Detection and Removal of Polycyclic Aromatic Hydrocarbon from Selected Areas in Tigris River in Baghdad City

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ABSTRACT

Aromatic hydrocarbons present in Iraqi national surface water were believed to be raised principally from combustion of various petroleum products, industrial processes and transport output and their precipitation on surface water.

Polycyclic aromatic hydrocarbons (PAHs) were included in the priority pollutant list due to their toxic and carcinogenic nature. The concern about water contamination and the consequent human exposure have encouraged the development of new methods for PAHs detection and removal.

PAHs, the real contaminants of petroleum matter, were detected in selected sites along Tigris River within Baghdad City in summer and winter time, using Shimadzu high performance liquid chromatography (HPLC) system.

Analysis of samples from selected sites proved that the most abundant component of aromatic hydrocarbons were phenanthrene naphthalene, and acenaphthylene, followed by fluorene, acenaphthene, fluoranthene, benzo (a) pyrene, anthracene. and pyrene were present in low concentrations ranging in a descending order. Chrysene and benzo (a) anthracene were found in very low concentration.

A laboratory unit was designed to optimize the factors which may influence the feasibility of degradation processes of naphthalene and phenanthrene in aqueous matrices by oxidation with Fenton reagent. The study proved that 83% and 79% removal of naphthalene and phenanthrene were achieved applying optimum conditions of pH=3, temperature=40 ° C, H_2O_2=50 ppm and Fe^{2+} catalyst = 6 ppm.

KEYWORD:

Polychlorinated biphenyls (PAH), phenanthrene ، naphthalene, acenaphthylene, fluorene, acenaphthene, fluoranthene, benzo (a) pyrene, anthracene, pyrene, chrysene, benzo (a) anthracene, Fenton reaction, Tigris River.

التحري عن المركبات الهيدروكاربونية العطرية وازالتها من مناطق مختارة في نهر دجلة في مدينة بغداد

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الخلاصة:

يمكن ان يعزى وجود المركبات الهيدروكاربونية العطرية (PAH) في مياهنا الوطنية بشكل رئيسي الى حرق المواد النفطية المختلفة وترسبها على سطح المياه من جهه والى طرح مخلفات العمليات الصناعية ومخلفات زيوت مكائن الحرق و صرفها الى المياه السطحية وانتقالها وجريانها مع النهرمن جهة اخرى.

صنفت المركبات العطرية متعددة الحلقة (PAH) ضمن قوائم المركبات الملوثة ذات الاولوية لما تمتاز به من سمية وخاصية مسرطنة. وقد دفع زيادة الاهتمام بالمياه الملوثة وما ينجم عن ذلك من تعرض المجتمع والمواطن لمخاطر التلوث الى استنباط طرق جديدة ومبتكرة في التحري عنها ومن ثم ازالتها من الماء .

تم العثور على مركبات ال PAH في مواقع مختارة من نهر دجلة وضمن مدينة بغداد من خلال سحب نماذج من تلك المواقع في شهر شباط و شهر حزيران من عام2011 وتحليل النماذج باستخدام تقنية الكروموتوكرافيا السائلة ذات الاداء العالي HPLC

اظهرت نتائج التحاليل ان اكثر المركبات وفرة كان الفينانثرين و النفثالين و الاسينافثالين يتبعهم الفلورين و والاسينافثين والفلورانثين و البنزو (a) بايرين و الانثراسين و البايرين وبتراكيز متناقصة. اما الكرايسين و البنزو (a) انثراسين كانت بتراكيز ضئيلة جدا.

تم تصميم وحدة مختبرية لاختيار افضل العوامل التي تؤثر في قابلية التدهور(الازالة) لمركبي النفثالين والفينانثرين في الماء بطريقة الأكسدة بواسطة كاشف فنتون . اثبتت الدراسة ان اضمحلال (تدهور) النفثالين بطريقة فنتون للاكسدة هي طريقة فعالة ومجدية اذ تم الحصول على نسبة ازالة مقدارها 83% للنفثالين و 79% للفينانثرين وباستخدام الظروف المثلى من الحامضية pH=3 و بحرارة C ° 40 وتركيز المادة المؤكسدة H_2O_2=50 ppm وايونات الرصاص كعامل مساعد وبتركيز 6 ppm

الكلمات الرئيسية

ثنائية الفينول متعددة الكلور،فينانثرين، نفثالين، اسينافثالين، فلورين ، اسينافثين ، فلورانثين،بنزو (a) بايرين ، انثراسين ، بايرين ، كرايسين ، بنزو (a) انثراسين ، تفاعلات فنتون ، نهر دجلة

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a class of diverse organic compounds containing two or more fused aromatic rings of carbon and hydrogen atoms. They are ubiquitous environmental contaminants found in air, water, and soil [Yang, 2002].

Natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as the conversion of steroids to aromatic hydrocarbons. They are also formed by incomplete combustion of carbon containing fuels such as wood, coal, diesel, fat and tobacco [King et al.,2002].

Some PAH are expected to be human carcinogens [Nieva, et.al. 2001]. Several organizations have proposed maximum values for PAH in food products. On the many hundreds of PAH, the most studied is benzo[a]pyrene, which is often used as a marker for PAH in ambient air and food [Grova, 2002]. The International Agency for Research on Cancer (IARC) has classified three PAH (benzo[a]anthracene, benzo[a]pyrene, and dibenzo [a,h]anthracene) as possibly carcinogenic to humans [Nieva, et.al. 2001].

The US EPA suggests determination of 16 PAH in food [US EPA, 1984]. Among these, eight (benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene) have high carcinogenic potential [Pino, 2003].

PAHs are usually analyzed with gas chromatography or liquid chromatography, often coupled with mass spectrometry. These methods are time-consuming and require laborious sample concentration and preparation steps. Mostly a solid-phase extraction step is performed to concentrate the PAHs in a hydrophobic sorbent [Guillen, et.al. 2008].

As a result of the low biodegradability Advanced Oxidation Processes (AOPs) have been studied to be applied as an alternative or a complement to the conventional treatments [ATSDR, 1999, Wischmann and Steinhart, 1997 and Buco, 2009].

Although many studies regarding PAH sources, fate and distribution in the aqueous environment have been carried out in the whole world much less attention has been given to the aqueous environment in the Arab Region. The great rivers of Euphrates and Tigris of Iraq a dynamically active area in the Middle East with unique physiographic and hydrodynamic characteristics its surface layers are directly influenced by the different industrial discharges and wastewater effluents, suggesting considerable amounts of petroleum and petroleum products contamination.

Other important sources of oil contamination in Iraqi Nation Rivers are the discharge of huge amounts of land drainage water from the highly polluted areas and sewage water; they may include the wastes of lubricants and other mineral oils.

Thus the present paper aims to detect and determine concentrations of 16 PAHs according to the US EPA procedure using Reversed Phase High Performance Liquid Chromatography (RP-HPLC) technique in selected sites in Tigris River through Baghdad City. In addition, the present work aims to study the feasibility of naphthalene and phenanthrene degradation (removal) at µg/l levels in water matrices by applying Fenton's reagent.

EXPERIMENTAL METHODS

PAHs are usually present in water and environmental samples at µg/l levels. As a result, their separation requires sensitive and good sample preparation. The algorithms of analysis include extraction, concentration, chromatographic separation, and determination. Analyses were conducted at the laboratory of Early Sensing of Cancer Diseases (ESCD), Directorate of Physical and Chemical Material Research, in the Ministry of Science and Technology.

Fixing Standards

Sample analysis were carried out using Shimadzu high performance liquid chromatography (HPLC) system, equipped with a variable wave length detector, a 20 µl volume injector (u6k model), and a 5µm RP-18 ODS column (250 x 4.6 mm).

All tests were run using a 31 minute linear gradient of H_2O: Acetonitrile (ACN) as a mobile phase.

Table 1 lists time gradient program of the separation process. Flow rate, UV lamp detection and sensitivity were 1.0 ml/min., 250 nm, and 2 x10^{-3} respectively.

Table1 HPLC gradient Separation program

Time(min)	% H_2O	% ACN
0	60	40
2	60	40
20	0	100
30	0	100
31	60	40

The components of the standard mixture were run individually for naphthalene and for phenanthrene to determine the order of elution of each component and as a blend to determine the order of elution with respect to the mixture components, as shown in figure 1, 2 and 3. Solutions were stored at 4ºC in the dark. All solutions were continuously degassed ultrasonically for one hour before use.

Stable base line and single corresponding peak for each chromatographed component are criteria for governing the purity of the components; no further purification was needed.

