105.47	1000	500
Total suspended solids (TSS) (mg/L)	3.00 (d)	84.50 (d)	18.58	±22.05	60	—
Turbidity (Tur) (NTU)	10.61 (w)	193.75 (d)	67.83	±65.36	5	5
Water flow (WF) (m/s)	0.31 (w)	0.71 (d)	0.47	±0.13	—	—
Water temperature (WT) (°C)	10.36 (w)	30.11 (d)	21.59	±6.83	>35	15
Chemical parameters (standard values)						
pH	7.43 (d)	8.25 (w)	7.75	±0.22	6–9.5	6.5–9
Nutrients (mg/L)						
Nitrite (NO <sub>2</sub> )	0.01 (d)	0.45 (d)	0.11	±0.12	0.06	0.06
Nitrate (NO <sub>3</sub> )	0.64 (d)	8.97 (d)	4.18	±2.82	15	13
Phosphate (PO <sub>4</sub> )	0.07 (w)	1.52 (w)	0.66	±0.43	0.4	0.1
Organic						
Biological oxygen demand (BOD) (mg/L)	0.53 (w)	3.67 (d)	1.5	±0.79	>5	—
Chemical oxygen demand (COD) (mg/L)	3.75 (w)	88.25 (d)	36.73	±34.9	>100	—
Dissolved oxygen (DO) (mg/L)	4.63 (d)	11 (w)	6.18	±2.06	≤5	5.5–9
Organic matter (OM) (%)	0.43 (d)	5.55 (d)	1.7	±1.44	—	—
Total organic carbon (TOC) (%)	0.27 (d)	2.24 (w)	0.88	±0.56	—	—
- = not applicable, w = wet season, d = dry season. Law 25/1967 = Iraqi River Maintaining System Law. CCME = Canadian Council of Management of the Environment.						

**Table 6.**  
*Physicochemical characteristics of Tigris River for wet and dry seasons.*

The pH value was between 7.43 in the dry season and 8.25 in the wet season. Nutrients include nitrite (NO<sub>2</sub>), nitrate (NO<sub>3</sub>), and phosphate (PO<sub>4</sub>). Concentration ranges recorded in dry and wet seasons were 0.01–0.45 mg/L

for NO<sub>2</sub>, 0.64–8.97 mg/L for NO<sub>3</sub>, and 0.07–1.52 mg/L for PO<sub>4</sub>, respectively. Naturally occurring ions in water as part of the nitrogen cycle are NO<sub>2</sub> and NO<sub>3</sub>. Concentrations were remarkably higher for all three nutrients in the wet season than those in the dry season except for PO<sub>4</sub> in the wet season. NO<sub>2</sub> displayed higher concentrations than dry season requirements, while NO<sub>3</sub> had declined significantly compared with acceptable values for both dry and wet seasons (**Table 6**).

In this study, the measured organic materials are biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved oxygen (DO), percent organic matter (OM%), and total organic carbon (TOC%). Ranges observed in wet and dry seasons were 0.53–3.67 mg/L for BOD, 3.75–88.25 mg/L for COD, while DO values ranged from 4.63–11.00 mg/L respectively in dry and wet seasons. In this study, the DO is within the allowed limit (**Table 6**).

OM% ranged from 0.43 to 5.55% in the dry season in the present study, although the TOC% in dry and wet seasons ranged from 0.27% to 2.24%, respectively. In this study, the highest values had been registered in dry season for OM% and in wet season for TOC% (**Table 6**).

6.2 Soil texture

The findings of the soil texture differed among the sites of the study as follows (**Table 7**): in S1 it was clay loam (40.4% silt, 30.6% sand, and 29% clay), in S2 it was clay loam (37.7% silt, 27.5% clay and 34.8% sand), S3 it was clay loam (38.6% silt, 33% clay and 28.4% sand) and silty clay loam (51.6% silt, 37% clay and 44.4% sand) at S4.

6.3 Descriptive analysis

Descriptive analysis for anionic surfactant (AS) and nonionic surfactant (NS) concentrations in sediment from the Tigris River sites during the study period by using photo lab S12 (PHD) and HPLC had demonstrated in **Table 8**.

