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THERMAL DECOMPOSITION OF SUNFLOWER OIL DURING DEEP FAT FRYING OF POTATO CHIPS AND EFFECTS OF USING RICE HULLS AND RICE STRAW AS NATURAL ADSORBENTS

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ABSTRACT

Deep-fat fried foods have exquisite taste, good flavour, excellent mouthful, and a characteristic texture. The primary function of oils during frying is to serve as a heat-transfer medium. Chemical and physical changes took place during frying leading to the odorous, flavours, and textures associated with fried foods. A myriad of less desirable products also are formed, which in turn affect heat-transfer efficiency and also the nutritional value of the incorporated oil. The objective of this work was to obtain a better understanding of using rice hulls (RHB) and rice straw (RSB) (10 % of oil weight) with citric acid (CA) (0.5 % w/w), carboxy methyl cellulose (CMC) (10 % w/w) and silica gel (SG) (10 % w/w), as inexpensive by-products as adsorbents for the heated oil used during deep-fat frying of potato chips at 180°C for 36h continuously. The degradation products that formed due to the heat treatments were investigated using the GC/MS. The degradative products included short chain free fatty acids, butyl esters, oxygenated compounds and hydroxylated products suggesting that the main mechanism involved was the thermooxidation mechanism. The concentrations of these products, however, were not quantitatively determined. The RHB and RSB were found to be more effective during the first 24h of heating and their effectiveness were reduced during the following heating hours up to 36h.

INTRODUCTION

Deep fat frying has by far received the most attention relative to changes in oils and fats during product use. Two important stimuli, which should receive considerable efforts, are: (1) safety / nutritive value *the possible formation of toxic or deleterious materials as a consequence of the exposure to heat and oxygen), and (2) changes in the frying medium that influence the sensory quality of the oil or fat and the food fried in it (Tyagi and Vasishtha, 1996).

In frying process the fat serves as a heat transfer medium rather than an important ingredient of the fried food. However, when oil is used repeatedly at elevated temperature in the presence of a wide variety of chemical reactions take place. This results in the accumulation of decomposition products that not only affect the quality of fried foods but also cause a potential hazard to human health and nutrition, particularly when frying or oil is highly abused (Nawar, 1997). Barbary *et al.* (1999) studied the effect of time and temperature of deep-frying on both sunflower oil and potato chips qualities by using corncob powder as a natural adsorbent material containing citric acid to regenerate the oil used for deep-frying as a trial to extend the life of oil and produce high quality fried foods.

The previous investigation dealt with the effect of using some rice by-products on the physicochemical properties of heated sunflower oil during deep fat frying of potato chips at 180°C for 36 h (Barbary *et al.*, 2003). The present study was carried out to investigate the products formed during deep-fat frying using sunflower oil as frying medium using GC/MS, and effects of rice hulls and rice straw as natural adsorbents on the chemical composition of heated oil.

MATERIALS AND METHODS

Materials:

Oils: Refined sunflower oil (a total of 30 L) was obtained from Alexandria Oils and Soap Company, Alexandria, Egypt.

Potatoes: Potatoes (*Solanum tuberosum*) (50 kg) were purchased from a local market, Alexandria, Egypt.

Methods:

Experimental procedures and frying performance were previously described as reported by (Barbary *et al.*, 1999) using the deep-fat fryers (Moulinex, France). Samples of potato chips (200 g) were fried at 180°C for 10 min every an hour to 36 h. RHB or RSB as filtering powders (10% of oil weight) was added to the whole oil at 180°C for 5 min after (8, 16, 24, 32 and 36 h of heating), then filtered with Wattman paper No (1) under pressure. Oil samples (50g) were collected every 8 hours before and after adding the RHB or RSB.

Identification of FAME's using GC/MS

FAME's of unheated, heated and filtered sunflower oil and their products that produced during deep fat frying of potato chips at 180°C for 36h were investigated and identified using gas chromatography/mass spectrometry (GC/MS) (Finnigan mat SSQ 7000, thermos instruments systems Inc., USA). The chromatographic conditions were as follow: H/P 5840 instrument with capillary column. (SGE BP-1, 75 m x 0.25 lid). Helium was used as a carrier gas at flow rate 37.9 cm/sec at 0.45 kg/cm was. Injector temperature was 375°C; column temperature, was 240°C with holding time for two min. The ramp rate was 7.5°C/min to 200°C. The mass spectroscopic conditions were: ion source temperature, 200°C, ion source pressure 0.5 to 0.8 tore, ion source voltage greater than 15 eV; electron multiplier, 2400 to 3000 volts, scanning 80 to 800 AMU in 3.6 seconds.

