THE USE OF CHITOSAN AEROGELS AS AN ADSORBENT FOR THE REGENERETION OF FRYING OIL

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THE USE OF CHITOSAN AEROGELS AS AN ADSORBENT FOR THE
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ABSTRACT

THE USE OF CHITOSAN AEROGELS AS AN ADSORBENT FOR THE REGENERETION OF FRYING OIL

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One of the most commonly used food preparation methods is frying. The improvement of the quality of used frying oil (UFO) is important because the reuse of regenerated oil could provide significant savings to the food industry. This study aimed to enhance the quality of used sunflower oil by using chitosan aerogels (CA), which can be considered as novel adsorbents with an increased surface area.

Aerogels are novel nanostructured materials with high porosity and large surface area. In this study, CA were produced by drying the 2% (w/v) chitosan gels using supercritical CO_2 (SC-CO_2) drying.

In the study, 32 consecutive deep-fat frying were performed using potato slices in sunflower oil at 180 ± 5 °C. The effect of the adsorbent concentration (0.5, 1, and 2% (w/w)) and different adsorption temperatures (90, 135, and 180 °C) were studied by examining the UFO before and after the adsorption treatments. The physicochemical properties of the oil were analyzed by determining free fatty acid (FFA) content, total polar compounds (TPC), smoke point, *p*-anisidine value (*p*-AnV), and color (CIE L, a*, b*). Moreover, the structural changes of aerogels after the adsorption process were investigated by Fourier Transform Infrared spectroscopy

(FTIR) and Nuclear Magnetic Resonance (NMR). FFA results showed that CA could reduce the % FFA values considerably due to the ionic interaction between CA and FFA. The results of TPC showed that CA could not adsorb the polar molecules formed during frying effectively. Yet, the smoke point increased significantly ($p<0.05$) after CA treatment, which means it effectively adsorbed nonpolar and low molecular weight molecules causing smoke. The *p*-Anisidine value was compensated with CA, indicating that secondary oxidation products, especially 2,4-dienals and 2-alkenals, were adsorbed. Additionally, color measurements (*L**, *a**, *b**) showed that CA caused a darker and reddish color after the adsorption treatments. Although CA improved the overall quality of UFO, it was not effective in reducing the TPC value and *L** values. The FTIR results of the CA showed that new peaks that belonged to FFA appeared after the adsorption process. Moreover, compared with MgSi, the same concentrations of CA were more effective in improving all the quality parameters of oil except for the *L** values.

Keywords: Chitosan Aerogel, Frying Oil, Regeneration, FFA

ÖZ

AEROJELLERİN KIZARTMA YAĞININ REJENERASYONUNDA ADSORBAN OLARAK KULLANILMASI

Delice, Feyza Nur
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Tez Yöneticisi: Prof. Dr. Mecit Halil Öztop

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En sık kullanılan gıda hazırlama yöntemlerinden biri kızartmadır. Kullanılmış kızartma yağının kalitesinin iyileştirilmesi önemlidir, çünkü rejenere yağın yeniden kullanılması gıda endüstrisine önemli tasarruflar sağlayabilir. Bu çalışma, yüzey alanı arttırılan yeni bir adsorban olan kitozan aerojeli kullanarak, kullanılmış ayçiçek yağının kalitesini arttırmayı amaçlamıştır. Aerojeller, yüksek gözenekliliğe ve geniş yüzey alanına sahip yeni nanoyapılı malzemelerdir. Bu çalışmada, süperkritik CO2 (SC-CO2) kurutma kullanılarak %2 (w/v) kitosan jellerinin kurutulmasıyla CA üretilmiştir. Çalışmada patates örnekleri ile, 180 ± 5 °C'de ayçiçek yağında art arda 32 kez derin yağda kızartma işlemi yapılmıştır. Adsorban konsantrasyonunun (%0,5, 1 ve %2 (w/w)) ve farklı adsorpsiyon sıcaklıklarının (90, 135 ve 180 °C) etkisi, adsorpsiyon işlemlerinden önce ve sonra kullanılmış kızartma yağı incelenerek araştırılmıştır. Yağın fizikokimyasal özellikleri, serbest yağ asidi (FFA) içeriği, toplam polar bileşikler (TPC), dumanlanma noktası, *p*-anisidin değeri ve rengi (CIE L, a*, b*) belirlenerek analiz edilmiştir. Ayrıca, adsorpsiyon işleminden sonra aerojellerin yapısal değişiklikleri Fourier Transform Infrared spektroskopisi (FTIR) ile incelenmiştir. Kitozan aerojelleri, kullanılmış kızartma yağının genel kalitesini iyileştirmesine rağmen, TPC değerini ve L değerini düşürmede etkili olmamıştır.