The concentrations of AS using PHD ranged from 41.83 µg/g to 72.05 µg/g during the wet season. In comparison, the minimum NS levels in the wet or dry season were not measurable while the maximum concentrations in the dry season had registered 56.19 µg/g. HPLC results showed concentrations of AS in dry season ranging from 10.80 µg/g to 135.74 µg/g. During the wet season the minimum NS level was not measurable, and the maximum concentration in the dry season was 467.31 µg/g.

The two measurement methods (PHD and HPLC) have been compared by using a T-test analysis. The results revealed no significant variations between the tests

Site	Soil percentage			Soil class
	Clay%	Silt%	Sand%	Soil texture
S1	29	40.4	30.6	Clay loam
S2	27.5	37.7	34.8	Clay loam
S3	33	38.6	28.4	Clay loam
S4	37	51.6	11.4	Silty clay loam

**Table 7.**  
*Soil texture of sediment samples.*



Parameters	Range		Mean	Standard deviation	Standard values	
	Minimum	Maximum			Law 25/1967	CCME for rivers
Phtolab (µg/g)						
Anionic Surfactant (AS)	41.83 (w)	72.05 (w)	52.85	9.88	—	—
Nonionic Surfactant (NS)	ND (w&d)	56.19 (d)	17.12	26.73	—	—
HPLC (µg/g)						
Anionic Surfactant (AS)	10.80 (d)	135.74 (d)	34.15	35.32	—	—
Nonionic Surfactant (NS)	ND (w)	467.31 (d)	163.80	147.38	—	—
- = not applicable, w = wet season, d = dry season. Law 25/1967 = Iraqi River Maintaining System Law. CCME = Canadian Council of Management of the Environment.						

**Table 8.**  
*Surfactant concentrations in the sediment of the Tigris River for wet and dry seasons.*

obtained by the two instruments for measuring AS at  $P<0.05$  ( $t = 0.088$ ), while considerable discrepancies for measuring NS had been obtained at  $P<0.05$  ( $t = 0.004$ ).

6.4 Cluster analysis

Two clusters diagram shows (**Figure 3a**) during the wet and dry season. Whereas two highest values (72.05 and 69.71 µg/g) for AS by PHD, (ND) for NS by PHD) had recorded, whereas during the wet season they were 14.83 and 18.20 µg/g for AS (HPLC) and 56.17 and 55.03 µg/g for NS (HPLC). No detectable (ND) for NS (by HPLC) was recorded in dry season, particularly in June and August 2017 and May 2017, which indicates a marked variation in the season.

During the study period the cluster diagram (**Figure 6a**) shows two clusters. The first consisted of two sub-clusters; first, the pair of S3-S4: HPLC (37.5 and 235.79 µg/g, respectively) had reported specifically high concentrations of AS and NS in these sites. However, measurement with PHD did not show any detectable NS levels. Second, the pair of S1-S2: PHD (57.88 and 53.17 µg/g) had registered at S1, the closest highest values for AS. In comparison, S2 registered the similarly highest by PHD values (34.32 and 34.17 µg/g) for NS.

6.5 Correlation matrix

**Table 9** shows the correspondence matrix of the results that recorded the following strong correlations ( $P<0.05$ ): Significant negative correlation of AT with NS (PHD) ( $r = -0.997$ ) and a strong positive correlation with AS (HPLC) ( $r = 0.999$ ) obtained. The correlation matrix also shows a strong degree of correlation between NS determined by PHD and TSS ( $r = 0.998$ ), COD ( $r = 0.998$ ), and  $\text{NO}_2$  ( $r = 0.999$ ).

6.6 Correlation between soil texture and surfactants in sediment

**Table 10** demonstrated the correlation matrix between soil texture and occurrence of AS and NS at Tigris River deposit. Nevertheless, the results revealed no clear correlation.

Parameters	AT (°C)	TSS (mg/L)	COD (mg/L)	NO <sub>2</sub> (mg/L)
AS (µg/g) PHD	-0.778 P = 0.432	-0.170 P = 0.892	-0.294 P = 0.810	-0.206 P = 0.868
NS (µg/g) PHD	-0.997 P = 0.050	-0.697 P = 0.509	-0.783 P = 0.428	-0.723 P = 0.485
AS (µg/g) HPLC	0.999 P = 0.029	0.720 P = 0.488	0.803 P = 0.407	0.745 P = 0.465
NS (µg/g) HPLC	0.787 P = 0.423	0.998 P = 0.036	0.998 P = 0.045	0.999 P = 0.012
The correlation marked is significant at P<0.05.				