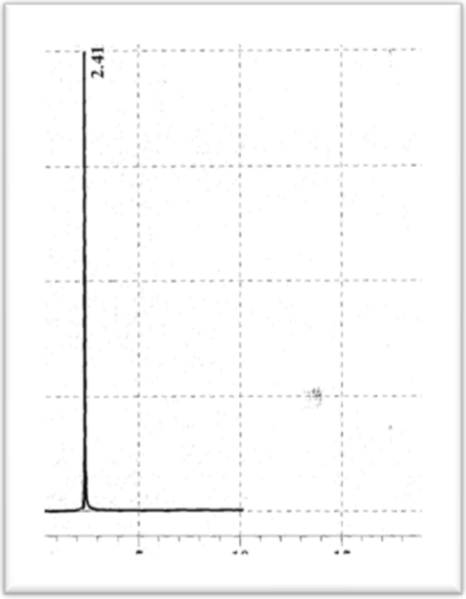

Fig.1. Fixing standard chromatogram of naphthalene

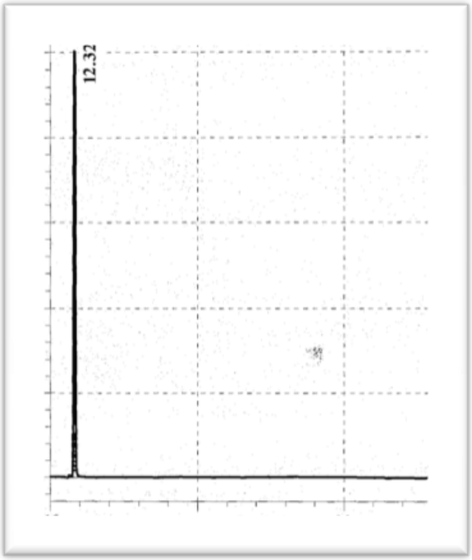

Fig.2. Fixing standard chromatogram of phenanthrene

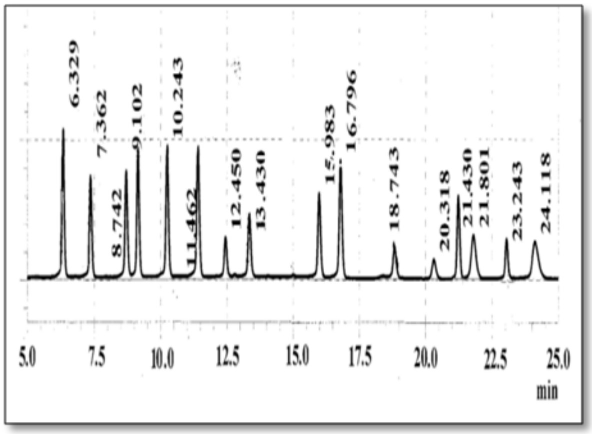

Fig.3. Fixing standard chromatogram of 16 PAH
1= naphthalene; 2= acenaphthylene;
3= acenaphthene; 4= fluorene;
5= phenanthrene; 6= anthracene
7= fluoranthene; 8= pyrene;
9= benzo (a) anthracene; 10= chrysene;
11= benzo (b) fluoranthene; 12= benzo (k) fluoranthene,13=benzo (a) pyrene, 14= dibenzo (a, h) anthracene , 15= benzo (ghi) perylene: 16=indeno (1, 2, 3-cd) Pyrenephenanthrene

SAMPLING

Sampling strategy depends on surface water analysis data reported by the Iraqi Ministry of Environment including stations believed to be directly influenced by effluents discharges.

Surface water samples (1 l volume) were collected from 4 different sites (Al-Rashid Treatment Plant, Al-Dorah Treatment Plant, Al-Jadriya Bridge, and Al-Muthna Bridge). Samples were taken in February and June 2011, brought to the laboratory, filtered using Whatman GF/F, 0.7 Im, filtrates were extracted using Sep-Pak cartridges, reduced to 2ml in a rotary evaporator and refrigerated at 4-5 ^{0}C [Grova, 2002]. Analyses were conducted within few hours.

Quantitative Analysis:

Calibration of HPLC was accomplished by individual injection of known concentration of naphthalene and phenanthrene solutions diluted with acetonitrile. The signal generated by the detector was presented as area under the curve. Concentration of unknown sample was determined using the equation below [Flotron, et, al, 2005]:-

$$C2= \frac{C1\ X\ A1}{A2} \qquad (1)$$

Where: C2 is the concentration of unknown sample in ppb.