FFA sonuçları, kitozan aerojeli ve FFA arasındaki iyonik etkileşim nedeniyle aerojel kullanımının % FFA değerlerini önemli ölçüde azaltabileceğini göstermiştir. TPC sonuçları, kitozan aerojellerinin apolar yapısından dolayı kızartma sırasında oluşan polar molekülleri adsorbe edemediğini göstermiştir. Ayrıca, kitozan aerojellerinin kullanımından sonra dumanlanma noktası önemli ölçüde artmış ($p<0.05$), bu da dumana neden olan apolar ve düşük molekül ağırlıklı bileşikleri etkili bir şekilde adsorbe ettiğini göstermiştir. *p*-Anisidin değeri kitozan aerojel kullanımı ile düşürülmüş, bu da ikincil oksidasyon ürünlerinin, özellikle 2,4-dienaller ve 2-alkenallerin adsorbe edildiğini göstermiştir. Ayrıca renk ölçümleri, adsorpsiyon işlemlerinden sonra kitozan aerojel kullanımının daha koyu ve kırmızımsı bir renge neden olduğunu göstermiştir. Kitozan aerojellerinin FTIR sonuçları, adsorpsiyon işleminden sonra FFA'ya ait yeni piklerin ortaya çıktığını göstermiştir. Ayrıca, eşit miktarda kullanılan kitozan aerojeli ve MgSi karşılaştırıldığında, kitozan aerojellerinin L değeri hariç yağın diğer kalite parametrelerini iyileştirmede daha etkili olduğu görülmüştür.

Anahtar Kelimeler: Kitozan Aerojeli, Kızartma Yağı, Rejenerasyon, FFA

To my beloved family and my love…

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ABBREVIATIONS

UFO: Used frying oil

FO: Fresh oil

FFA: Free fatty acids

CA: Chitosan aerogels

p-AnV: *p*-Anisidine value

AdsT: Adsorption temperature

TPC: Total polar compounds

CHAPTER 1

INTRODUCTION

1.1 Deep-fat Frying

Deep-fat frying is a widely used method for producing and preparing foods both industrially and at home. Fried foods produced with deep-fat frying have a desirable color, flavor, and texture thanks to a complex thermal chemical process (Das et al., 2013). Deep-fat frying requires immersing a food item in a large amount of oil at a temperature between 130 and 190 °C, which is routinely replenished and reused multiple times before being discarded (Das et al., 2013; Wroniak et al., 2021).

In Türkiye, one of the most common oils used in the frying of foods is sunflower oil. Sunflower oil contains monounsaturated and polyunsaturated acids. The fatty composition of sunflower oil is shown in the table below. Considering the fatty acid composition, sunflower oil with a high monounsaturated fatty acid content can be more resistant to oxidation during deep fat frying (Ramroudi et al., 2022). Furthermore, research conducted by Ramroudi et al. (2022) showed that sunflower oil had a high smoke point of 266 °C (Ramroudi et al., 2022). Therefore, sunflower oil is a good alternative for frying with good fatty acid composition and high smoke point (Gharachorloo et al., 2009).