RESULTS AND DISCUSSION

Fatty acid composition of unheated sunflower oil

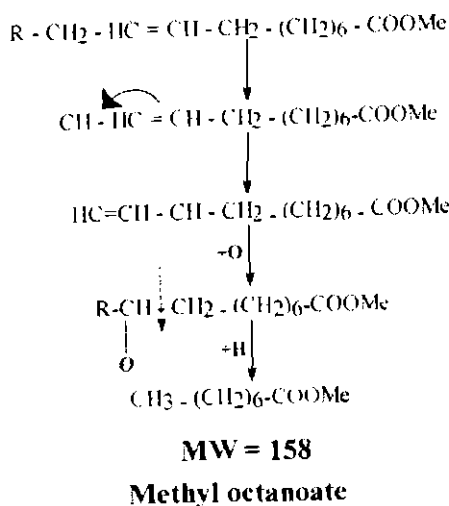
Fatty acid composition of unheated sunflower oil was identified using GC/MS as shown in Table (1). Data revealed that the fatty acid composition of oil is a typical pattern of sunflower oil and consisted of 14:0; 15:0; 16:1; 16:0; 17:0; 18:2; 18:1; 18:0 and 20:0. The GC/MS detected the presence of odd numbered fatty acids which have not been reported before in sunflower oil.

Table (1): GC/MS of FAME's, of unheated sunflower:

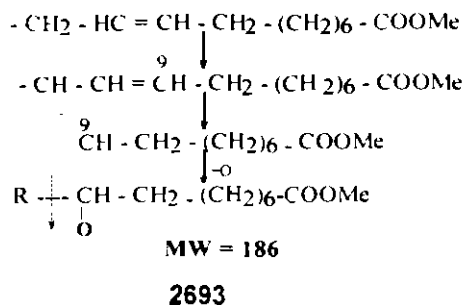
Identified FAME's	Molecular Weight
Methyl Tetradecanoate (C14:0)	242
Methyl Pentadecanoate (C15:0)	256
Methyl Hexadecenoate (C16:1)	268
Methyl Hexadecanoate (C16:0)	270
Methyl Heptadecanoate (C17:0)	284
Methyl Octadecadienoate (C18:2)	294
Methyl Octadecenoate (C18:1)	296
Methyl Octadecanoate (C18:0)	298
Methyl Eicosanoate (C20:0)	326

FAM's of heated sunflower oil

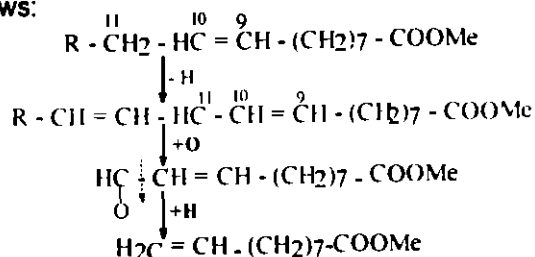
FAME's and other products that formed from the sunflower oil during deep-fat frying of potato chips at 180°C for 36 h were identified using the GC/MS and are shown in Table (2). Methyl octanoic acid methyl ester (C8:0) was not identified in the unheated oil and is considered as a product of thermal decomposition of the oil during heating. The formation of this fatty acid may be due to secondary processes, i.e. shortening of the original hydrocarbon chain followed by scission of the alkyl oxygen bond (or vice versa) or shortening of the alkyl chain in the original free fatty acids (linoleate) as follows:



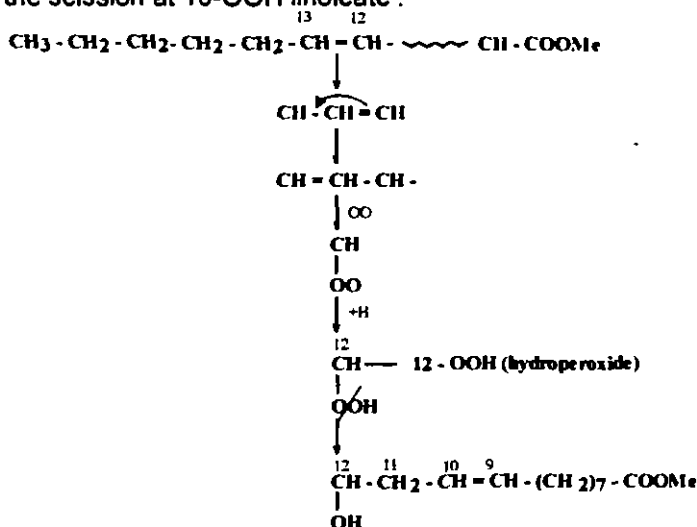
The 9-oxo octanoate is formed as a secondary product of oxidation of oil during heating as follows:



The 10, 11-undecenoate is believed to be formed from thermal degradation of linoleic acid and the possible mechanism for its formation can be explained as follows:

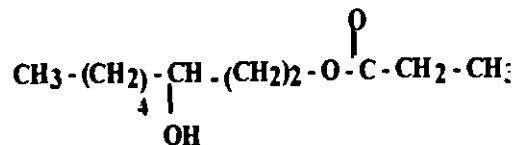


The 12-hydroxy dodecenoate is another product of oxidation of the linoleate by the scission at 10-OOH linoleate :

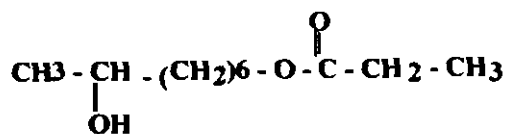


12 - hydroxy dodecenoate

The 3-hydroxy octyl or 7-hydroxy octyl propanoate are:



3 - hydroxy octyl propanoate

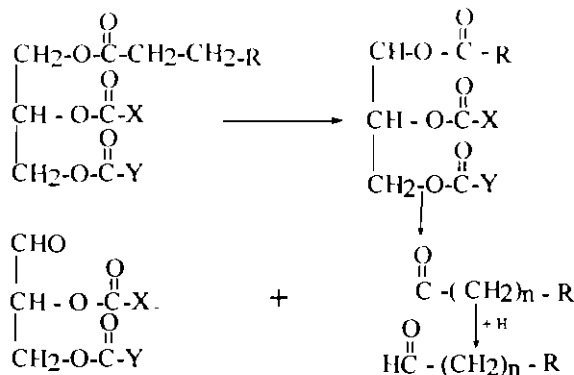


7 - hydroxy octyl propanoate

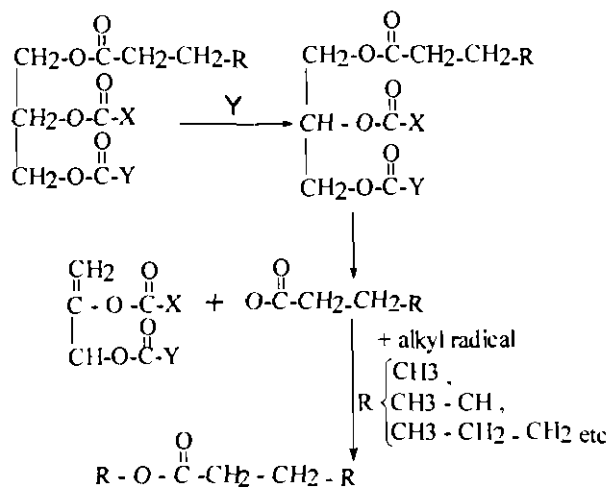
Thought to be formed from linoleic acid and the possible mechanism for the formation of these products can be explained by H-abstraction from C11 and rearrangement on C9 or C12, which then reacts with oxygen to form

ultimately the alkoxy radical, which in turn is converted into a product via 11-atom addition. These products have been formed in autoxidized linoleate (Nawar, 1986).

The 13-oxo-dodecenoate is also a product formed during thermal degradation of the oil as a secondary product. The possible mechanism for the formation of 11-oxo-butyl undecanoate is from the degradation of triglyceride (TG) to form this product.