C1 is the concentration of known sample (standard component) in ppb.
A1 is the area under the curve of the known sample (standard component) in units
A2 is the area under the curve of the unknown sample in units

Detection of pollutants in selected sites

Identification was achieved by comparing the retention times of the unknown peaks with those of known standards, while quantification of the identified and integrated peaks is performed by comparing area under the unknown peaks with areas under fixed standards peaks.

However the distribution of aromatic hydrocarbons detected in surface water through the four recommended sites were exposed in figure 4 through 7.

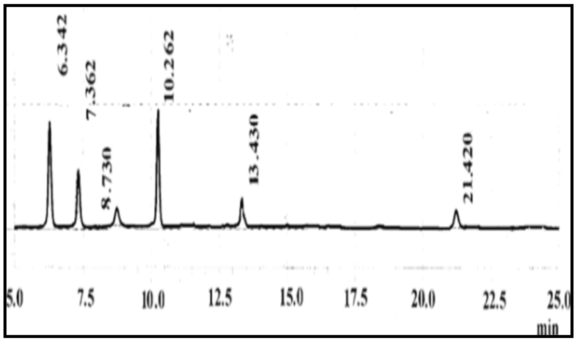

Fig.4. Al-Rashid water treatment plant, raw water, overlaying standard mixture: naphthalene = 9.87, acenaphthylene=7.03, acenaphthene=1.88 phenanthrene=11.28, pyrene=1.87, benzo (a) pyrene=1.26)ppb

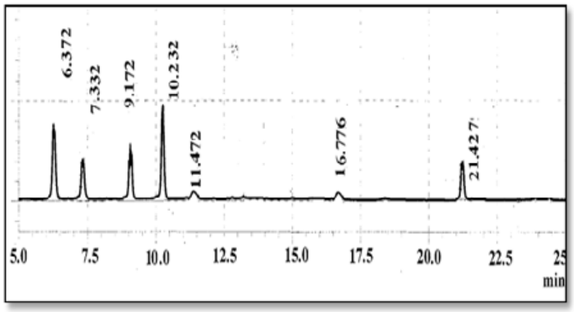

Fig. 5. Al-Dora water treatment plant, raw water, overlaying standard mixture: (Naphthalene = 9.17, acenaphthylene=5.34, fluorene =4.23 phenanthrene=10.64, anthracene =0.79, chrysene = 0.88, benzo (a) pyrene=3.11) ppb

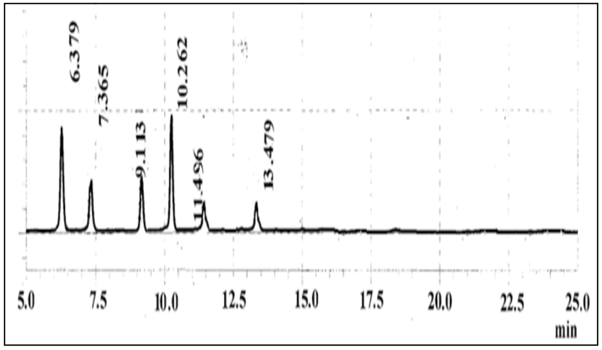

Fig. 6. Al-Jadriya Bridge, raw water overlaying standard mixture. (Naphthalene = 3.70, acenaphthylene=3.82, fluorene =3.90 phenanthrene=2.10, anthracene =0.68, fluoranthene =2.49) ppb.

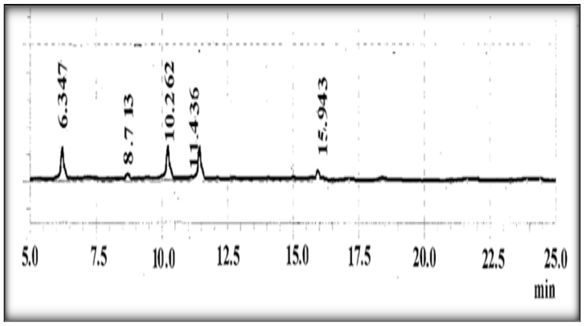

Fig.7. Al-Muthna Bridge, raw water, overlaying standard mixture:(naphthalene = 0.82, Acenaphthene =0.17 Phenanthrene=1.10, Anthracene =1.82, Benzo(a)anthracene =0.23)ppb.

