Determination of PAHs Concentration in Some Types of Phoenix Dactylifera L. Samples from Al-Diwaniyah Markets by Using Soxhlet and Gas Chromatography-Mass Spectroscopy Technique

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Abstract

The concentration of poly aromatic hydrocarbons in three types of Phoenix Dactylifera L. fruits (Iraqi, Iranian, Saudi) which are all collected from Iraq-Al-Diwaniyah city have been investigated. The PAHs levels in our samples were estimation by using Gas Chromatography Mass Spectroscopy (GC-MS). The technique of GC-MS was used for determination of ten of prior sixteen of carcinogenic PAHs compounds that are globally approved. The data indicated that there are four PAHs in Iraqi dates, where fluorene was the highest level of these compounds with concentration of 124.509 µg/mL followed by Acenaphthylene, Naphthalene, and Anthracene with concentration about 16.227 µg/mL, 15.850 µg/mL, and 3.035 µg/mL respectively. While the Saudi dates found that there are five types of PAHs with different concentrations, where the highest concentration is for Naphthalene with concentration about 269.491 µg/mL followed by Acenaphthylene, Phenanthrene, Anthracene and Pyrene with levels of 23.670 µg/mL, 8.340 µg/mL, 1.761 µg/mL and 0.543 µg/mL respectively. Six types of these compounds are hydrophobic, toxic, non-polar, water solubility, high stability, high melting point, and low vapor pressure. The number of aromatic rings in the Skelton of PAHs effect on some properties like solubility, volatility and hydrophobicity where the solubility and volatility increase and the hydrophobicity decrease with the increasing the number of aromatic rings [5-8]. United State-Environmental Protection Agency (US-EPA), Food and Drug (FDA), National Oceanic Atmospheric Administration (NOAA), and European Union priority Pollutants (EUPP) have been classified sixteen PAHs as pollutant compounds because of the carcinogenic and mutagenic properties that they have in their natures [9]. The International Institute for Occupational Safety and Health (NIOSH) recommends that the average air-to-air ratio for coal tar products should not exceed 3 for a 10-hour working day and within a week of 1.0 mg/m of work of 40 hours [10]. There are other limits imposed on-site exposure to items containing polycyclic aromatic hydrocarbons, such as coal, coal tar, and mineral oil [11]. However, the tests cannot of explain whether any
Health effects will occur or not, or appear the extent for polycyclic aromatic hydrocarbons or their source [12]. The main source of food crops pollution with polycyclic Aromatic Hydrocarbons is deposition of these compounds. Heavy mass of PAHs are associate particular matter such as dust while those compound consist of two or three rings are predominantly present in vapor phase [13]. Polycyclic aromatic hydrocarbons can degrade through their interaction with sunlight and other of chemicals circulating in the atmosphere over a period of the days to weeks or by using adsorbent surfaces [14]. Polycyclic aromatic hydrocarbons seep from wastewater in industrial wastewater treatment plants and wastewater [15]. The aim of this work is to study the concentrations of poly aromatic hydrocarbons in three of types from dates are marketed in Iraq, were collected in Al-Diwaniyah city, central Iraq, where the samples were processed accurately before the tests.

2. Material and Methods

2.1. Material and instrument

Shimadzu GC-MS has been use in estimation of ten of poly aromatic hydrocarbons. A mixture of 10 polyaromatic reference standards containing acenaphthylene, naphthalene, anthracene, benz[a]anthracene, Dibenzo[a,h]anthracene, benz[a]fluoranthene, fluroene, chrysene, pyrene, and phenanthrene have been purchased from Supelco Inc., USA., PAHs workingsolutions (10 µg/mL) was prepared from a stock solution of PAHs containing 200 µg/mL. N-hexane, cyclohexane, acetonitrile, anhydrous sodium sulphate, acetone (BDH chemicals), were obtained from Merck, Germany. All chemicals and reagents were used in HPLC grade and not need more purification.

