An-Najah National University

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Analysis of Leachate Production and other Organic Outcomes in Pickling Cucumbers in Plastic Bottles.

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Dedication

I dedicate this work

To my beloved parents, who raised me to be I am today... ….

To my husband and daughter…….

To my brothers, my sisters and their families ……

To all who have supported me …

Acknowledgement

First of all, I would like to express my gratitude to ALLAH, who granted me the ability to finish this work.

Many thanks and gratitude to my supervisor; Prof. Shehdeh Jodeh for his academic, technical guidance and full help and support throughout this study.

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Finally, thanks to all my family for their care and support which gave me the courage that I need.

الإقرار

أنا الموقعة أدناه مقدم الرسالة التي تحمل العنوان:

Analysis of Leachate Production and other organic Outcomes in Pickling Cucumbers in Plastic Bottles.

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أية درجة أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

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The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

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Analysis of Leachate Production and other organic Outcomes in Pickling Cucumbers in Plastic Bottles.

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Abstract

This study investigated the potential migration of plastic components or additives from plastic bottles during keeping cucumber as pickle for a long time. The compounds studied were bisphenol A (BPA), nonylphenol (4-NP), bis (2-ethylhexyl) phthalate (DEHP) and bis (2-ethylhexyl) adiapate (DEHA).

In addition, the plastic bottles were tested with four different contents and three different days of storage. In all cases, samples were analyzed using gas chromatography mass spectrometry (GC/MS) and High Pressure Liquid Chromatography (HPLC).

Four target compounds appeared in all samples with variety concentrations. Indicating that migration from plastic bottles can occur at the experimental cases tested. Result showed the effect of increasing the day of storage and increasing the amount of compound release, and so the effect of changing the contents of plastic bottles in the variety of concentration of each compound at the same number day of storage.

The highest concentration of compounds migrated was for 4-NP and the lowest for BPA. 4-nonylphenol was found in plastic bottle which contain tap water with range from 23 to 47 ng/L, in plastic bottle which contain the

additives from 112 to 170 ng/L, in plastic bottle contain cucumber from 120 to 179 ng/L and in plastic bottle contain cucumber with pesticide residue from 320 to 420 ng/L. bisphenol A was found in plastic bottle which contain tap water with range from 17 to 27 ng/L, in plastic bottle which contain the additives from 101 to 145 ng/L, in plastic bottle contain cucumber from 113 to 152 ng/L and in plastic bottle contain cucumber with pesticide residue from 290 to 370 ng/L. Although the compounds migrate levels measured in these samples pose no risk for human health because of very little concentration, the presence of more source of exposure to our body to such compounds pose a health risk.

Chapter One

1.1 General Introduction

Plastic bottles are everywhere you turn. Drinking water, soda, juices, baby bottle and various food products.

Plastic popularity has grown considerably with plastic can easily molded into a wide range. Their availability benefits provide manufactures with a cheap and convenient way for packaging their products that other material does not.

Plastic is a synthetic material that is manufactured using all soft's of compounds, while some plastic is safe for using once only. In the bottling industry, bottles are manufactured from different polymers, each with its characteristics regarding bottle strength and storage time.

High density polyethylene (HDPE), polyethylene terphthalate (PET) and poly carbonate (PC) for primary packaging (baby bottle, water bottle, etc….), while high-density polyethylene (HDPE), low density polyethylene (LDPE) and ply styrene (PS) for caps.

Mixture of plastic components and additives can be made to obtain improved plastic characteristic, several water bottle format, shapes and colors.

The safety of some polymeric material is a subject of concerns in the bottling sector, due to potential migration of plasticizers and additive to our food and water. The washing and reusing of plastic bottle is making a

problem. These plastics become dangerous; they break down over time, releasing chemicals into our food and water [1].

The chance that chemicals will leak out of tiny cracks increases with repeated wash and reusing of such bottles. This leads to exposing human, animal, plant and microorganism to a very large number of chemical that are released from many different sources and so entering the organisms by different routes.

Many of these chemicals may not cause harm individually, they occur in low concentrations, but the combination effect from exposure to all these chemicals, even at low concentration, during a prolonged period time, may lead to adverse effect for human health and environment.

Plastic bottle monomers and additive can migrate to water and change its organoleptic properties [2]. Which can endanger the health of consumer if it is presented at high concentration due the potential toxic properties of some chemicals [3].

The potential migration of plasticizer and additive to water diffusion process attracted a lot of attention in the last decade and now a days [4], due to their potential endocrine disrupting effect toxicity to wild live; [5] as described for, Phthalates [6,7] , Alkyl phenol such as Octylphenol (OP), Nonylphenol (NP) [8,9] , and Bisphenol A (BPA) which is one of the chemicals that take a lot of attention from public and the scientific community [8,10-13].

Pesticides are synthetic chemicals that are widely used for preventing, destroying, repelling or mitigating any pest [14] and their applications eventually lead to higher productions yield and quality.

Pesticide residue refers to small amount of pesticides that may remain in or on food crop after harvesting and storage [15] and make their way into the food chain.

By bio accumulation of pesticides residue through the food chain, they could build up to risk or threat to both animals and human life [16].

Some of their effect causes Harmon disruption, birth effect and neurological [17].

In this study a plastic bottle will be used after filling it with cucumbers as pickles. A complete scan for both metals and organics which leaked out from plastic bottles will be studied, and the impact of substances on human health.

Also we are using pesticides as a marker or indicator for what’s happening after chemical migration from plastics. We also used in this study insecticide such as Abamectin which is one of the most widely used insecticides and can be applied by soil injection, tree injection, application to the skin, or broadcast foliar or ground application as granular or liquid formulation or as pesticide coated seed treatment.[18, 19].

1.2 Objectives

The study aims to achieve a set of goals and the most important of which are the following points:

1- To know the materials leachate from plastic bottles in cucumber pickling.

2- To make comparison between storage in plastic bottles and glass bottles.

3- To know which of the additives that are used in cucumber pickling process help in releasing more of the material from plastic bottles wall.

4- To know the interaction between the compound leachate and pesticide residue.

5- To educate the Palestinian communities about the risk regards using plastic bottles in pickling process.

1.3 Research justification.

Palestinian housewives depended mainly on the plastic bottle for keeping beverage and food, in spite of the repeated warning of using of such tools. These tools contain a substance which was the most important reason for the defenders of the environment to refuse reuse such tools.

Of the most bottles in and outside the home are the water bottles and beverage plastic, and experts note that the danger of reusing these packages is that they contain certain chemicals and contamination of food

and beverages as a result of the interaction with them, leading to interference with the system of the body for communication natural hormonal.