Removal of naphthalene and phenanthrene by oxidation

Evaluation of the feasibility of two PAHs compounds degradation (at μg/L levels) in water matrices was studied by applying Fenton's Reagent.

Fenton's reagent is a strong oxidant mixture consisting of hydrogen peroxide and iron (II) salt that acts as a catalyst [Flotron et. al, 2005].

The effect of variables that influence Fenton degradation (temperature, initial concentrations of the ferrous salt, hydrogen peroxide, and analyte) was determined for naphthalene and phenanthrene only as they were chosen to be as model for PAHs removal due to their different molecular properties and prevailing presence in surface water [Lee, et. al., 2008].

The experiments were conducted in a 250 ml jacketed thermostatic batch reactor (inner diameter: 7.5 cm, height: 11.5 cm). Solutions of 100mL of naphthalene and phenanthrene at different initial concentration were inserted in the reactor separately in sequence. An aliquot was withdrawn each 10 min. for further analysis. Total running time was 90 minutes.

Degradation of the concerned compounds was accomplished by HPLC. Analyses were performed with mobile phase consisted of acetonitrile (90%) and water (10%) running in isocratic conditions at a flow rate of 1.2 ml min$^{-1.}$ The injection volume was 50 μL on 5μm RP-18 ODS column (250 x 4.6 mm). The column was operated at ambient temperature [Beltr´an et.al .2008].

The excitation and emission wavelengths were 297 nm and 405nm for naphthalene and phenanthrene respectively [Pino, 2009].

Quantification was performed by calculating the area under the curves according to equation (1).

RESULTS AND DISCUSSION

The main observations obtained is the abundance of naphthalene, phenanthrene and acenaphthylene, pronouncedly in Al-Rashid and Al-Dora treatment plants as exposed in fig. 8 and 9

Predominance of naphthalene, acenaphthylene and phenanthrene in Al-Rashid and Al-Dora water treatment plant sites may give an assumption that PAHs in these two regions are probably derived from the same types of petroleum products and/or crude oils. Meanwhile, Tigris River receives relatively little inputs of PAHs originated from crude oil and its products, but receives high amount of run-off of road washings through rain water pumping stations and refinery discharge.

Naphthalene is considered among the main components of the kerosene fraction of crude oils.

The occurrence of this aromatic in surface water might be originated from incomplete combustion of kerosene in generators followed by dispersion into the atmosphere in the form of vapors and its precipitation on water surface. Fluorene, acenaphthene, fluoranthene, benzo (a) pyrene, anthracene and pyrene were present in low concentrations ranging in a descending order, as shown in figures 8 through 11.

Chrysene and benzo (a) anthracene were found in very low concentrations comprising less than 1% of the total PAHs.

A relative elevation was found in PAH levels during winter compared with that of summer reflecting the effect of temperature on dissolution of low-boiling aromatics.

Temperature raise increase microbial activities thus enhancing biodegradation and oxidation process which lead to moderate decrease in the concentration of most of PAH compounds detected in summer. Figures 8 to 11 expose average PAH concentration in the four concerned sites in winner and summer and toxic equivalent factor TEF of each [Nisbet and LaGoy, 1992].

Removal of Naphthalene and phenanthrene by Oxidation

a. Effect of pH.

The Fenton’s reaction is pH dependent, because this value affects the hydroxyl radical’s generation and consequently, the oxidation efficiency. For this degradation process, the optimal pH range was studied to achieve the most effective removal. The removal efficiency was significantly changed with the pH increase from 3 to 6, pH = 3.0 was used as the pH optimum removal value.

b. Effect of Temperature

Experiments were conducted under the same conditions at four different temperatures between 20 and 50°C to investigate the effect of temperature on the degradation kinetics of aqueous naphthalene and phenanthrene solutions.

An enhancement in the rate and even in the extent of degradation reaction was observed with the temperature increase. Despite this, at higher temperatures the thermal decomposition of hydrogen peroxide may be accelerated, resulting in a decrease of the concentration of hydroxyl radicals, with consequent reduction in the reaction extent [Beltr´an et.al .2008].