**Table 9.**  
Correlation between physicochemical and surfactants in Tigris River sediment during the study period.

Parameters	Clay %	Silt %	Sand %
AS (µg/g) PHD	0.269 P = 0.73	0.191 P = 0.81	-0.232 P = 0.77
AS (µg/g) HPLC	0.940 P = 0.06	0.807 P = 0.19	-0.897 P = 0.10
NS (µg/g) HPLC	0.389 P = 0.61	0.824 P = 0.18	-0.678 P = 0.32
he analysis had done according to temporal variation for all four sites.			

**Table 10.**  
Correlation between soil texture and surfactants in sediment.

7. Discussion

7.1 Physicochemical parameters of Tigris River water

All the data for AT and WT during the study period was within the permissible limit of weather rates for Baghdad city during wet and dry seasons (Table 6) [48]. This result is consistent with the previously reported role of AT for the heat budget of the Tigris River [49].

The excellent indicator assessment for total dissolved solids (TDS) in the water of the aquatic ecosystem is electrical conductivity (EC) [41]. During the wet season, such high concentrations of major ions have recorded as those of the dry season may be attributed to increased surface runoff, the flow of irrigation water return, soil salinity, and increased human activities [50].

High values of S‰ and TDS parameters may result from increased surface runoff, river geological erosion, increased evaporation rate, and increased human activity, all of which may result in increased ion concentrations [50].

The factors that can lead to an increase of the TSS level are silt, decaying plant and animal matter, industrial wastes, and sewage. But such high TSS values will cause many stream health and aquatic life problems [51, 52]. River sediments represent suspended solids that are reliant on discharge [41]. Turbidity found values above the allowable limits, with turbid water evident by the eye, probably due to the presence of organic, inorganic matter, bacteria, silt, algae, etc. [53].

WF determines the degree and type of deposition and, thus, the nature of sediment [54]. Water flow is an essential factor that moves the pollutants into regions far from their origin. The reason that might cause an increase in flow rate is melting

snow in the summer season; this explains much lower levels of sediment-measured pollutants [55].

The values of pH indicating river water is typically alkaline slightly and within the permissible amount for aquatic living [56].

In the environment, the  $\text{NO}_3$  had known to be more stable than  $\text{NO}_2$  [57]. The microbial activity, especially during the summer season because most biological processes take place during this season, is one of the reasons that led to a decrease in the nitrate concentration in the Tigris River due to the uptake process by these microorganisms [58]. For the concentration of  $\text{PO}_4$ , it was higher than the permitted level of aquatic life for both seasons, and the highest value had recorded in the wet season. In the water body, the  $\text{PO}_4$  is an important nutrient, and only the soluble form, inorganic phosphorus, can be directly utilized by aquatic biota [59]. The presence of phosphorus in the environment is either through the natural or activities of humans. Natural phosphorus sources include atmospheric precipitation, natural rock, and mineral dissolution, weathering of inorganic soluble minerals, biomass decomposition, runoff, and sedimentation. The anthropogenic source, by comparison, contains detergents, animal wastes, fertilizers, wastewater, and effluent from the septic tank, and industrial discharge [60].

BOD is a function of the amount of oxygen the bacteria consume, which decomposes organic matter into both surface water and waste [58]. The BOD in this study is within the permissible limits [45]. COD is a measure of the number of chemicals, usually organics, that consume dissolved oxygen [61]. All values in wet and dry seasons were within the permissible limits, and they agree with those found by previous investigations [62]. One of the parameters that maintain biological life in water is DO, and its variations depend on temperature and the presence of algal communities [63]. Raising a water body's flow rate would increase the amount of dissolved oxygen in the water, due to the flow rate increases the atmospheric oxygen diffusion and movement from and into the water. Organic matter (quantity) in the water impacts the dissolved oxygen levels by decreasing it [64].

TOC% estimate in sediment and soil samples is an essential criterion for determining environmental quality. In the ecosystem, organic matter exists in components of soil, ground, water, and sediment. The presence of these compounds in the sediment results in their interaction with metal ions allowing soluble or insoluble complexes to form. Such complexes, in effect, associate with minerals in the sediment to form particles capable of absorbing them into other pollutants [65]. TOC indicated river pollution because of the proportionality between TOC content and organic matter, which has an affinity for trace anionic and nonionic surfactant contaminants [66].

