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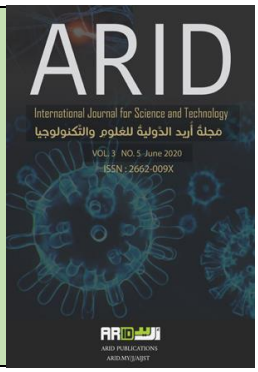

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EFFECT OF WASHING ON HEAVY METALS CONTENTS ON DATE FRUITS

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تأثير الغسل على محتويات العناصر الثقيلة في التمور

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ABSTRACT

The quantities of aluminum (Al, Cadmium (Cd), nickel (Ni) and tin (Sn) were estimated in twenty samples of packaged dates imported from the Middle East and North Africa countries collected from the Malaysian markets in Selangor - West Malaysia. The varieties include, Ajwa, Deglet Nour, Lulu, Mariami, Zahdi (two samples from different suppliers), Medjool, Mabroom, Khudri, Lamri, two unidentified species under trade marks (nomades standard, palm dates), Safawi (two samples from different suppliers), Khasouei, Khalas-Ihsa, fard, Roshdi, Mashrook and Rabbi .20 g of each sample was washed with 15 mL of deionized distilled water for 90 second. Washing residues and washed date tissues were dried and digested by mixture of nitric acid and hydrogen peroxide (15:20). The effectiveness of water washing on the removal of residues of heavy elements accumulated on dates was measured by comparing the contents in both washing residues and date tissue after washing. where the effectiveness ranged from 9.35 to 34% of the total content according to type of element. The study concluded that washing dates before direct consumption or manufacturing can play an important role in the removing some of the contents of heavy elements and reduces the health risk that can be caused to the consumer.

Keywords: washing residues, date fruits, heavy metals, washing activity, direct consumption

الملخص

تم تقدير كميات عناصر الألومنيوم (Al) والكادميوم (Cd) والنيكل(Ni) والقصدير(Sn) في عشرين عينة من التمور المعبأة المستوردة من دول الشرق الأوسط وشمال إفريقيا والتي جمعت من الأسواق الماليزية في منطقة سلنقور – غرب ماليزيا، وتشمل الفصائل الآتية: عجوة، دقلة نور، لؤلؤ، مريمي، زهدي (عينتين من مصدرين مختلفين)، مبروم، مدجول، خضري، لامري، صفوي (عينتين من مصدرين مختلفين)، خصوي، خلاص الإحساء، فرد، رشدي، مشروك، رابي. بالإضافة لعينات غير معروفة التصنيف تباع تحت العلامات التجارية الآتية (palm dates و Nomads standard)، تم غسل 20 جراماً من كل عينة ب 15 مليلتر من الماء المقطّر منزوع الأيونات لمدة 90 ثانية. كلا من ناتج الغسيل وأنسجة التمر المغسولة جففت وتم هضمها بواسطة خليط حامض النيتريك وبيروكسد الهيدروجين بنسبة 20:15 زتم قياس فاعلية الغسل بالماء على إزالة بقايا العناصر الثقيلة المتراكمة على التمور عن طريق مقارنة محتوياتها في كلا من ناتج الغسل وأنسجة التمور بعد الغسل حيث تراوحت الفاعلية من 9.35 إلى 34% من المحتوى الكلي حسب نوع المعدن. وخلصت نتيجة البحث إلى أن غسل التمورقبل الاستهلاك المباشر أو التصنيع يُمكن أن يلعب دوراً مهماً في التخلص من بعض محتويات العناصر الثقيلة ويقلل من الأضرار الصحية التي يمكن أن تلحق بالمستهلك.

الكلمات المفتاحية: بقايا الغسيل، ثمار التمر، المعادن الثقيلة، فاعلية الغسل، الاستهلاك المباشر.