The 9-hydroxy undecenoate n-butyl propanoate and 9, or 10-keto dodecenoate n-butyl propanoate are also thought to be formed from decomposition of TG as esters as follows:



The formation of methyl 9 or 10 keto acids involves analogous way for the formation of 9,10 epoxy 12-octadecenoate from linoleic acid. This product has not been observed in heated oils before. The most probably mechanism for formation of these products are as follows:

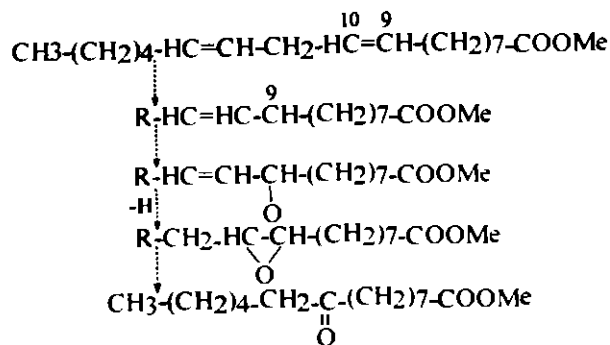


Table (2): GC/MS Identified products (FAMS's) of heated sunflower oil during deep-fat frying of potato chips at 180°C for 36 h:

M.S. peak number	Identified FAME's	Molecular Weight
1	Methyl octanoic acid (C8:0)	158
2	9-Oxo octanoate	186
3	10, 11-Undecenoate	198
4	12-Hydroxy dodecenoate	227
5	3 or 7-Hydroxy octyl propanoate	202
6	13-Oxo dodecenoate	226
7	11-Oxo butyl undecanoate	242
8	Methyl tetra decanoate (C14:0)	242
9	9-Hydroxy undecenoate n-butyl propanoate	242
10	9 or 10-Keto dodecenoate butyl propanoate	254
11	Hexadecenoate (C16:1)	268
12	Hexadecanoate (C16:0)	270
13	9 or 10-Keto pentadecanoate	270
14	12-Oxo hexadecenoate	282
15	Methyl heptadecanoate (C17:0)	284
16	Methyl Octadecadienoate (C18:2)	Isomer 294
17	Methyl Octadecadienoate (C18:2)	Isomer 294
18	Methyl Octadecadienoate (C18:2)	Isomer 294
19	Methyl Octadecadienoate (C18:2)	Isomer 294
20	Methyl Octadecadienoate (C18:2)	Isomer 294
21	Methyl Octadecadienoate (C18:2)	Isomer 294
22	Methyl octadecenoate (C18:1)	296
23	Methyl octadecanoate (C18:0)	298
24	9-Keto 12, 13- octadecenoate or 13-Keto 9, 10- octadecenoate	310 310
25	9-Hydroxy 12, 13- octadecenoate or 13-Hydroxy 9, 10- octadecenoate	312 312
26	9-Hydroxy octadecenoate	314
27	10-Epoxy octadecenoate	314
28	12-Epoxy octadecenoate	312
29	Methyl eicosanoate (C20:0)	326
30	9-Hydroxy 12, 13-epoxyoctadecanoate	
31	13-Hydroxy 9, 10-epoxy octadecanoate	326

The 9- or 10-keto hexadecenoate are formed from linoleic acid, by hydrogenation by formation of hydroperoxides on C12 or C13 to form two isomers of methyl 12-oxo hexadecenoate. This product has been previously reported to be formed in heated soybean oil (Meltzes *et al.*, 1981).

Different isomers of linoleate were detected by GC/MS, however, the position of the double bonds can not be located using the GC/MS under such condition used. These isomers might be originated from the heat treatment. Trans geometrical isomers of C 18:2 were identified as easily in several foods (Ackman, 1974), such as vegetables oils and frying oils (Martin *et al.*, 1998), industrial refining of oil, by thermally induced mechanism (Wolf, 1993). Their presence in food are of concern because they have been shown to be desaturated and chain elongated into higher metabolites (Martin *et al.*, 1998). These latter can modify physiological functions in comparison to their cis homologues, such as platelet aggregation and eicosanoid metabolism (Berdeaux *et al.*, 1996). They also changes in electroretinograms of rat pups whose mothers were fed trans n-3 fatty acid (Chardigny *et al.*, 1996). Keto acids such as 19, keto 9, 10 octadecenoate and 9 keto 12, 13 octadecenoate and epoxy acids were reported on fried foods.

From the above mentioned results and products detected in sunflower oil during fat frying of potato chips at 180°C for 36 h, it could be concluded that these products were of decomposition products of unsaturated fatty acids mainly linoleic acid.