Table 1. 1 Fatty acid composition of sunflower oil (Erickson, 2007)

	$C_{16:0}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$
	Palmitic Acid	**Stearic Acid**	**Oleic Acid**	**Linoleic Acid**
g/100g Oil	5.9	4.5	19.5	65.7

1.2 Chemical and Physical Changes During Frying

During frying, oil is exposed to high temperatures in the presence of moisture and atmospheric oxygen. Under these circumstances, chemical processes such as hydrolysis, polymerization, oxidation, and degradation take place (Figure 1.1), which negatively affect the quality of the oil. Additionally, these modifications result in the production of oxidized and polymerized chemicals, which are undesirable in terms of health aspects (Gharachorloo et al., 2009).

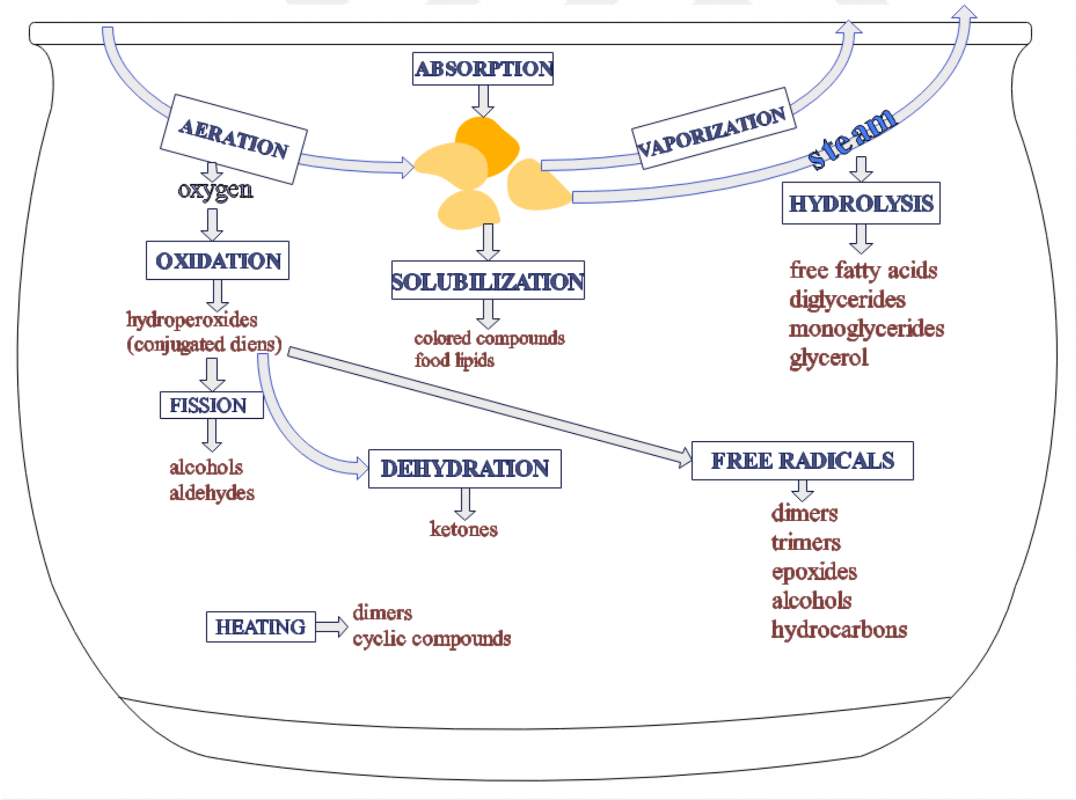

Figure 1. 1 Reactions taking place during frying (Adapted from Orthoefer & List, 2007a)