1.Introduction:

For the past few decades, higher plants are used as bio-monitors of heavy metals pollution in the environment [1]. The date palm has been reported as a bio-monitor for heavy metal contamination [2,3]. Many studies from the Middle East have confirmed the presence of significant quantities of heavy metals in date fruits [3,4,5]. Essential heavy metals play a significant role for maintaining health [Anonymous. 2000]. However, non-essential heavy metals like, Cadmium (Cd), Lead (Pb), Nickle (Ni) and chromium Cr, are non-biodegradable thus, these metal elements can deposit in various body organs which possess a great threat to the human health [6,7]. Heavy metals emission of from natural sources, industrial activities and vehicles may cause deposition of heavy metals on the surface of the fruits and vegetables and might seriously harm human health e.g. neurological disorders, intrauterine growth retardation, decrease in immunological protection [8]. hence, regular monitoring programs of heavy metal contamination in food stuff were mainly centered for decades in developed countries [9]. Several analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), neutron activation analysis (NAA), differential pulse anodic stripping voltammetry (DPASV), energy dispersive X-ray fluorescence (EDXRF) etc. have been employed for the determination of trace metals in different environmental samples [10]. Graphite flam atomic absorption spectrophotometer (GFAAS) was used for quantifying the heavy metal contents in date fruit samples in the present work as it is, sensitive, accurate, highly selective and cost effective. There are many studies on investigating the heavy metals in date fruits; Mineral Ion Contents of seeds of Bahraini date palm were determined by [11] Evaluation of Sewy date palm cultivars irrigated by both treated wastewater and Nile water was studied by [12]. Heavy

metals in the date fruits collected from different locations of Riyadh was studied by [2], the study reported a significant effect of washing date fruits on Pb and Cd contents. Growth and heavy metals uptake by date palm grown in mono-and dual culture in heavy metals contaminated soil was determined using AAS [13]. In a comparative study conducted by [3], concentrations of some trace elements ; Silver (Ag), Aluminum (Al), boron(B), barium (Ba), cadmium (Cd), copper (Cu), chromium (Cr), Iron (Fe), nickel (Ni), lead (Pb), selenium (Se) and zinc (Zn) in the date palm fruits and their washing solutions were investigated in the residential and urban locations of Jeddah. The levels of these elements were found to be greater in the urban site than in the residential one, increasing with the harvest time. The study showed that date palm has a strong potential for environmental biomonitoring. In the study conducted by [14], concentrations of calcium(ca), magnesium (Mg), iron (Fe), copper (Cu), and lead (Pb) in palm oils (Elaeis guineensis) at various steps of the purifying process were determined using microwave digestion and ICP-MS analysis. determination of some trace elements as pollutants in date fruits and agricultural soils at Zilfi area was carried out by [15]. The concentrations of the elements in soil were found as follows: Ag (0.7-42) , Al(1628.7-6264.5), As(40-59.8), Bi(0.02-0.1), Cd(0.08-4.2), Co(1.1-11.5), Cr(19.2-126.2(ppm),while, the concentrations in date fruits were found as follows: Ag (0.3-1.2) , Al(24.6-152.9), As(4.3-6.5), Bi(0.004-0.008), Cd(0.03-0.2), Co(0.03-1.6),and Cr(4.1-15.5).The concentrations of the elements were lower in washed date samples than unwashed ones. In the study carried out by [16] on date fruit samples from the type Segae, washed and unwashed samples were analyzed for metal contents using flame photometry inductivity coupled plasma and atomic absorption. The study revealed that the dates have considerable contents of Fe and Mn which are important to human health. The toxic elements like As, Cd, Ni and Bi was found to be less in washed samples compared to unwashed samples. The aim of this study is to study the effect of washing on heavy metals contents in packed imported date fruits sold in the Malaysian supermarkets.

2-Materials and methods:

2.1 Instruments and chemicals

The equipment used comprised the Agilent AA200 atomic absorption spectrometer (AAS) with Zeeman background correction system equipped with graphite furnace (GTA 120) and an auto sampler (PSD 120). Also used were hollow cathode lamps for Cd (228.8 nm and slit 0.5 nm), Ni 352.5 nm slit 0.2nm), Al (257.4 nm slit 0.5 nm) Sn (286.3 nm slit 0.5 nm). The instrument was operated following the manufacturer's instructions. atomic signals were measured in peak aria mood. The working standard solutions (100ppm) were prepared using 1000 ppm stock standard solutions (purchased from Sigma-Aldrich) using 0.05M analytical grade nitric acid (supplied by Merck, KGaA, Germany) and deionized distilled water. Moreover, palladium (II) nitrate (from Merck, KGaA Germany) and ascorbic acid (supplied by Sigma-Aldrich) were used as modifiers during the sample analysis. All containers and glassware were cleaned by sonicating into 20% nitric acid solution and rinsed with deionized water distilled (DDW) water prior to use.