The recent status of the California Research and Environmental Studies addressed the risks of using these reused materials which can be damaged through daily use or washing. It also increases the chance of leakage of chemicals from small cracks, which develops over time and use. These studies have linked between this article and the incidence of breast and uterine cancer and increased the risk of miscarriage. It also causes low level of testosterone hormone in the body, and contributes to substance BPA in plastic bottles in the corruption of the immune systems of children.

Chapter Two

2. Background

It is known for years that the rule of some chemicals can be leachate to water and food and this causes people to have small amount of chemicals in their blood and urine.

In water bottling sector, polyethylene terphthalate (PET) and poly carbonate (PC)for single use bottle and repeated use [20], scientists have found that both plastic monomers and additives among many other common products may also harbor hormone disrupting chemicals that migrate to the water, change its organoleptic properties [21, 22].

It's too soon to say wither drinking out of PET plastic bottles is harmful to human health, said leader researcher Martin Wager, an ectoxicologist at Goethe University in Frankfurt. But it now appears possible to interfere with estrogen and other reproductive hormones just as the plasticizers BPA and Phthalates [23].

2.1 Substance investigated in plastic container content.

2.1.1 Bisphenol A

Bisphenol A (BPA) is the common name of 2,2-(4,4 dihydroxy diphenyl propane) and the chemical structure show in figure 2.1.

It is an monomer used to make certain plastic and epoxy resins, it entered into variety of common consumer products, such as water bottles, sports equipment, carboys, CDs, DVD and food container [24-28].

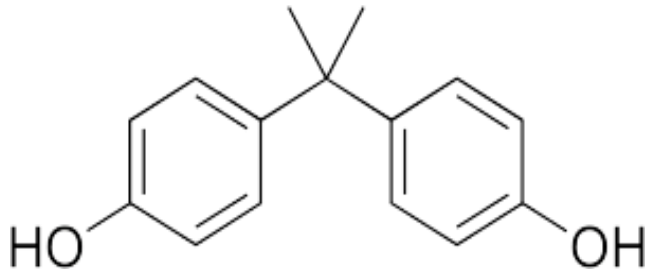


Fig 2.1: Chemical structure of Bisphenol A.

For plastic bottle, the chemicals BPA one of major concerns, which used in manufacture of many plastic bottles. It is known that the rule of BPA can be leachate from the container that made with BPA to our water and food , when they're washed, heated or stressed and then enter the human body, this reason to have a small amount of BPA in their urine and blood. [9] [29, 30] This take a lot of attention due to BPA health, environment disruption, so the study continue on BPA and its migration under different condition [31, 32].

Some of research study the migration of BPA from plastic bottle water and carboy, under different temperature, and the studies shows that the increasing in temperature lead to more BPA was released [33-37].

In other hand some studies done under different period storage to investigated the BPA migrate level, and found that, the leach of BPA from

plastic container increased with increase the storage time, and also the number of sample that showing BPA migrate in it was increase with the increase storage time.[38, 39]

There are study done under controlled time / temp condition and the study showed the migrate of BPA range from 7 to 58 mg/kg [27].

In other study, the BPA was detected in eleven canned soft drinks including soda, cola, tea and energy drinks at concentration ranging from 0.044 to 0.6 mg/L. [30].

During manufacturing process, unreacted BPA will be present in the PC products and some residual free BPA is still available for receptor binding, migrate of BPA will be from PC to the food [32, 40].

There is some studies work in showing the level of migration of BPA from the new and from the used plastic bottles to water, study noticed that the BPA concentration leached increase at the used plastic bottles more than the new plastic bottles, water from used plastic bottles contain BPA migrate level at the range from 4 to 60 mg, but the BPA migrate determined in water from new plastic bottles ranged from 0.6 to 0.3mg [41].

2.1.2 4–Nonylphenol.

4-nonylphenol (4-NP) is the common name of 4-(2,4-dimethylheptan-3-yl)phenol and the chemical structure show in figure 2.2, it is widely used in

domestic product such as surfactant and food packaging films and it is used to improve the plastic bottles properties[42-44].

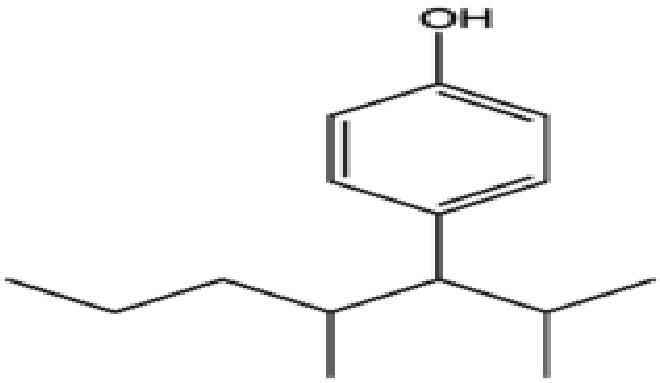


Fig 2.2: Chemical structure of 4-nonylphenol.

4-nonylphenol is one of the chemicals that concerns the human and takes attention due to it disrupting the endocrine system and that can harmful consequences on wild life and human health [45-47].

Nowadays, bottling sector is a subject of concern due to the potential migration of plasticizers to water such as 4-nonylphenol [8].

Alkyl phenol such as nonylphenol (NP) and octylphenol (OP) detected by several author in bottled water and after migration assay, detected of 4-NP in samples, indicating that 4-NP able to migration from plastic food [9], [48, 49].

Using gas chromatography-mass spectrometry with negative chemical ionization for investigated the level of 4-NP in bottled water, and the study show that 4-NP present in all sample of the bottled water and the concentration of 4-NP in bottled water ranged from 108 to 298 ng/L [36],

Also by using gas-chromatography-mass spectrometry chemical ionization another study detected the amount of 4-NP in human urine samples [50].

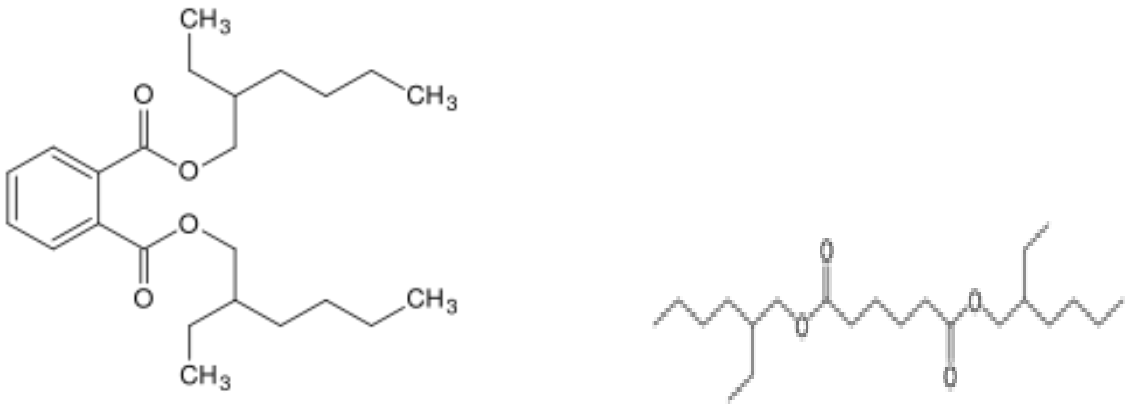
2.1.3 Plasticizers.