2.2. Extraction

Three packed samples of Phoenix Dactylifera L. (Iraki, Saudi, Iranian) have been collected during the month of July 2017 for determination the levels of toxic poly aromatic hydrocarbons. The samples kept in refrigerator and then clean up before doing the extraction. The cooled samples of Phoenix Dactylifera L.s (30 g for every sample) were extracted with 300 mL of solvent mixture (n-hexane and acetone 1:1) by using quick fit unit for 24 h. soxhelt extraction method. The cleaning up process for the samples was done after the extraction by using (5 g) the anhydrous sodium sulfate to each sample independently followed by eluting process that done by using of mL n-hexane and ml methyl chloride to 10 mL for each sample.

2.3. GC-MS analysis of Phoenix Dactylifera L. samples

All the extracted samples were analyzed by using an Shimadzu GC equipped with a MS, HP-5 column, nitrogen gas as carrier gas. The GC oven temperature was programmed to increase from 50 °C (2 min.) to 200 °C (2 min) at a speed of 20 °C/min, to 240 °C (2 min) at 5 °C/min, and to 290 °C at 3 °C/min and then held for 15 min. The injector temperatures was 275 °C.

3. Results and discussion

The concentrations of ten detected polycyclic aromatic hydrocarbons from Phoenix Dactylifera L. of 3 traditional types in Al-Diwaniyah City-Iraq were shown in Table 1. which illustration that concentration of polycyclic aromatic hydrocarbons compounds in the three types (in µg/mL). These high levels of PAHs may be come backed to the effect of the source that found in these types. The variable in the kind of pollutant sources that produced polycyclic aromatic hydrocarbons compounds contributed to variation in results, another reason for different may be return to the degradation factors, which presented in this sites (sun light intensity, bacterial, temperature degree, and flouting body), which act some of them as a good absorbent to the polycyclic aromatic hydrocarbons compounds such as flouting residue plants or flouting died plants. Another reason had been contributed that effect of crowded traffic, which arise the percent of polycyclic aromatic hydrocarbons compounds if we take in consideration the sites are distributed in urban and rural places. The results as shown in table1:

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Table 1: Concentration of PAHs in (µg/mL) in *Phoenix Dactylifera L.* Samples.

| PAHs Compound          | No. of rings | Concentration (µg/mL) | Iraqi    | Saudi    | Iranian  |
|------------------------|--------------|-----------------------|----------|----------|----------|
| Naphthalene            | Two rings    | 15.850                | 269.491  | 114.401  |          |
| Acenaphthylene         | Three rings  | 16.227                | 23.670   | 3.723    |          |
| Fluorene               | Three rings  | 124.509               | ND       | 5.102    | 3.754    |
| Phenanthrene           | Three rings  | ND                    | 8.340    |          | 3.030    |
| Anthracene             | Three rings  | 3.035                 | 1.761    | 3.030    |          |
| Pyrene                 | Four rings   | ND                    | 0.543    | 0.376    | 0        |
| Benz[a] anthracene     | Four rings   | ND                    | ND       | ND       | ND       |
| Chrysene               | Four rings   | ND                    | ND       | ND       | ND       |
| Benzo[a] fluoranthene  | Five rings   | ND                    | ND       | ND       | ND       |
| Dibenz [a,h] anthracene| Five rings   | ND                    | ND       | ND       | ND       |
| Total                  |              | 159.621               | 303.805  | 130.3856 | 0        |

Where found four of toxic PAHs with high concentration. The highest concentration was for fluorene 124.509 ppm, Acenaphthylene 16.227ppm, Naphthalene 15.850 ppm, then Anthracene 3.035 ppm respectively. Another six compounds of PAHs are not existed in Iraqi sample. Where found five of toxic PAHs with high concentration. The highest concentration was for Naphthalene 269.491 ppm, Acenaphthylene23.6670 ppm, Phenanthrene 8.340 ppm, Anthracene 1.761 ppm, and Pyrene 0.543 ppm respectively. Five of toxic PAHs compounds of PAHs are not exist in Saudi sample. Six compounds of PAHs have been found in Iranian sample while four are not. The highest concentration of these compounds was for Naphthalene 114.4 µg/mL, Fluorene 5.102 µg/mL, Phenanthrene 3.754 µg/mL, Acenaphthylene 3.723 µg/mL, Anthracene 3.030 µg/mL, and Pyrene 0.3766 µg/mL respectively. The priority PAHs is classified in to five types according to the number of rings (two, three, four, five and six) fused aromatic rings. Table 2. shows the summation of every type of PAHs class in all studied samples:

Table 2: Summation of concentrations of PAHs which are classified according to number of rings

| Type of sample | Summation of concentrations (µg/mL) |
|---------------|-----------------------------------|
|               | 2-rings  | 3-rings  | 4-rings  | 5-rings  |
| Iraqi         | 15.850   | 143.771  | 0        | 0        |
| Saudi         | 269.491  | 33.771   | 0        | 0        |
| Iranian       | 114.4    | 15.609   | 0        | 0        |
The lowest concentration was for 2-ring PAHs (Naphthalene) 15.850 in Iraqi sample while the highest concentration (269.491) was recorded for Saudi sample was most abundant than others samples. The concentrations for PAHs class those consist of three rings were for the Iraqi sample higher than others samples as shown above. The pollution with PAHs compounds can was done by direct exposure to the known sources or indirect via irrigation intake by water. PAHs which mainly enter in surface waters via atmospheric in fall out, municipal industrial effluents, urban runoff and oil spillage or leakage (H. Zhang and references therein) [16]. Relative concentration values in general of PAH compounds that different molecular weights were used frequently to distinguish of PAHs sources. PAHs were regarded as two types, including 4-6 rings (high relative molecular weight(HMW) and low-rings from 2-3rings (low relative molecular weight LMW). The results showed in table 2 that the PAH concentrations of HMW was lower than LMW from studied samples. Special PAH compound ratios, such as Phenanthrene /Anthracene, Flurene/Pyrene, LMW/HMW and Fluorenthenel / (Fluorenthene & Pyrene), were widely used to identify that sources of PAH. Previous researchers were suggested that the possible sources of PAHs were petroleum when the ratio of Phenanthrene/Anthracene > 10, while possible input of PAHs was incomplete combustion of fuel such as oil and coal when Phenanthrene/Anthracene <10. Meanwhile, according to the conclusions of other researchers, when the rate of Fluoranthene/(Fluoranthene+Pyrene) <0.5, it was frequently considered as an indicator of petroleum; when the rate of Fluorene /(Fluorene/Pyrene)>0.5, it was usually considered as an indicator of combustion [17].

In this work, the ratio of Phenanthrene/Anthracene is used to identify the possible sources of PAHs in samples of *Phoenix Dactylifera L*. The results in table 3 shows that the ratios of Phenanthrene/Anthracene are almost in the range of 1.238 to 4.735 Iranian & Saudi samples respectively, both ratios were less than 10, which indicate that sources of PAHs from incomplete combustion of fuel.

| Type of Sample | Ratio of Phenanthrene to Anthracene |
|---------------|-----------------------------------|
| Iraqi         | ---                               |
| Saudi         | 4.735                             |
| Iranian       | 1.238                             |

**Conclusion**

Ten polycyclic aromatic hydrocarbons compounds of sixteen of priority of PAHs had been determined in the three samples of *Phoenix Dactylifera L*. (Iraqi, Suadi, Iranian) selected from Al-Diwniyah Markets by using GC-MS technique. The results refer that all the three types were contaminated in different percent of polycyclic aromatic hydrocarbons compounds according to human activity which present in these sites. The results were referred that the Saudi and Iranian *Phoenix Dactylifera L* containing five and six compounds respectively of PAHs with various and high concentration, while the Iraqi *Phoenix Dactylifera L* was less pollution than other types and contain just four types of PAHs compound with low concentrations. The pollution with three rings class of PAHs was higher than tow rings class of PAHs. The study is indicating that sources of PAHs were incomplete combustion of fuel.

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**List of abbreviations**
### Abbreviation and Symbols

| Abbreviation | The meaning |
|--------------|-------------|
| PAHs         | Polycyclic Aromatic Hydrocarbons. |
| GC-MS        | Gas Chromatography-Mass Spectroscopy |
| US-EPA       | United State-Environmental Protection Agency |
| FDA          | Food and Drug |
| NOAA         | National Oceanic Atmospheric Administration |
| EUPP         | European Union priority Pollutants |
| NIOSH        | International Institute for Occupational Safety and Health |
| ND           | Not Detection |

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