Results also revealed that the hydroperoxides formed during deep fat frying break down in several steps, yielding a wide variety of decomposition products. The decomposition products can themselves undergo farther oxidation and decomposition, thus contributing to a large and varied free radical pool (Frankel, 1982). It should also be mentioned that hydroperoxides begin to decompose as soon as they are formed. In the first stages of oxidation, their rate of formation exceeds their rate of decomposition. The reverse takes place at latter stages.

Heating foods causes various chemical changes, some of which can be important to flavors, appearance, nutritive value, and toxicity. The chemistry of lipid oxidation at high temperatures is complicated by the fact that both thermolytic and oxidative reactions are simultaneously involved. Both saturated and unsaturated fatty acids undergo chemical decomposition when exposed to heat. In the course of deep-fat frying, food contacts oil at higher temperature and are partially exposed to air for various periods of time. Thus, frying, more than any other standard food processor handling method, has the greatest potential for causing chemical changes in fat and sizeable amounts of this fat are carried with the food (5-40% fat by weight is absorbed) (Nawar, 1997).

Effect of RHB on the chemical composition of heated oil

Heated sunflower oil for 36 h was filtered using the RHB and the chemical composition of the filtered oil is shown in Table (3). Results revealed that the low molecular weight products, in the heated oil has been totally disappeared from the filtered oil. Some of the products with high

molecular weights were still found in the filtered oil, however, no quantification has been made. These results suggested that the RHB absorbed the products with low molecular weights along with some products with high molecular weight.

Table (3): GC/MS identification products (FAME's) of filtered heated sunflower oil using RHB:

M.S. peak number	Identified FAME's	Molecular Weight
1	Methyl octanoic acid (C8:0)	148
2	Methyl tetra decanoate (C14:0)	242
3	Hexadecenoate (C16:1)	268
4	Hexadecenoate (C16:0)	270
5	3 or 7-Hydroxy octyl propanoate	282
6	13-Oxo dodecenoate	284
7	Methyl octadecadienoate (C18:2) Isomer	294
8	Methyl octadecadienoate (C18:2) Isomer	294
9	Methyl octadecadienoate (C18:2) Isomer	294
10	Methyl octadecadienoate (C18:2) Isomer	294
11	Methyl octadecadienoate (C18:2) Isomer	294
12	Methyl octadecadienoate (C18:2) Isomer	294
13	Methyl octadecadienoate (C18:2) Isomer	294
14	Methyl octadecadienoate (C18:2) Isomer	294
15	Methyl octadecadienoate (C18:2) Isomer	294
16	Methyl octadecenoate (C18:1)	296
17	Methyl octadecanoate (C18:0)	298
18	13-Epoxy 9, 10-octadecenoate	308
19	9-Epoxy 12, 13-octadecenoate	308
20	13-Hydroxy 9, 10-octadecenoate	312
21	9-Hydroxy 12, 13-octadecenoate	312
22	8, 13-Diketo- octadecenoate	326
23	Methyl eicosanoate (C20:0)	326
24	9-Hydroxy 12, 13-epoxy octadecenoate	326
	13-Hydroxy 12, 13-epoxy octadecenoate	

Effect of RSB on the chemical composition of heated oil

Heated sunflower oil for 36 h was also filtered using the RSB and the chemical composition of the filtered oil is shown in Table (4). Results revealed that, again, the products with low molecular weight along with some of high molecular weights were absorbed on the RSB as they did not show up in the identified products in the filtered oil using GC/MS. Using these two blends (RHB) and (RSB) improved the oil quality during the first stages of frying up to 24 h (Barbary *et al.*, 2003), afterwards their effects became gradually less up to 36 h of frying. Investigation also indicated that these two blends were capable of adsorbing considerable degradation products as shown by GC/MS analysis. The adsorption mechanism and the sorts of adsorbed polar material is still unknown, as a few number of studies have dealt with this subject. Proctor *et al.* (1995) suggested that alkaline metal ions, especially K⁺, present in the ash will react with the fatty acid products forming oxylate ions. This mechanism was suggested to contribute the adsorptive capacity of the RHB. They also showed that the adsorption mode of oleic acid onto RHB partially occurred by surface hydrogen bonding of the

carboxylic acid.