Most of the volatile compounds produced as a consequence of these reactions evaporate, and the rest are either absorbed by the food or exposed to further chemical reactions. The physical and chemical characteristics of oil and fried foods are impacted by the non-volatile components in the oil. Frying increases the viscosity concentration of polymeric compounds, and polar materials, makes the oil darker whereas it decreases the unsaturation (Figure 1.2) (Choe & Min, 2007; Gertz, 2014; Orthoefer & List, 2007b). It is important to control the quality of frying oil after using it several times. One of the important quality parameters is the total polar materials (TPM), which is the main “chemical index” used to examine the degree of cumulative degradation of oil (Miyagi Atsushi et al., 2003). The maximum permitted value of TPM is set in many European countries at 25% (Kmiecik et al., 2018). The smoke point is the other parameter that indicates the temperature when the first bluish, continuous smoke is seen. It must be below the value of 170 °C defined as a limit by the *Statement of the Working Group of Food Chemistry Experts* (Matthäus, 2006). Additionally, the *p*-anisidine value (*p*-AnV) is important to measure the secondary oxidation products formed during the frying process (Miyagi Atsushi et al., 2003). Another quality parameter is the free fatty acids (FFA), which are produced due to the hydrolysis reactions taking place during the frying process. According to the literature, the accepted maximum value of FFA is 0.3% (de ALMEIDA et al., 2019).

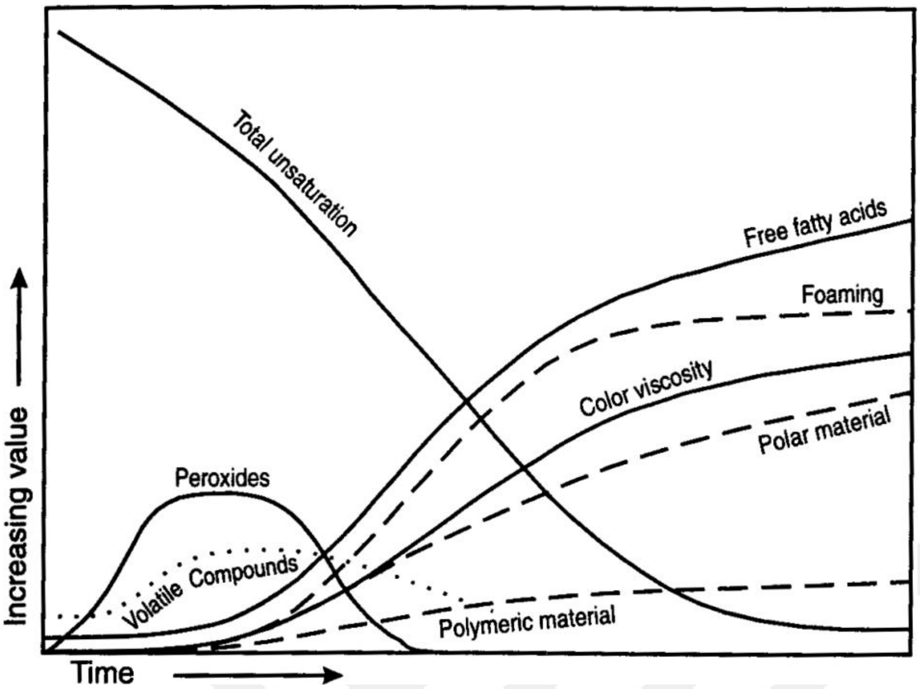

Figure 1. 2 The physical and chemical changes of oil during deep-fat frying (Choe & Min, 2007)

1.3 Major Reactions During Frying

Although frying is a complicated process and there are a variety of reactions taking place simultaneously, the main reactions are known as hydrolysis, oxidation, and polymerization.

1.3.1 Hydrolysis

During frying, water evaporating from the food results in hydrolytic reactions which break the bonds between free acids and glycerol (Figure 1.3). High temperature speeds up hydrolysis, which leads to the production of glycerol, diglycerides, monoglycerides, and FFA (Dana & Saguy, 2006).

Compared to the original triglycerides, these molecules have a lower molecular weight and higher polarity (M. C. Dobarganes & Márquez-Ruiz, 2007).