Plasticizers are small compound with relative small molecular weight; the addition of plasticizers to plastic is wide spread, plasticizers added to mixture polymers to improve their softness and flexibility.

2.1.3.1 Bis (2-ethylhexyl) phthalate

Bis (2-ethylhexyl) adiapate.

Bis (2-ethylhexyl) phthalate (DEHP) and bis (2-ethylhexyl) adiapate (DEHA) figure 2.3(a, b), are widely used as a plasticizer in manufacturing due to their suitable properties and low cost.



(a) (b)

Fig2.3: Chemical structures of: (a) bis(2-ethylhexyl)phthalate, (b) bis(2-ethylhexyl)adiapate.

As another chemicals, DEHA and DEHP take attention by several study, like these studies determination of the DEHA and DEHP in plastic bottles, the plasticizer could migrate from the wall to the contains[51]

A university of Idol survey revealed that the reuse of water and soda bottles widely in the university, with some people using a single bottle for several weeks.

The UI study tested water samples from soft drink and water bottles, analysis of the samples showed that the chemicals in plastic can break down and migrate into the liquid inside with repeated use. Di (2-ethylhexyl) adiapate was one of the toxins that present, a carcinogen that has been shown to cause liver damage and reproductive problems [52].

Potential migration of plasticizer and additives to water by different process is form concern to human as described for phthalates, phthalates used as polymerization acceleration or agent to make high flexibility [6, 8]. Detected of phthalate in water bottles by several author, phthalate may come from, bottling lines [53], cap-sealing resins [54], water treatment facilities [55, 56] or during storage [8, 57, 58]. Migration of plastic components or additive during bottling and storage was studies in Spanish water bottled and the study found that target compound such as Diethyl hexyl phthalate and Bi phenol A were detected in bottled water.

DEHA and DEHP were observed in most of the samples irrespective of the condition (heating, without heating and under solar light), DEHP detected

in varied concentration from 0.006 to 0.532 mg/L and DEHA present in water samples with concentration between 0.001 to 0.256 mg/L [59] .

In a study done to determined the level of phthalate that migration from plastic bottle to mineral water and soft drink, results showed that the highest rate of migration to soft drink was recorded for dimethyl phthalate, and highest rate of migration to the mineral water recorded to dibutyl phthalate and diethyl hexyl phthalate [60].

2.2 Health

In last year's, evidence has indicated adverse changes in the reproductive health of animals and humans, studies indicated that some chemicals in the environment have the potential to disrupt the endocrine system, endocrine disruptors are compounds that mimic the action of natural estrogens.

The presence of plastic component or additives in water and food have been attracted the attention of the scientific world because of their endocrine disrupting and possible negative effect on human health, especially when chemicals present at high concentration [61, 62].

Drinking out of plastic bottles is harmful to human health it appear unidentified chemicals in plastic bottle that have potential to interfere with estrogen and other reproductive hormones, as the plasticizers BPA and phthalates [13].

Alkyl phenol, such as Bisphenol A and 4-nonylphenol are a potential endocrine disruption, that mimics the action of hormone estrogen [63][64] , some estrogenic compounds, such as bis phenol A and nonylphenol can alter cell cycle kinetics, produce chromosomal aberrations and produce telomeric associations, the chemical bis phenol A can binding to DNA after metabolic activation [65].

The endocrine disruptors can produce many health related problems, such as puberty in females, reduced sperm counts, altered function of reproductive organs, obesity, altered gender specific behavior, and increased rate of some breast, ovarian, testicular and prostate cancer [66].

In addition to BPA negative effect endocrine systems low dose BPA might also result in increased risks of a diabetes mellitus, cardiovascular diseases and liver enzyme abnormalities [67].

2.2.1 Pesticides

Pesticides are toxic chemicals used to control or kill pests, there are different types of pesticides and classification is offered according the target organism. Herbicide, fungicides and insecticides, use of these products has played a significant role in raising the yield of crops from agricultural land. When pesticides are applied improperly, resulting residue can pose significant health risk to consumer [68].

Public concern over pesticide residue in food has been increasing in the last decades for example, a recent 1988 national survey by the Marketing

Institute showed that approximately 75 percent of consumers are very concerned about pesticide in their food, that percentage is higher than that of consumers worried about cholesterol, fat, additives or any components [69].

The control operation and control the spraying in some countries, In the habit is spraying pesticides in the day or hours before the harvest of crop, such crops may contain pesticide residue in vegetable and fruit therefore these residues is reflected in the pickles [70] .

2.2.2 Abamectin

Abamectin is a mixture of avermectins B1a (80%) and avermectins B1b (20%) these two components, B1a and B1b have very similar biological and toxicological properties. Abamectin is an insecticides well as acaricide and anematicide.

Abamectin is used to control insect and mite spests and average of a gronomic, fruit, vegetable and ornamental crops.

In the sun light the photoisomer 8,9-2-avermectin is produced and becomes part of the residue, it is also described as the D-8,9 isomer.

Analytical methods that measure the components of the residue involve the HPLC separation and fluorescence detection of derivatives formed by converting the cyclohexene ring to an aromatie ring. Analytical method for

abamectin residue in crops, soil, animal tissue, milt and water were measured [71].

Harvesting of the product should be controlled and not sold before the tenth day of spraying like in cucumber due to existence of pesticide residue. The study showed that residue of abamectin remains in vegetable, tomato, cucumber and pepper with a high amount after first days of spraying and until the fifth day amount of abamectin was high and form dangerous problem. The result obtained that the quantity of abamectin residue in plant part decrease by time due to photodegradation of pesticides [72].

Chapter Three

3. Material and methodology

The research experimental work basically depends on determining of chemical leachate out of plastic bottle wall, which contain cucumber as pickle, the samples were collected at different time after storage, on the fifth day, tenth day and twentieth day.

To avoid the contamination of chemicals (BPA, 4-NP, DEHA and DEHP), no plastics were allowed to be used in the experiment, and all glass vessels used were cleaned and dried before use.

3.1 Materials.

All reagents which used in this experiment were purchased from Aldrich chemical company and highly selected and purely chosen. The following list is for all chemicals used in this study:

Abamectin.

BPA.

DEHA.