Table (4): GC/MS Identification products (FAMS's) of filtered heated sunflower oil using RSB.

M.S. peak number	Identified FAME's	Molecular Weight
1	11-Oxo-butyl undecanoate	242
2	Metyl Tetra decanoate (C14:0)	242
3	Hexadecenoate (C16:0)	268
4	10 or 12-Oxo-hexadecenoate	270
5	3 or 7-Hydroxy octyl Propanoate	282
6	13-Oxo dodecenoate	284
7	Methyl octadecadienoate (C18:2) isomer	294
8	Methyl octadecadienoate (C18:2) isomer	294
9	Methyl octadecadienoate (C18:2) isomer	294
10	Methyl octadecadienoate (C18:2) isomer	294
11	Methyl octadecenoate (C18:1)	296
12	Methyl octadecanoate (C18:0)	298
13	9-Epoxy 12, 13-octadecenoate	308
14	12-Epoxy 9, 10-octadecenoate	
	9-Oxo 12, 13-octadecenoate	310
15	9, 13- Diketo-octadecenoate	324
16	Methyl eicosanoate (C20:0)	326
17	9-Hydroxy 12, 13-epoxy octadecenoate	326
	13-Hydroxy 9, 10-epoxy octadecenoate	

The organic chemical analysis of the RHB and RSB revealed that silicon was the only element detected 20.55% in RHB and 13% in RSB. Jones (1954) reported that 94.5% silicon oxide and 1.1% potassium oxide in raw ash, smaller amounts of the oxides of Ca, Mg, Na, and P are also present.

Adsorption of RHB and RSB

Adsorbed oils on the RHB and RSB are shown in Figure (1). Data revealed that the two materials showed different mode of adsorption. In case of the RHB, it seems that, as a corn cob appearance, it adsorbed more non polar triglycerides rather than pigments or components with higher molecular weights. In contrast, the RSB mode a net form appearance and adsorbed more pigments or components with high molecular weight. These results confirmed the previous results (Barbary *et al.*, 2003) and results obtained from GC/MS analysis. These results are supported by those of Barbary *et al.* (2003).

The RHB removed the fragment components with low molecular weights from the heated oil, whereas the RSB removed both the low and high molecular weight products. However, the quality of the heated oil improved better with RSB than that treated with the RHB. This is because the former removed the most effective components accelerating the thermal oxidation of the oil. The latter removed the terminal products formed during the thermal oxidation process.