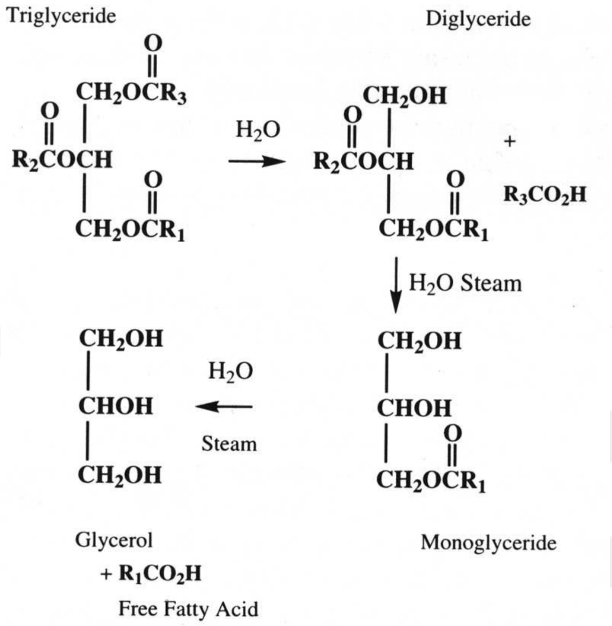

Figure 1. 3 Hydrolysis of the triglycerides

1.3.2 Oxidation

During frying at high temperatures (180 °C), oil reacts with oxygen, and thermal oxidation takes place. The mechanism of thermal oxidation is mostly the same as that of autoxidation (Choe & Min, 2007). Oxidation includes initiation, propagation, and termination processes. Autoxidation takes place when lipid-containing fatty acids, especially polyunsaturated fatty acids like linoleic and linolenic acids, are exposed to oxygen (Perkins, 2007). In the initiation stage, the hydrogen atom in the fatty acids is abstracted, and lipid alkyl radicals are formed. The alkyl radicals may also react with alkoxy radicals, alkyl radicals, and peroxy radicals to produce dimers and polymers (Choe & Min, 2007).

$$\text{Initiation: } RH \rightarrow R\bullet + H\bullet$$

In the propagation step, alkyl radical reacts with $^1O_2$ and forms lipid peroxy radical. Then, the hydrogen is abstracted from other unsaturated lipid molecules to produce hydroperoxide and another alkyl radical.

$$\text{Propagation: } R\bullet + {}^1O_2 \rightarrow ROO\bullet$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet$$

The hydroperoxides are quite unstable at the frying temperature, therefore they are decomposed to alkoxy radicals and hydroxy radicals (Choe & Min, 2007; Perkins, 2007).

The alkoxy radical is degraded or reacts with other alkoxy radicals to form nonradical molecules. At the end of the oxidation, the production of nonradical volatile and nonvolatile components having different stability, polarity, and molecular weight is known as the termination stage.

$$\text{Termination: } R\bullet + R\bullet \rightarrow \text{Nonradical Products}$$

During frying, most of the volatile molecules are lost because of the decomposition, evaporation, and reaction of volatile components with other food compounds (Choe & Min, 2007) The volatile components affect the flavor quality of the fried foods and frying oil.

1.3.3 Polymerization

High temperature and the presence of air promote the growth of polymerization processes, which are responsible for the most complex group of new substances observed in the UFO. The main degradation products of frying oil are non-volatile polar molecules and triglyceride dimers and polymers. Compared to these major products, the amounts of cyclic components are relatively small (C. Dobarganes et al., 2000).

During polymerization, a tiny number of dimers form via carbon-oxygen bonds, while most of the dimeric and polymeric triglycerides are intermolecularly synthesized from carbon-to-carbon links. It implies that those created by oxidation at low temperatures are linked by oxygen bridges, whereas those formed at high temperatures are connected by carbon-carbon bonds. An intermolecular addition of one radical to a triglyceride molecule, combination of the two free radicals, or the Diels-Alder reaction (a conjugated diene reacts with an alkene (dienophile) to produce unsaturated six-membered rings.) is considered as the primary pathways of dimers and polymers during autoxidation. (Figure 1.4) (Kochhar & Gertz, 2004).