DEHP.

4-NP.

Ethyl acetate.

Sodium sulfate.

Distilled water.

Acetone.

Methanol.

3.2.1 People survey.

The objective of the survey is to compare the people who used plastic bottles in pickling cucumber in the study area, the survey includes question about personal characteristics, household and buys pickles and market orientation and many detailed question about different aspects of the use of plastic bottles in the pickling cucumber, materials added during the pickling process and the storage time of the pickles.

Another objective of the survey is to identify more of pesticides that used in the study area.

3.2.2 People survey results.

This survey consists of two parts, the first shows the information about the containers that used in pickling cucumber, the material uses in pickle process and the storage time of the pickle, the second part shows the information about pesticides used on cucumber crops.

After the survey distributed to 50 people the results we obtained, the first part shows that the container most housewife used was plastic bottles to

keep cucumber as pickle, and very small percentage that used glass container to keep cucumber as pickle, also from the survey we noticed that large percentage used these material or additives in cucumber pickle process (salt, vinegar, lemon and garlic), and the cucumber pickle storage time ranged from five day to six month.

The second part of the survey answering by farmer and shows that more pesticides used on cucumber crops was Abamectin as acaricided and the harvest of crop after one day of spraying with pesticide.

3.3 Pesticides residue in cucumber fruit.

We are using pesticides as a maker or indicator for what's happening after chemical leachate from plastic bottles. So we are going to measure it in cucumber only in the fruit itself.

3.3.1 Sample preparation.

This study carried out planting a cucumber and spraying with pesticides, then the cucumber collected after one day of spraying with pesticide to sure of the existence of the material inside the fruit, after that we measure the pesticide residue inside the fruit using HPLC.

3.3.2 Extraction procedure.

Cucumber fruit sample (20g) were blended for three minutes using high speed blender with 60 mL of acetone were added and 100 mL ethyl acetate. The solution was filtered and rinsed twice with 50 mL acetone, the solution

was evaporated at 40^{o} under reduced pressure using rotary evaporator, and then the residue was transferred and diluted with 5 mL of methanol into small vials and stored until analysis.

3.3.3 Analysis instrumentation.

High performance liquid chromatography HPLC instrumentation was used for pesticides residue analysis, type of Perkin Elmer series 140 LC pump chromatograph, with AL 95UV/visible spectra photometer detector, C_{18} stainless column, the wave length was 210 nm for Abamectin.

3.3.4 Pesticides residue results.

After the sample was collected, cucumber fruits was extracted, and analyzed by HPLC and the following results were obtained:

The day 0 original concentration of Abamectine which spraying on the cucumber fruits was 26.00 mg/L, after one day of spraying the concentration of Abamectine at cucumber fruit was found 15.94 mg/L.

We noticed that the concentration of Abamectine was high after one day of spray, so in this work we collected the cucumber fruit after one day of spray to make cucumber as pickle using plastic bottles, used the pesticide residue as indicator and know what’s happing after chemical leachate.

3.4 Testing cucumber pickles.

Testing cucumber pickles and the water after pickling process at different storage time, in this study we used tap water to make cucumber pickle, so we test the tap water to know if there any chemicals which we will study present in the tap water itself.

3.4.1 Sample collection and preparation.

Cucumber that were characterized by small to medium sized fruit and did not ever spray with any pesticide were collected, and used in the present work.

Cucumbers that were characterized by small to medium sized fruit and spraying with pesticide also were collected and used in the present work.

The sample preparation was as the following:

1. Glass and plastic bottles filled with tap water only.

2. Glass and plastic bottles were filled with tap water and additive that most people as noticed from the survey used it in pickle process which are, salt, lemon, vinegar and garlic.

3. Glass and Plastic bottles filled with tap water, additives, and cucumber that never spray with pesticides.

4. Glass and plastic bottles filled with tap water, additives and cucumber that is collected after one day of spraying with pesticides, all plastic bottles

prepared and storage period 5,10and 20 days, the samples were taken and stored in a cooler until analysis. Table (3.1).

Table 3.1: Samples collection and preparation.

Sample no.	Day of storage	Tap water	Additive	Cucumber	cucumber, pesticide residue
1	5	✓			
2	10	✓			
3	20	✓			
4	5	✓	✓		
5	10	✓	✓		
6	20	✓	✓		
7	5	✓	✓	✓	
8	10	✓	✓	✓	
9	20	✓	✓	✓	
10	5	✓	✓		✓
11	10	✓	✓		✓
12	20	✓	✓		✓

3.4.2 General procedure.

The procedure was operated under room temperature, and all equipment used were glass that was cleaned and dried before using to investigate the compound that migrates from plastic bottle.

The procedure step as follows:

1. The sample extraction with ethyl acetate $C_4H_8O_2$ (chromasolve for HPLC ≥ 99.7%) 3X50mL.

2. Combine ethyl acetate fractions.

3. Dry over sodium sulfate Na_2SO_4 (it is drying agent remove residual water for ethyl acetate).

4. To remove drying agent, filter ethyl acetate.

5. By using Laborta evaporator ethyl acetate evaporated under vacuum and temperature doesn't exceed 50^oC.

6. Remove ethyl acetate until about 1mL is left, the sample stored and ready for GC/MS analysis.

3.4.3 Analysis instrumentation.

Samples were analyzed by gas chromatography coupled to quadruple mass spectrometer, an Agilent 6890N gas chromatograph connected to an Agilent 5975B MSD mass spectrometer, the system was operated in electron ionization mode (CL) source (Agilent, USA). The target compounds separation was achieved with a capillary column DB5_MS (30mX0.25mm, 0.25Mm film thickness).

Helium was used as the carrier gas (1.2mL min^{-1}). A 1ML was injected in split less mode at a temperature of 300^oC. The GC oven temperature program applied was as follows, 80^oC (hold 1 min) to 220^oC at 10^oC/min, from 220^oC to 260^oC at 4^oC/min, and 260^oC to 300^oC (8min) at 5^oC/min, finally to 310^oC at 20^oC/min.

Peak detection and integration were carried out; full scan data was used for the identification of target compounds in the migration test.

Chapter Four

Results and discussion.

After cucumber fruit was collected and kept as a pickle at three storage periods, we used GC/MS to investigate the chemicals that have the potential to migrate from plastic bottles.

Previous reports showed that chemicals such as (BPA, 4-NP, DEHA and DEHP) can leach out from plastic containers. The present study confirmed the continuous release of such chemicals from plastic bottle under normal condition.

Many different sources of exposure human to the chemicals (BPA, 4-NP, DEHP and DEHA), one of the sources we found in this work was cucumber pickle that kept in plastic bottles.