On the other hand, there was practically no difference between the experiments carried out at 40°C and 50°C (removal of 90%). The economic aspect is often a limiting factor; thus the best option would be working at 40°C.

c. Effect of Ferrous Ion Concentration

It was noticed that there is an increasing degradation with the increasing of ferrous ion concentration, in fact significant differences were found between 2 and 6 mg/l, where removal efficiency were increased from 62 % to 83% for naphthalene and from 54 % to 79% for phenanthrene. The homogeneous Fenton process has the disadvantage of commonly using high concentrations of ferrous ion (50 to 80 mg/L), which is beyond the legal limit of 2.0 mg/ L for treated water to be released directly into the environment [Lee et, al., 2008].

In this work, a maximum ferrous ion concentration of 2.0 mg/L was applied.

d. Effect of Hydrogen Peroxide H_2O_2 Concentration

Experiments were performed to determine the effect of hydrogen peroxide concentration on the process.

In all experiments, it was observed that the maximum degradation of aqueous naphthalene and phenanthrene solutions was reached after 90 minutes.

On the other hand, the increase of hydrogen peroxide concentration from 20 to 50 mg/L yields rising removal efficiencies. However, increasing H_2O_2 concentrations lead to lower degradation rates.

The recombination of hydroxyl radicals and the reaction between them and hydrogen peroxide may explain this fact [Flotron, 2005].

e. Effect of Initial Naphthalene and Phenanthrene Concentrations

The reaction occurs quickly in the first 30 minutes and then stabilizes at the maximum degradation value, for all cases studied. After a period of 90 minutes a removal of 83%, 76%, 65%, and 57% was achieved with 10, 20, 50, and 100 µg/L of naphthalene, and a removal of 79%, 74%, 61%, and 51% was, achieved with 10, 20, 50, and 100 µg/L phenanthrene, plus 6 mg/l Fe^{2+} and 50mg/L H_2O_2 at 40 ^{0}C as temperature optimal conditions for both.

CONCLUSION

Naphthalene and phenanthrene appeared in the four selected sites showing extremely high-level in water treatment plants, indicating high rate of pollution comparing with the standard TEF value.

Acenaphthylene, acenaphthene, and fluorene were detected in most of the selected sites indicating moderate pollution yet still higher than the TEF standards.

Anthracene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo(a) Pyrene were detected scattering but less than the TEF standards.

Benzo (b) Fluoranthene, Benzo (k) Fluoranthene and Indeno (1, 2, 3-cd) Pyrene were not detected in all the proposed sites.

Dibenzo (a,h)anthracene and Benzo(ghi) perylene have no adequate data to compare with in the TEF values, though they were not detected.

More over the study revealed that Fenton’s reagent is an appropriate method for the degradation of naphthalene and phenanthrene in water matrices, providing that the ferrous ion and hydrogen peroxide are present in suitable concentrations.

An increase in temperature from 20 to 40◦C led to an increase in the removal efficiency from 70 % to 83% for naphthalene and from 64 % to 79% for phenanthrene but the best option for both was 40◦C.

The same effect was verified with the increase of ferrous ion concentration from 2 to 6 mg/l removal efficiency were increased from 62 % to 83% for naphthalene and from 54 % to 79% for phenanthrene.

Hydrogen peroxide was the only reagent with a double role during the oxidation: despite the degradation of naphthalene and phenanthrene increased with the H_2O_2 concentration, at higher oncentrations of oxidant the removal was reduced.

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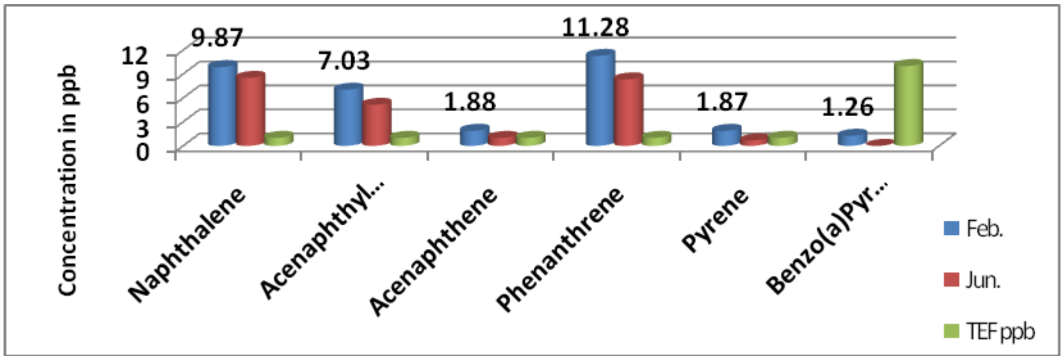