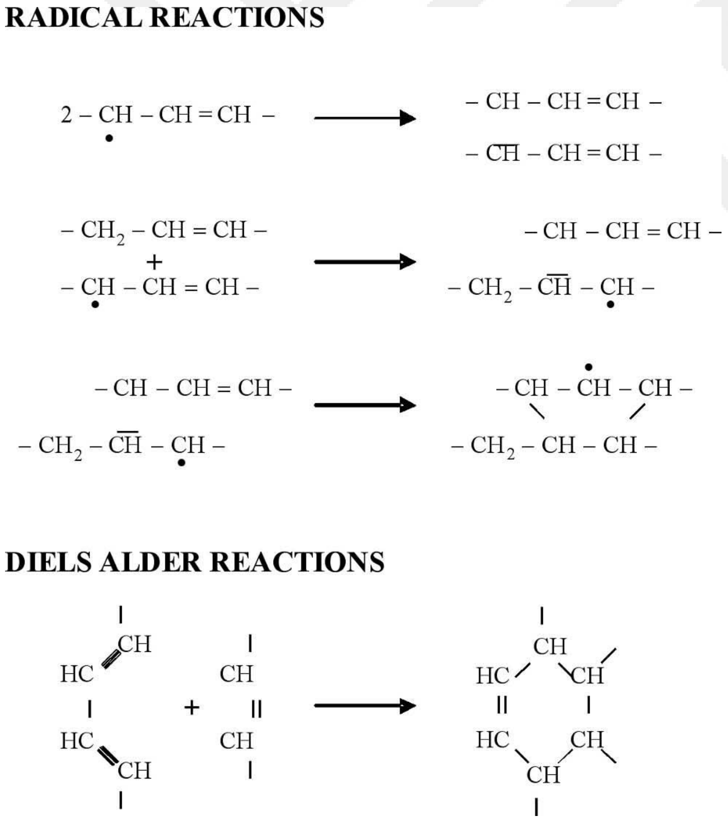

Figure 1. 4 Pathways of formation of the dimers and polymers (M. C. Dobarganes & Márquez-Ruiz, 2007)

1.4 Regeneration Methods for Used Frying Oil

Waste disposal problems are widely prevalent today, which raises the risk of damaging the ecology. According to the United States Department of Agriculture, around 60 million tons of edible vegetable oil are produced annually throughout the world (Bhattacharya et al., 2008). The majority of this oil is used to fry meals. The UFO is replenished and reused several times before being discarded. It is crucial to determine the quality of oil to prevent using deteriorated oil, which may result in adverse health effects if consumed as part of the fried product (Das et al., 2013). In order to regenerate UFO and prolong its life cycle, the fast-food industry has developed several techniques. The main methods are the addition of natural additives to frying oil, the usage of oil dilution techniques, frying under a vacuum or natural gas atmosphere, membrane processing, and the utilization of active and passive filtration (Bhattacharya et al., 2008; Buket Aydeniz & Emin Yilmaz, 2016; Bulut & Yılmaz, 2010; Choe & Min, 2007; Miyagi Atsushi et al., 2003; Udomkun et al., 2018). Active filtration, one of the most prevalent treatment methods, relies on combining an adsorbent material with the UFO to selectively adsorb oxidized molecules, FFA, polar compounds, dimers and polymers, and other particles to remove from the oil by filtration to regenerate the oil and enhance its shelf life (Yılmaz & Güner, 2018). The commonly used adsorbent materials are magnesium silicate, diatomaceous earth, zeolites, and alumina. On the other hand, passive filters remove the solid particles, microemulsified water, and compounds including copper, iron, or free radical oxygen, which enhance the oxidative reaction (Bhattacharya et al., 2008).