Urano et al. [67] showed that the sediment's adsorption potential tends to be independent on the residual surface area but is more related to the organic carbon content. Also found adsorption of AS and NS values on the microbiota equal to their sediment adsorption values. Organic matter (quantity) in the sediment supplies matrices for the adsorption of hydrophobic compounds and disposed them incomplete slowly [33].

## 7.2 Soil texture

The soil texture differed among the sites in this study (**Table 7**) from clay loam at S1, S2, S3, and silty clay loam at S4 [68, 69].

## 7.3 Descriptive analysis

**Table 8** illustrates the descriptive analysis for anionic surfactant (AS) and nonionic surfactant (NS) concentrations in the sediment of the Tigris River. There

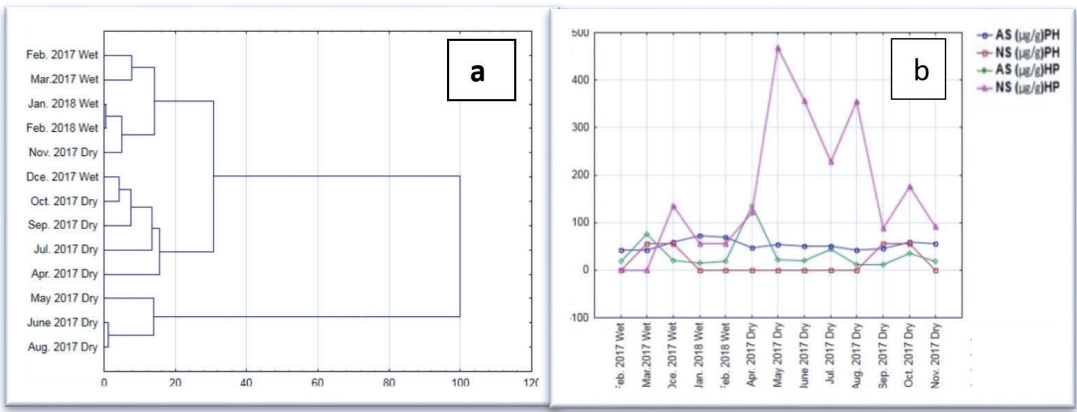
is no standard has found, whether Iraqi or international, about the permissible limits of the presence of the surfactants in river sediments to compare with data of the present study [70].

The main important factor to absorption surfactants compound on sediment is the different charges of these compounds, so the cationic surfactants (CA) can undergo sorption in sediment much more significant in contrast to AS such as sodium dodecylbenzene sulfonate (SDBS) [39]. The coefficient of equilibrium distribution for CS is twice more significant than that for SDBS. Also, low organic carbon content and neutral pH provide CS with more excellent sorption capability to the sediment, due to the electrostatic interactions between the positively charged ammonium groups ( $[(CH_3)_3NR]^+$ ), forming the heads of CS and the overall negatively charged sediment surface. SDBS shows lower sorption than CS, because the negative charge of SDBS compared to CS, which has positively charged [39]. And the adsorption of surfactant forms in sediment as Cationic > Nonionic > Anionic may be classified in the sequence. No measurable NS concentrations were reported using PHD in this study during 9 of the 13 months of the study period (3 in the wet season and 6 in the dry season), as opposed to higher AS concentrations. Lif and Hellsten [71] have shown that the NS has an amide group, comprising a small portion of the total volume of NS. However, their development and use are growing due to excellent chemical stability with rapid biodegradation and relatively simple processes of manufacture based mainly on renewable raw materials.