4.1 Tap water in glass and plastic containers.

Tap water was used in the cucumber pickle process, so we determined the concentration of the compounds in tap water itself, the concentration of compounds (BPA, 4-NP, DEHA and DEHP) in tap water listed in table 4.1.1. All four target compounds were detected in tap water and the BPA concentration in the tap water sample was the highest among the four target compound (11ng/L) see figure 4.1.1, as for 4-NP(10ng/L), DEHP (9ng/L) and for DEHA (7ng/L).

Table 4.1.1: concentration of (BPA, 4-NP,DEHP and DEHA) in tap water in glass bottle.

Sample/ compound	BPA ng.L^{-1}	4-NP ng.L^{-1}	DEHP ng.L^{-1}	DEHA ng.L^{-1}
Tap water	11	10	7	9

Plastic bottle filled with tap water and stored at room temperature, table 4.1.2 lists the concentrations of each compound detected in plastic bottles at different three storage time (5,10 and 20 day). All four compounds BPA, 4-NP, DEHP and DEHA were detected in the three storage time with varied concentration ranged from 17 to 27 ng/L, 23 to 47 ng/L, 19 to 32 ng/L and 20 to 37 ng/L respectively.

Table 4.1.2: concentration of (BPA, 4-NP,DEHP and DEHA) detected in tap water in plastic bottle.

Sample no.	Day of storage	BPA ng.L^{-1}	4-NP ng.L^{-1}	DEHP ng.L^{-1}	DEHA ng.L^{-1}
1	5	17	23	19	20
2	10	20	29	26	31
3	20	27	47	32	37

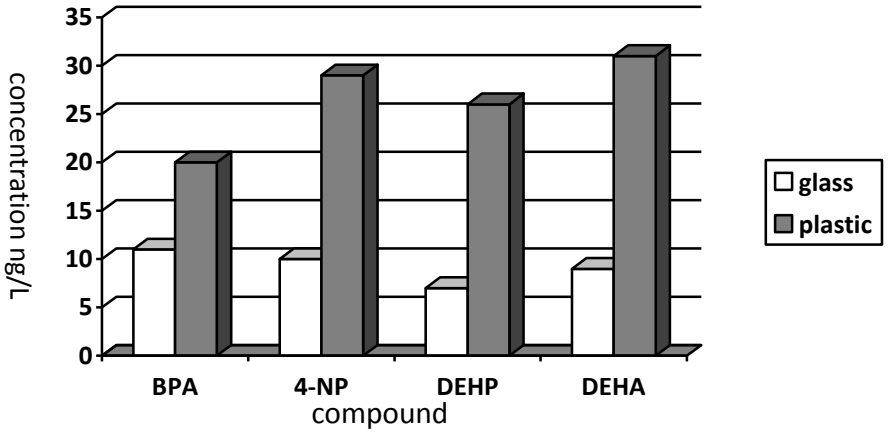


Fig 4.1.1: Concentration of compound investigated in plastic and glass container contain tap water.

From the figure 4.1.1 we noticed the increase of concentration of each compound when the tap water kept at plastic bottle compare with the concentration of these compound when the water keep at glass container, this give us the evidence of happen migration of such compound from plastic bottle to the water .

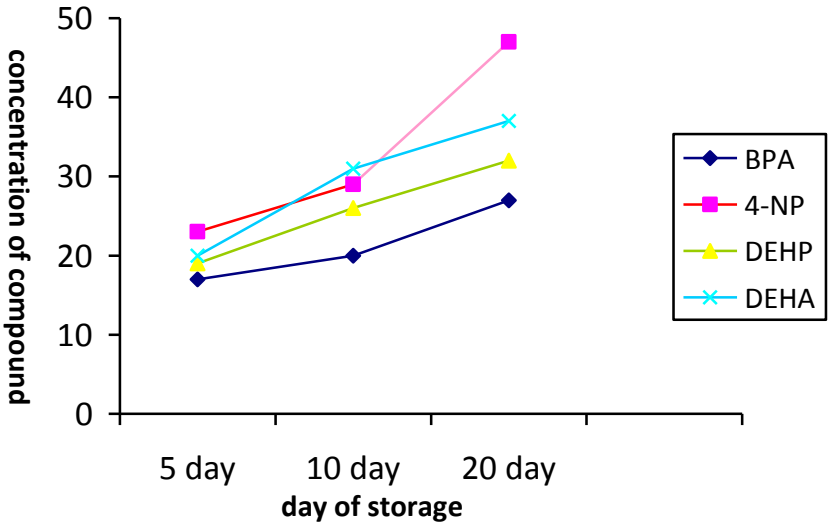


Fig 4.1.2: Concentration of BPA, 4-NP, DEHP and DEHA in plastic bottle contain water at three storage time.

From Figure 4.1.2 we noticed that the highest concentration detected of all four target compound 47ng/L for 4-NP, 37ng/L for DEHA, 22ng/L for DEHP and 27ng/L for BPA. Which were found at the twentieth day of storage.

The concentration of BPA, 4-NP, DEHP and DEHA migrate in water storage in plastic bottle samples were increasing as we noticed from the figure 4.2 with increasing the day of storage.

4.2 Additives in glass and plastic containers.

After observing the glass container with the water and additives that enter the pickle process (lemon, salt, vinegar and garlic), we found the four target compound and the concentration list in table 4.2.1

Table4. 2.1: Concentration of BPA, 4-NP, DEHA and DEHA in the glass container contain the additives.

Sample/ compound	BPA $ng.L^{-1}$	4-NP $ng.L^{-1}$	DEHP $ng.L^{-1}$	DEHA $ng.L^{-1}$
Additives	**15**	**13**	**10**	**11**

The plastic bottle contain tap water plus additives (salt, lemon, vinegar and garlic) storage at the room temperature, this study showed that the four chemicals released from plastic bottle and at the three storage time.

Table 4.2.2: Concentration of (BPA, 4-NP, DEHP and DEHA) in plastic bottle which contain the additives.

Sample no.	Day of storage	BPA ng.L^{-1}	4-NP ng.L^{-1}	DEHP ng.L^{-1}	DEHA ng.L^{-1}
4	5	101	112	107	109
5	10	117	133	123	128
6	20	145	170	152	167

Table 4.2.2 list the concentration of BPA, 4-NP, DEHP and DEHA that ranged from 101to 145ng/L, 112 to 170ng/L, 107 to 152ng/L and 109to 167ng/L respectively.