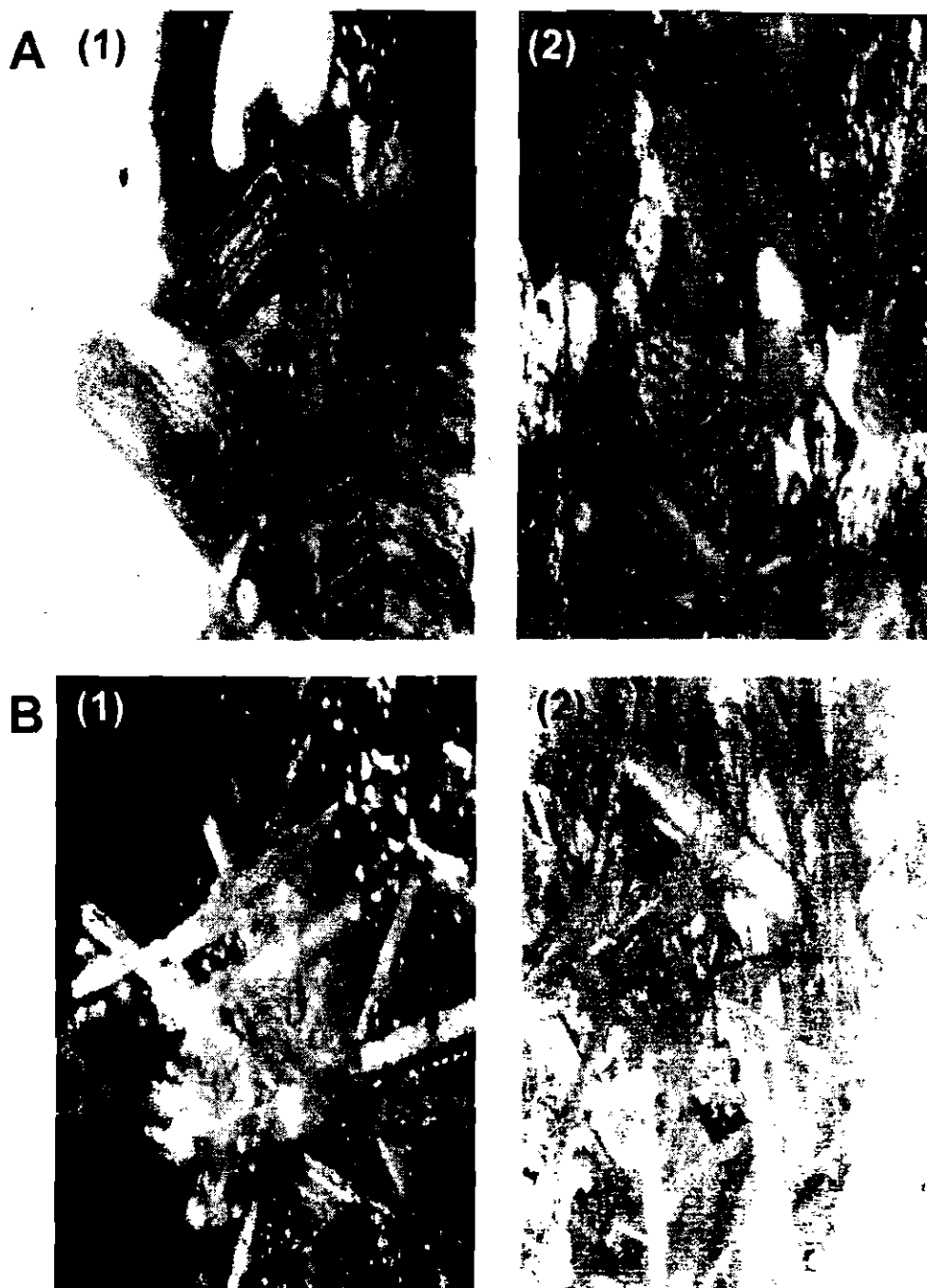


Figure (1): SEM micrographs of (A) RHB, (B) RSB as adsorbent material, magnification (1) x100 and (2) x 200.

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نواتج التكسير الحرارى لزيت عباد الشمس اثناء تحمير البطاطس وتأثير إستخدام قش و قشر الأرز كمواد إدمصاص طبيعية
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تمتاز الأغذية المحمرة بالطعم المميز والرائحة الجيدة والمذاق الممتاز وكذا القوام الخاص. ويعتبر الزيت وسط ناقل للحرارة أثناء عملية التحمير. ويحدث للزيت بعض التغيرات الطبيعية والكيميائية أثناء التحمير تؤدي إلى تكوين الرائحة والطعم والقوام المرتبطة بهذه الأغذية المحمرة. وقد تتكون أثناء عملية التحمير بعض المركبات غير المرغوبة والتي تؤثر على كفاءة عملية نقل الحرارة وتؤثر بالتالى على القيمة التغذوية للزيت. ولذا فإن هذه الدراسة تهدف إلى دراسة المركبات التي تتكون أثناء عملية تحمير البطاطس على درجة حرارة ١٨٠ م لمدة لمدة ٣٦ ساعة باستخدام جهاز GC/MS وأيضا باستخدام قش وقشر الأرز كمواد إدمصاص طبيعية لتفقية الزيت.

ولقد أوضحت النتائج أن المركبات المتكونة هي نتيجة التكسير الحرارى للزيت وشملت الأحماض الدهنية قصيرة السلسلة ، المركبات الأوكسجينية والهيدروكسيلية وكذا الإسترات. وأوضحت الدراسة أن ميكانيكية تكوينها يتم من خلال الأكسدة الحرارية للزيت. وقد أوضحت النتائج أيضا أن إستخدام كل من قش الأرز وقشر الأرز كان فعالا فى المراحل الأولى من عملية التحمير ونقل فاعليتها فى المراحل الأخيرة حيث أن إستخدام الأول قام بإدمصاص المركبات ذات الأوزان الجزيئية الصغيرة والثانى قام بإدمصاص المركبات ذات الأوزان الصغيرة بالإضافة إلى المركبات ذات الأوزان الجزيئية الكبيرة.