Magnesol XL is a synthetic adsorbent that is widely used in industry to enhance oil quality (Farag & Basuny, 2009). This material is a white, amorphous, hydrous, odorless synthetic magnesium silicate powder (Farag & Basuny, 2009; Lin Song et al., 1999). The ionic pattern of Magnesol XL was examined by Farag & El-Anany, (2006) and it was reported that it contained basic ions of Si (34.75%) and Mg (27.33%).

In recent studies, researchers develop alternative materials for regeneration of UFO. In a study conducted by Farag & Basuny, (2009), the effectiveness of the organic (normal and modified cellulose powder) and inorganic (normal and modified silica gel) materials in improving the quality of used sunflower oil was compared with the Magnesol XL. In the study, it was reported that organic and inorganic adsorbents improved the quality of used sunflower oil to a great extent by reducing the levels of acid, polymer, oxidized fatty acids. Thiobarbituric acid (TBA) values were comparable to that of used sunflower oil treated with Magnesol XL. Additionally, normal silica gel with small particle size provided a high adsorbing capacity and it was comparable to that caused by Magnesol XL.

1.5 Chitosan

Chitosan is a naturally occurring polysaccharide that is generated by the deacetylation of chitin (Figure 1.5). Chitin is the second-most prevalent biomass after cellulose and can be extracted from different natural sources like shellfish, crabs, fungi, lobsters, and algae (Behr & Ganesan, 2022). Chitosan is a copolymer composed of D-glucosamine and N-acetylglucosamine with 1,4-glycosidic linkages (Wei et al., 2020). Chitosan has demonstrated considerable potential for a variety of purposes in different areas such as the medical field and the food industry, due to its high biocompatibility, biodegradability, non-toxicity, and functional properties (Aider, 2010; Saenz-Mendoza et al., 2020; Yuan et al., 2016). Deacetylation means removing acetyl groups from the molecular chain (Figure 1.5). The basic definition of DDA of chitosan is the ratio of D-glucosamine to the total amount of N-acetylglucosamine and D-glucosamine (Weißpflog et al., 2021). In general, deacetylation is achieved by heating the chitin in an alkaline medium (Moura et al., 2011). Deacetylation provides the highly reactive free amino group, which is important for the functionality of chitosan.

Additionally, chitosan can produce hydrogel either chemically or physically. Chemical hydrogels are produced by the irreversible covalent bonding including crosslinked chitosan hydrogels. On the other hand, various reversible links, such as those found in entangled gels, polyelectrolyte complexes, and ionically crosslinked hydrogels, are used to form physical hydrogels. In order to create a chitosan hydrogel, chitosan should be dissolved in an acidic aqueous medium and precipitated in an alkaline solution (Quignard et al., 2008).

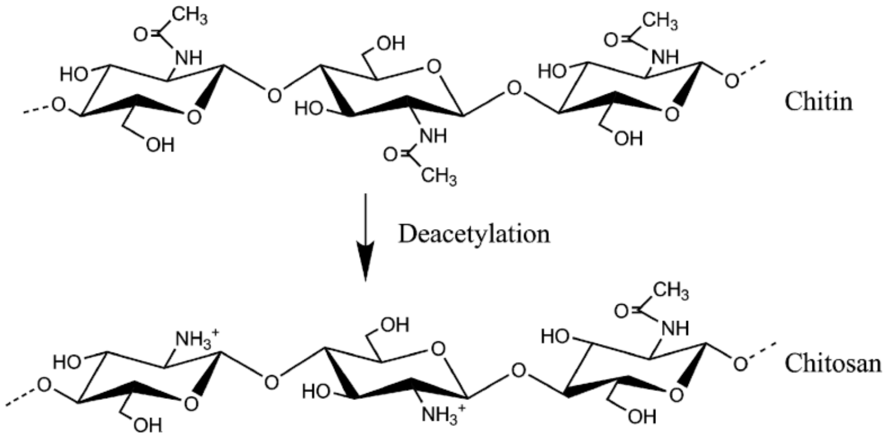

Figure 1. 5 Structure of chitin and chitosan (Nilsen-Nygaard et al., 2015)