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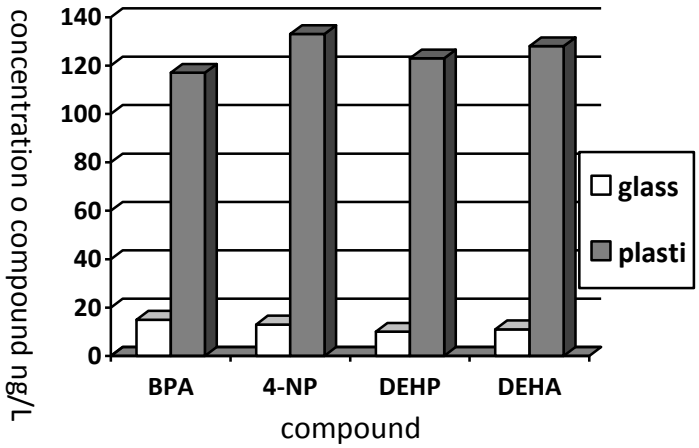

Fig 4.2.1: Concentration of compounds in glass and plastic container contain the additives

From the Figure 4.2.1 we noticed the increase of concentration of each compound when the water and additives keep at plastic bottle compare with the concentration of these compound when the water and additives keep at glass.

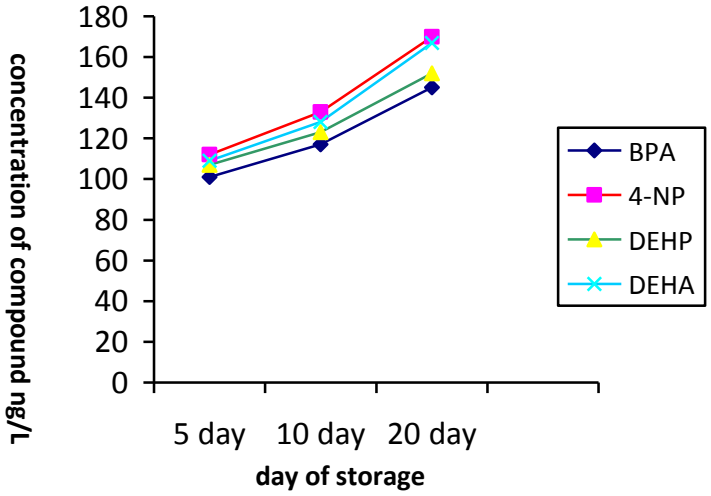

Fig 4.2.2: Concentration of BPA, 4-NP, DEHP and DEHA in plastic bottle contain additives at three storage time.

From figure 4.2.2 we noticed that among the four target compound, 4-NP had the highest concentration (170ng/L) and BPA had the lowest concentration (145ng/L), we also noticed that the concentration of each compound that migrates from plastic bottles wall increase with increasing the day of storage, the four target compound had the highest concentration at the twentieth day of storage.

4.3 Cucumber in glass and plastic containers.

The glass container with the water, additives and cucumber keep as pickle, we found the four target compound and the concentration list in table 4.3.1

Table4. 3.1: Concentration of BPA, 4-NP, DEHA and DEHA in the glass container contain the cucumber.

Sample/ compound	BPA $ng.L^{-1}$	4-NP $ng.L^{-1}$	DEHP $ng.L^{-1}$	DEHA $ng.L^{-1}$
Cucumber	**19**	**16**	**14**	**15**

Plastic bottle filled with tap water, additives and cucumber which never sprayed with pesticides before, table 4.3.2 list the varied concentration of the compound that migrate of plastic bottles wall, the concentration ranged from 113 to 152 ng/L for BPA, 120 to 179 ng/L for 4-NP, 115 to 163 ng/L for DEHP and from 117 to 177ng/L for DEHA.

Table 4.3.2: Concentration of (BPA, 4-NP, DEHP and DEHA) in plastic bottle contain cucumber.

Sample no.	Day of storage	BPA $ng.L^{-1}$	4-NP $ng.L^{-1}$	DEHP $ng.L^{-1}$	DEHA $ng.L^{-1}$
7	5	113	120	115	117
8	10	126	142	132	136
9	20	152	179	163	177

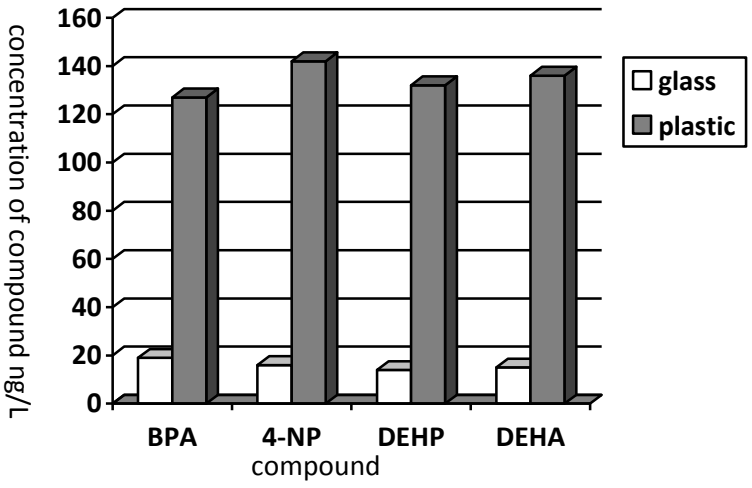

Fig 4.3.1: Concentration of compounds in glass and plastic container contain cucumber.

We found that there is release of the four target compound (BPA, 4-NP, DEHP and DEHA) from these plastic bottles, which is clear from the

figure 4.3.1 we also noticed the increase of concentration of each compound when the water, additives and cucumber are kept in plastic bottle compared with the concentration of these compound when the water, additives and cucumber are kept in glass.

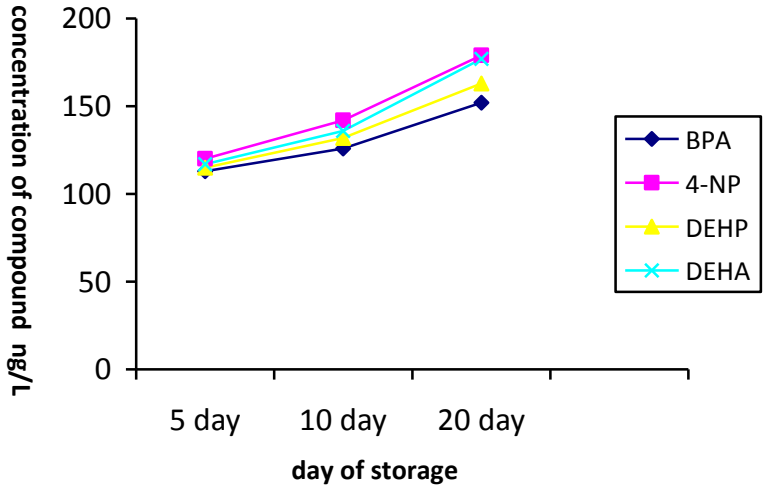

Fig 4.3.2: Concentration of BPA, 4-NP,DEHP and DEHA in plastic bottle contain cucumber at three storage time.