Fig 8 Average PAH concentration detected in Al Rashid treatment plant raw water samples in winter and summer

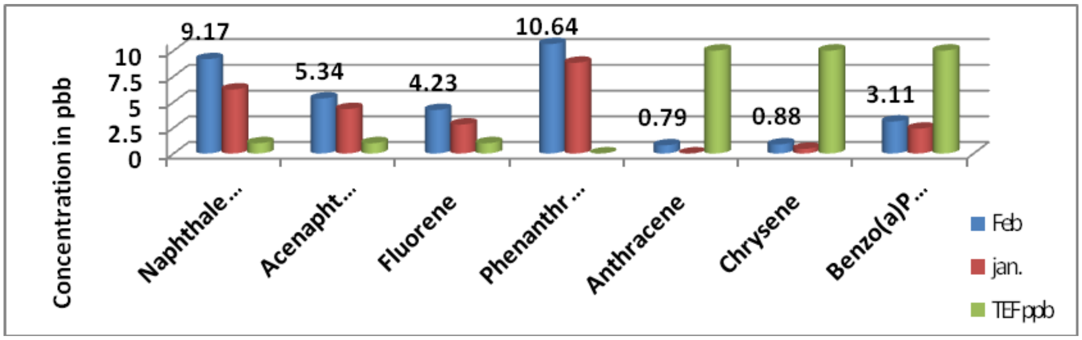

Fig 9 Average PAH concentration detected in Al -Dorah treatment plant raw water samples in winter and summer

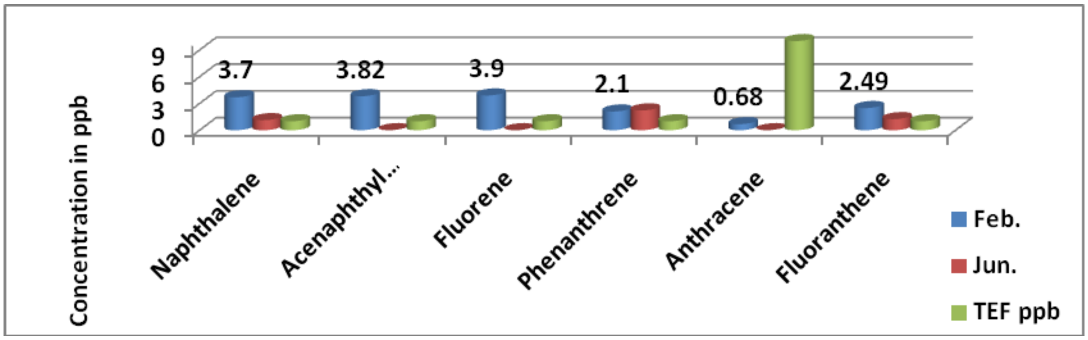

Fig 10 Average PAH concentration detected in Al-Jadryia bridge site raw water samples in winter and summer

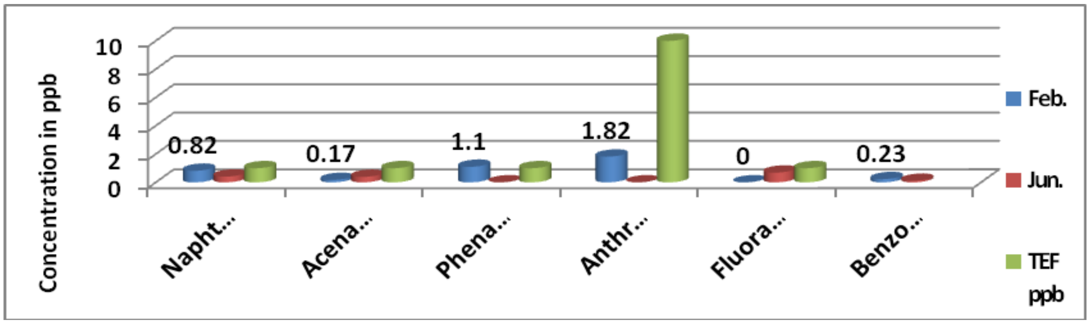

Fig 11 Average PAH concentration detected in Al-Muthna bridge site raw water samples in winter and summer