2.2 Sample collection.

Twenty imported packet date fruit samples were purchased from the local supermarkets in the state of Selangor in West Malaysia. These samples were namely Ajwa, Deglet Nour, Lulu, Mariami, Zahdi (two samples from different suppliers), Medjool, Mabroom, Khudri, Lamri, two unidentified species under trade marks (nomades standard, palm dates), Safawi (two samples from different suppliers), Khasouei, Khalas-Ihsa, fard, Roshdi, Mashrook and Rabbi (Table(**1)**).

Table (1): characterization of samples

Sample No.	Sample variety	Sample case	COUNTRY OF ISSUE	EXPIRATION DATE
1	Ajwa	loose	KSA	23/12/2018
2	Deglet Nour	packed	TUNISIA	12/2018
3	Lulu	packed	UAE	13/11/2019
4	Mariami	**loose**	**UAE**	**22/1/2019**
5	Zahdi -1	**packed**	**UAE**	**11/5/2019**
6	Medjool	**packed**	**UAE**	**2/12/2018**
7	Zahdi. -2	**packed**	**UAE**	**19/1/2019**
8	Mabroom	**packed**	**UAE**	**26/7/2018**
9	Khudri	**packed**	**KSA**	**20/2/2018**
10	Lamry	**packed**	**-**	**3/2/2019**
11	Palm dates	**packed**	**UAE**	**28/12/2018**
12	Nomades(Promel)	**packed**	**TUNISIA**	**-**
13	Safawi	**packed**	**UEA**	**6/2/2019**
14	Khasouei	**packed**	**KSA**	**29/1/2019**
15	Khalas-Ihsa	**packed**	**KSA**	**2/2018**
16	Frad	**packed**	**UAE**	**-**
17	Roshdi	**packed**	**KSA**	**-**
18	Mashrook	**packed**	**KSA**	**2017**
19	Rabi	**packed**	**IRAN**	**19/9/2018**
20	Safawi	**packed**	**KSA**	**23/3/2020**

2.3 Removal of dust by washing

To determine the heavy metals in fruits' dust, 20 g from each sample were washed thrice with 15 mL in three portions for 30 seconds each with deionized water (DDW). Washing residues were collected in 150 mL beakers and put on hot plates to dry. The residues were kept in a refrigerator for digestion and analysis. After washing, all date samples were dried and cut into slices, and kept for digestion and analysis.

2.4 Digestion procedure

The digestion method was partly modified from [2].1g of each sample was added into a conical flask containing 15 mL of HNO_3 65%. Hot plates were used for heating the mixtures

in fume cupboard for 30 min at 70°C, 20 mL of hydrogen peroxide H_2O_2 were added in portions (5ml each). To get a clear solution, the mixtures were heated at 130 °C until almost dry. The flasks were left to cool and then10mL of DDW was added to the digested samples and the solutions filtered using Whatman No 0.42 filter paper. The filtrate was made up to 50mL with DDW and kept for GFAAS analysis. All washing residues were treated the same way.

2.5 Validation Method

The accuracy of the method was evaluated by recovery study on spiked samples with known concentrations of examined heavy metals (two different concentrations each). Samples were digested and analyzed by the same procedure used for examining samples. The mean recoveries of the analyzed heavy metals were between 84.86 % and 114.56%, indicating a good agreement with estimated and measured values (Table 2). RSD ranged from 6.1to 0.5. The estimated value was calculated as following: Added mount (Spiked) – Sample' heavy metal content.

The recovery % was calculated from the equation.

$$\left\{\frac{\text{Added mount (Spiked)} - \text{Sample's heavy metal content} * 100}{\text{Added mount}}\right\}$$

2.6 Determination of washing effect on heavy metals content

After determination of heavy metals content in all date samples using GFAAS ,the washing effect was calculated as follows: washing effect = C.D /(C.D + C.F).where, C.D is concentration of metal in dust and C.F is concentration of metal in the flesh of the fruit Table (3).

Table (2): Heavy metal recoveries and relative standard deviations (RSDs) at two different concentrations (n =3)

	Concentration 1(ppb)		Concentration 2(ppb)		Recovery %		Relative STD	
element	estimated	measured	estimated	measured	RECOVERY (1)	RECOVERY (2)	RSD% (1)	RSD% (2)
Ni	20	19.5	100	110.07	97.5 ± 4.43	110.07 ±1.7	4.55	1.51
Cd	2	2.291	10	11.45	114.56± 5.5	114.53 ± 3.78	4.85	3.30
Sn	20	19.798	100	105.33	98.99 ± 8.71	105.33 ± 4.41	8.80	4.19
Al	100	101.34	400	410.54	101.34 ± 0.54	102.63 ± 1.42	0.535	1.388