From figure 4.3.2 we noticed that the concentration reading of 4-NP was the highest 179ng/L, then to EDHA was177ng/L, for DEHP 163ng/L and finally the lowest on for BPA 152ng/L. we can also noticed that the concentration of each compound migrate increasing with increasing the day of storage.

4.4 Cucumber with pesticide residue in glass and plastic container.

The glass container contain the water, additives and cucumber with pesticides residue keep as pickle, we found the four target compound and the concentration list in table 4.4.1

Table4. 4.1: Concentration of BPA, 4-NP, DEHA and DEHA in the glass container contain the cucumber with pesticide residue.

Sample/ compound	BPA ng.L^{-1}	4-NP ng.L^{-1}	DEHP ng.L^{-1}	DEHA ng.L^{-1}
Cucumber with pesticide residue	**26**	**22**	**19**	**20**

Plastic bottle filled with tap water, additives and cucumber with pesticide residue, table 4.4.2 list the concentrations of each compound detected in plastic bottles at different three storage time (5, 10 and 20 day), the four target compound were detected in all samples with range from 290to 370ng/L for BPA, 320 to 420ng/L for 4-NP, 311 to 389ng/L for DEHP and from 309 to 377ng/L for DEHA.

Table 4.4.2: Concentration of (BPA, 4-NP, DEHP and DEHA) in plastic bottle contain cucumber with pesticide residue.

Sample no.	Day of storage	BPA ng.L^{-1}	4-NP ng.L^{-1}	DEHP ng.L^{-1}	DEHA ng.L^{-1}
10	5	290	320	311	309
11	10	320	380	350	333
12	20	370	420	389	377

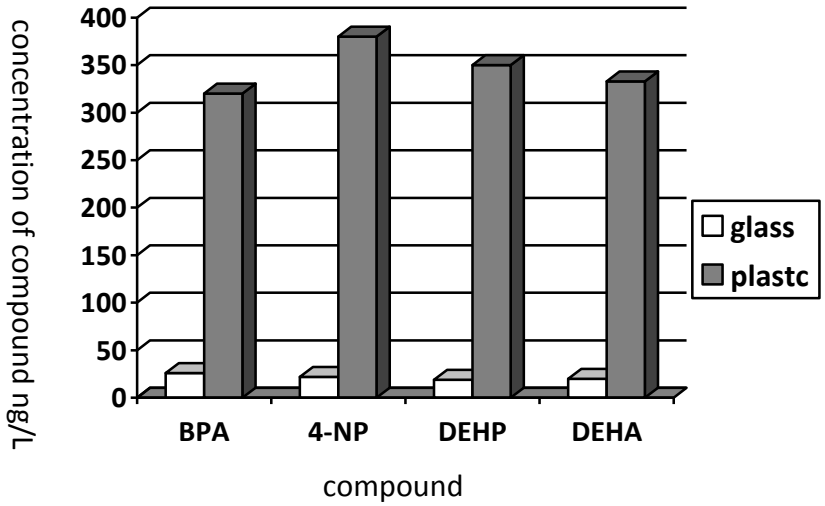

Fig 4.4.1: Concentration of the compounds in plastic bottle contain cucumber with pesticide residue.

From the figure 4.4.1 we noticed the increase of concentration of each compound when the water, additives and cucumber with pesticide residue when kept in plastic bottle compared with the concentration of these compounds when the water, additives and cucumber are kept in glass. This is an evidence of the migration of such chemicals from plastic bottles.

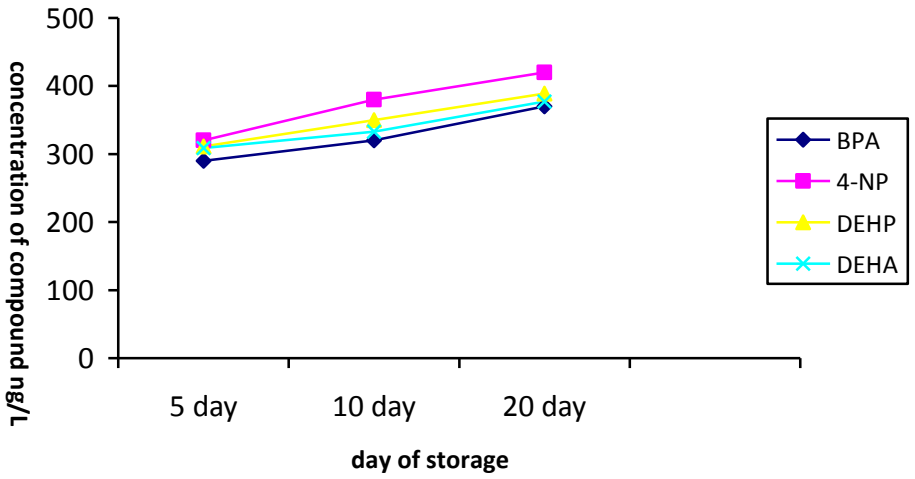

Fig 4.4.2: Concentration of BPA, 4-NP, DEHP and DEHA in plastic bottle contain cucumber with pesticide residue at three storage time.

From figure 4.4.2 we noticed that the amount of migrate was increasing with increase the storage time for each target compound, and we find that the highest concentration was for 4-NP 420 ng/L at the twentieth day, then for DEHP 389 ng/L,DEHA was 377 ng/L and for BPA 370 ng/L.

4.5 The effect of content on migration of compounds.

To know the effect of the different content on the migration of the four target compound we take the concentration of each compound at the twentieth day of storage the cucumber pickle figure 4.6.

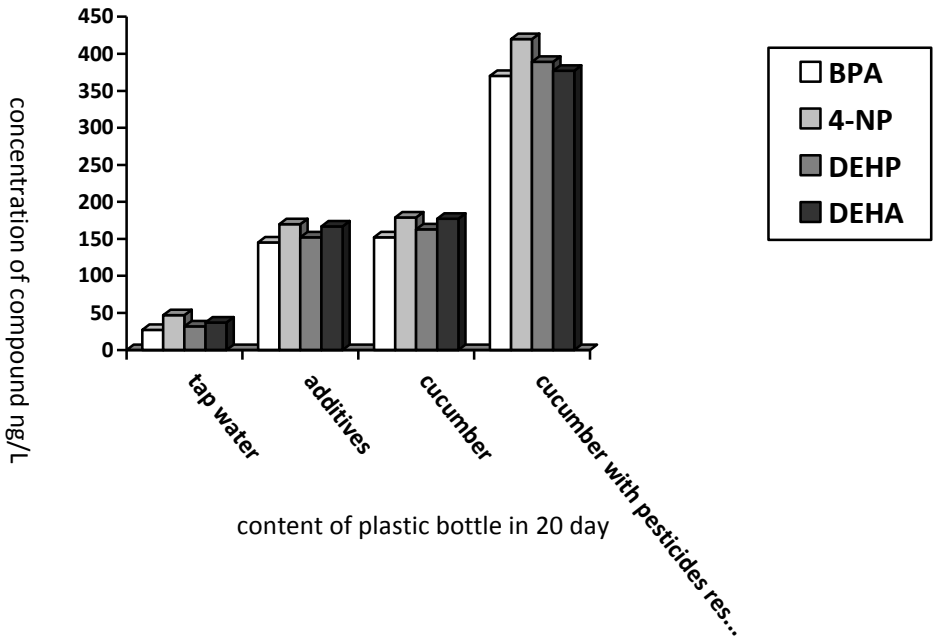

Fig 4.5: Concentration of BPA, 4-NP, DEHP and DEHA in plastic bottles with different content at the twentieth day of storage.