7.4 Cluster analysis

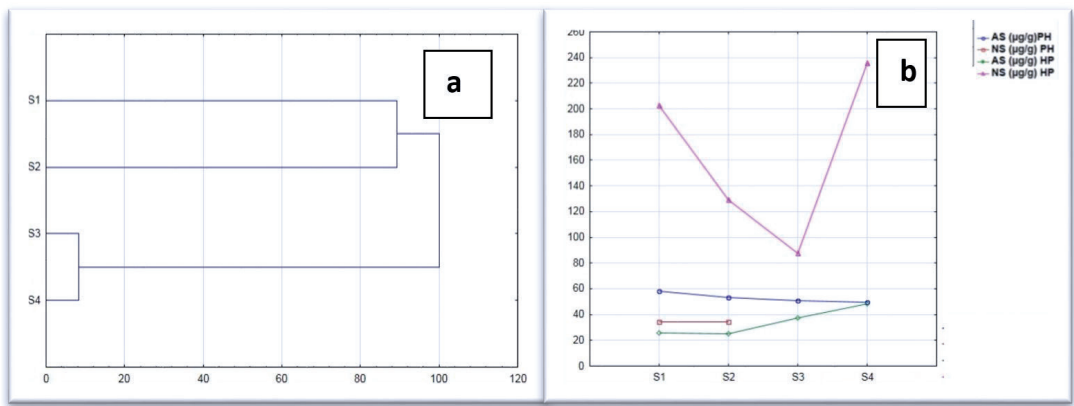
The seasonal variation illustrates in **Figure 5b**. In comparison to the wet season with lower temperatures, concentrations of NS and AS (by HPLC) observed the highest values in the dry season. The explanation could be either to lower pollutant (surfactant) inputs into the river or to more effective biodegradation of compounds studied in the dry season in the river water. Marcomini et al. [40] observed a significant seasonal variation in LAS and nonyl-phenol ethoxylates (NPEOs) concentrations at Lake Venice. Mainly due to increased biodegradation at temperatures above 20°C (late spring and summer). In 1994, coworkers observed the similar seasonal variation of some compounds in the Glatt River (Switzerland) [30]. Such as nonyl-phenol (NP), lipophilic nonyl-phenol monoethoxylate, and nonylphenol diethoxylate (NP<sub>1</sub>EO, and NP<sub>2</sub>EO).

A significant difference had observed for NS (HPLC) in which the two highest values at S1 and S4. At the same time, the lowest NS (HPLC) levels were at both S2



**Figure 5.** *a- Cluster diagram of temporal of the sampling period for wet and dry seasons, b- temporal variation of surfactants in sediment for wet and dry seasons.*





**Figure 6.** a-cluster diagram of spatial clustering of sampling sites for the wet and dry season, a b-spatial variation of surfactants in sediment for dry and wet seasons.

and S3. Nevertheless, during the study period, no apparent difference was found for other surfactants (**Figure 6b**), which suggests that S1 and S4 reported the highest levels of pollution with NS (by HPLC) relative to the lowest in S2 and S3, indicating these sites as hot spots for point sources of municipal and industrial discharges.

### 7.5 Correlation matrix

The correlation matrix between Physicochemical and surfactants in Tigris River sediment during the study period (**Table 9**) shows strong correlations ( $P < 0.05$ ) of (AT, TSS, COD, and  $\text{NO}_2$ ) with AS and NS, which means that only these parameters affect on the presence and degradation of anionic and nonionic surfactants either positive and negative correlation.

### 7.6 Correlation between soil texture and surfactants in sediment

Cano and Dorn [72] and Brownawell et al. [73] reported that the alcohol ethoxylate surfactant sorption is better associated with the sediment's clay content than to its organic carbon content (**Table 10**). This study found no clear correlation.

## 8. Conclusions

Several conclusions that drawn based on the findings of this study:

1. Two measuring techniques had applied with similar efficiency to measure anionic (AS) in river sediments while HPLC was more efficient for nonionic surfactants (NS)
2. The sediment serves as a sink for the sedimentation of AS and NS, the residual in the river water.
3. Four environmental parameters (air temperature, total suspended solids, chemical oxygen demand, and nitrite) were more critical factors impact on surfactants.
4. Nonionic surfactants and, most likely, their degradation products, nonyl-phenol, are significant contaminants because of toxic impacts in the aquatic environment, especially during the dry season. The highest concentration in



the dry season recorded (467.31 and 56.19 by HPLC and PHD, respectively) due to the high temperature that has likely led to the higher microbial organism's activity for compound degradation than in the wet season.

5. It was possible to use surfactants as markers for the presence of organic pollutants in sediments.
6. In fertilized soils, surfactants may also be possible to used to remove the organic compound.
7. The texture of soil does not affect the efficiency of the adsorption precipitation of AS and NS on river sediment.

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## Author details

Rana R. Al-Ani<sup>1</sup>, Fikrat M. Hassan<sup>1,2\*</sup> and Abdul Hameed M. Jawad Al-Obaidy<sup>1</sup>

<sup>1</sup> Environment Research Center, University of Technology, Baghdad, Iraq

<sup>2</sup> Department of Biology, College of Science for Women, University of Baghdad, Baghdad, Iraq

\*Address all correspondence to: fikrat@csw.uobaghdad.edu.iq

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