3. Results and Discussion

The activity of washing on some heavy metals deposited on date fruits was studied using wet digestion technique and GFAAS for analysis. Heavy metal contents in all samples were significantly reduced by washing for about 90 seconds at room temperature, and the results agree with those reported in the literature [2]. The washing effect (Table .2) ranged from 34.78 to 9.35% and seemed to be in descending order as follows: Cd> Ni> Al> Sn. The highest washing activity was found for Cd (34.78%) followed by Ni (31.02%), Al (30.32%) and Sn (9.35%). Several previous studies have been conducted in the Middle East to investigate the amount of dust accumulated on date palm trees and the effect of location on the quantities of accumulated dust [17,18,19]. In a study carried out by [17] on adult palm trees of Al-Khalas variety in Saudi Arabia, the amount of dust collected on the leaves of palm trees was estimated according to the distance of these trees from unpaved streets and agricultural roads. The mean dust deposit

(mg/cm2) according to the distance between (in meters) the roads between the year1984 and 1985 was found, 0.67,0.26 ,0.21, and 0.13 for distances of 10,40,80 and120 meters from the roads. The study observed a decrease in the amount of dust accumulated on the leaves as the trees away from agricultural roads and unpaved streets. The study also revealed that, the accumulation of dust on date palm leaves can affect the quality and quantity of date products because it exposes the trees to the stress of dust pollution that affects the vital activities and the efficiency of leaves in providing the fruits with the carbohydrates and thus the productivity of fruits. In the study carried by [18], a positive relationship was found between the amount of dust deposited on date palm trees cultivated of Halawi variety distributed over three regions in the province of Basra and wind speed and temperature of palm planting area. The amount of dust falling on the leaves were calculated according to the fruit growth months The study showed that the productivity of trees in the study sites decreased, reaching 36 kg in Abu al-Khaseeb area, followed by Al-Hartha region where the average production of palm trees was 32 kg. The variability in date palm yields in the three study areas may be due to the effect of the deposited dust on fruit surfaces, as well as deposited dust on the leaves reduces the leaves' efficiency in providing the fruits with the carbohydrates needed for their growth and development. Similar results were found by [19] in the study carried out on sampled palm leaves from growing trees in different environments (industrial environment, marine environment, agricultural environment, desert environment, urban environment). The study revealed three important results: first, that palm trees have a significant role in the absorption and sedimentation of large quantities of heavy metals and the highest sedimentation of heavy metals was found on leaves taken from the industrial environment and the lowest concentration was in the agricultural environment and then the desert. Second, the percentage of heavy elements absorbed and deposited by palm leaves (cobalt, chromium, nickel, lead, ranged between 22-91%). The third, palm trees capture 40-80% of the amount of dust suspended in the air and the total amount absorbed by the leaves ranges

between 22-91. However, the presence of heavy metals in the air is caused by air contamination by vehicles, nickel-cadmium batteries, oil industries and mining [20]. Pesticides and packing materials may also contribute to the deposition of metals on the surface of fruits and vegetables. However, presence of heavy metals such as Pb an Cd in washing residues and flesh of date fruits was reported previously in many studies i.e. [2, 13,15].

Table (3): Effect of washing on total heavy metal contents in date fruits (n=3)

Element	Average flesh heavy metal contents (µg/g) fruit fresh weight	Average dust heavy metal contents (µg/g) fruit fresh weight	Total	Washing effect %
Ni	0.258	0.116	0.374	31.02
Cd	0.009	0.0048	0.0138	34.78
Al	7.238	3.150	10.388	30.32
Sn	0.188	0.0194	0.2074	9.35

4. Conclusion

The results showed that washing can remove a considerable quantity of total heavy metals contents adhered to date fruits and minimize the risk to consumers' health. More studies are required to optimize the suitable washing time, temperature and washing liquid**.**

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List of Abbreviation

(DDW) Deionized distilled water

(GFAAS) Graphite flame atomic absorption spectrophotometer

(AAS) Atomic absorption spectrometry

(ICP-AES) Inductively coupled plasma-atomic emission spectrometry

(ICP-MS) Inductively coupled plasma-mass spectrometry

(NAA) Neutron activation analysis

(DPASV) Differential pulse anodic stripping voltammetry

(EDXRF) Energy dispersive X-ray fluorescence

(nm) Nanometer

(ppm) Part per million

(ppm) Part per billion (ppb)

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