From the figure 4.5 we noticed the variety concentration of the compound (BPA, 4-NP, DEHP and DEHA) with change the content in the plastic bottles.

First, when the plastic bottle contain just tap water we found that there is a migration of the four compounds, when we compare the concentration in this case and with the concentration of the compound for the tap water that not keep in plastic bottle we found an increase of the concentration, this give us evidence that migration happen from the plastic wall to the water.

Secondly, plastic bottles contain tap water plus additives (lemon, salt, vinegar and garlic), in this case we found an increase in the concentration of the four target compound compare with the concentration of the compound in plastic bottle that contain just water. We might that the increase in concentration is reveled to that the additives help the migration to happen more of the compound from plastic wall. As a previous studies the amount of migration dependent of the content of plastic container, the level of BPA detected in 50%ethanol as a food stimulant were higher relative to the levels of BPA detected into water [73].

Third, plastic bottle contain water, additives and cucumber that never sprayed with any pesticides, in this step we noticed that there is a very small increase of concentration of the target compound compare with concentration of the same compound with previous step (plastic with additives), this increase may due to presence of such compound in cucumber itself, as we noticed from previous studies that detected of the

compound as BPA or 4-NP appearance in the air, soil and water [33, 35, 74, 75].the compound spread at the environment.

Finally, plastic bottles contained water, additives and cucumber with pesticides residue, the large concentration of the compound observed at this step, we noticed a high increase of the concentration of the four target compound compare with the last three step. This high increasing may explain by,

The cucumber with pesticides residue forcing or help the migration of such compound from plastic bottle which leads to more migration and increase of the concentration.

Or, the increase due to happen type of interference between the chemicals and the pesticides residue. Which lead to broaden the peak area.

In this work although a very small concentration of the target compound were detected, but we sure that the exposure anticipated from cucumber pickle to the target compound is just one of many source contamination. Other source as food should be includes in order having a proper risk assessment for the compounds.

4.6 The effect of day of storage cucumber pickle on migration of compounds.

Its seem slightly the increase of the concentration of each compound with increase day of storage the cucumber pickle in plastic bottles from previous

figures(4.1.2)(4.2.2)(4.3.2)(4.4.2) This result confirm the previous studies that found the increasing of storage time lead to more migration of the chemicals from plastic bottle [38, 39] .

Conclusion.

We have used GC/MS in scan mode to identify compound which can migrate from plastic bottle. The study demonstrated that BPA, 4-NP, DEHP and DEHA were detected in cucumber pickle sample, that is kept in plastic bottles.

1. The chemicals can be released into the water from plastic bottles at room temperature.
2. The concentration of chemicals migration increases with the increase of the storage period.
3. The concentration of chemicals migration was affected by the content of the plastic bottles.
4. The additives (lemon, salt, vinegar and garlic) help the migration of chemicals.
5. Highest concentrations were obtained when the cucumber with pesticide residue used in pickle process.

The exposure to the four target compound from cucumber pickle poses little risk to human health, but further studies are important to consider mixture effects and combined ingestion routs, including food and water to make more risk assessment of intake of BPA, 4-NP,DEHP and DEHA.

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جامعة النجاح الوطنية

كلية الدراسات العليا

تحليل المواد والمركبات العضويه الراشحه من الاوعيه البلاستيكيه المستخدمه في تخليل الخيار

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قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس، فلسطين.

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الملخص

هذه الدراسة هدفت إلى التحقق من الهجرة الممكنة للمكونات البلاستيكية والمواد المضافة من الأواني البلاستيكية خلال حفظ الخيار بشكل مخلل. المركبات التي تمت دراستها كانت ثنائي الفينول أ، نونيل فينول، مكرر الفثالات ومكرر اديبات .

بالاضافه إلى ذلك تم اختبار الأواني البلاستيكية مع أربعة محتويات مختلفة وبثلاث ايام،GCMS مختلفة من التخزين. في جميع الحالات، العينات تم تحليلها باستخدام جهازHPLC. وجهاز المركبات الأربعة قد ظهرت في كل عينة بتراكيز مختلفة. مبينا أن الهجرة من الأواني البلاستيكية ممكنة مع الحالات التي تم اختبارها.

أظهرت النتائج تأثير زيادة أيام التخزين في زيادة كمية المواد الراشحة وتأثير تغيير محتويات الأواني البلاستيكية في اختلاف التراكيز لكل مركب عند نفس عدد أيام التخزين.

وأدنى مستوى كان لمركب4-NP أعلى تركيز من المركبات المهاجرة كان لمركب BPA .

تم العثور على مركب نونيل فينول في الأواني البلاستيكية التي تحتوي على مياه الصنبور 23–47 نانوغرام/لتر، في الأواني البلاستيكية التي تحتوي على المواد المضافة 112–170 نانوغرام/لتر، في الأواني البلاستيكية التي تحتوي على الخيار 120–179 نانوغرام/لتر وفي الأواني البلاستيكية التي تحتوي الخيار مع بقايا المبيدات 320–420 نانوغرام/لتر. تم العثور على مركب ثنائي الفينول أ في الأواني البلاستيكية التي تحتوي على مياه الصنبور 17–27 نانوغرام/لتر، في الأواني البلاستيكية التي تحتوي على المواد المضافة 101–145

نانوغرام/ لتر، في الأواني البلاستيكية التي تحتوي على الخيار 113–152 نانوغرام/ لتر وفي الأواني البلاستيكية التي تحتوي الخيار مع بقايا المبيدات 290–370 نانوغرام/ لتر.

على الرغم من أن قياس مستويات الهجرة في هذه العينات لا تشكل خطرا على صحة الإنسان بسبب التراكيز المنخفضة جدا، إلا أن وجود أكثر من مصدر لتعرض الجسم لمثل هذه المركبات يشكل المخاطر الصحية.