1.6 Aerogels

Aerogels are novel nanostructured materials with high porosity and large surface area that have the potential to provide excellent efficacy in various types of applications, including drug delivery, thermal insulation, and adsorption matrixes (Mißfeldt et al., 2020). The production of aerogels is achieved by the drying of organic (such as polysaccharides or proteins), inorganic (such as silica, oxide, graphene, or clay), or hybrid gels using supercritical CO_2 (SC-CO_2) drying which protects gel networks by preventing pore collapse (López-Iglesias et al., 2019; Y. Wang et al., 2019).

Polysaccharides are relatively new as an aerogel-forming substance and have several advantageous features in both food and non-food industries since they are nontoxic, renewable, sustainable, and, eco-friendly (Mikkonen et al., 2013; Y. Wang et al., 2019). Chitosan has great potential to be an environmentally benign material for the production of aerogels to be utilized in absorbent applications for the medical, catalysis, or as an adsorbent for environmental applications (Takeshita & Yoda, 2015). While chitosan is converted from chitin through the deacetylation process, the amino groups of chitosan become protonated, making the matrix positively charged and it can be able to interact with a range of negatively charged molecules like lipids, proteins, and nucleic acids (Q. Z. Wang et al., 2006; Wei et al., 2020).

1.7 Objective of the Study

Deep-fat frying is one of the most commonly used ways of preparation of food all around the world. Due to the rise in the price of oil, health concerns about reused frying oil, and environmental worries regarding pollution, the current study aimed to increase the quality of used sunflower oil by regenerating the oil with chitosan aerogels (CA) as a novel material. In the study conducted by Widiastuti et al. (2022), it is reported the positively charged chitosan molecules could make a great connection with the negatively charged FFA, therefore the FFA reduction could be achieved. In the literature, however, there is no study done to regenerate UFO with aerogels. In the presented study, it is hypothesized that the compounds formed during frying which reduce the quality of the frying oil can be adsorbed more efficiently with the CA which have increased surface area and potential to improve the quality of frying oil by using environmentally friendly materials rather than synthetic ones.

1.8 Design of Experiments

Table 1. 2 Design of Experiments

Factors	**Levels**	**Responses**
Aerogel Concentration During Adsorption (%)	0.5, 1, 2	○ Free Fatty Acids ○ Total Polar Compounds ○ Smoke Point ○ Colour Measurement ○ *p*-Anisidine Value ○ FTIR ○ TD-NMR
Adsorption Temperature (°C)	90, 135, 180	
Adsorbent Type	Chitosan Aerogels, Magnesium Silicate (as the reference material)	

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

Refined sunflower oil (Sole, Tekirdag, Türkiye) and frozen crispy potato sticks (7 cm x 7 mm, SuperFresh Kerevitas¸ Gıda San. Tic. A.S, Türkiye) were purchased from a local market. Magnesium Silicate was obtained from Aropi Kimya (Konya, Türkiye). All other chemicals were purchased from Sigma-Aldrich and all of the reagents were of analytical grade.

2.2 Methods

2.2.1 Preparation of Chitosan Aerogels

The preparation of chitosan aerogel mainly consists of three steps which are hydrogel production, alcogel production (replacing solvent with ethanol), and aerogel production by using supercritical drying.

2.2.1.1 Production of Chitosan Hydrogels

Chitosan can be dissolved in a weak acid solution. A 2% (w/v) chitosan solution was prepared by dissolving chitosan in a 1% acetic acid solution. To get a homogenous hydrogel solution, it was first mixed with ultra-turrax at 15 rpm for 10 minutes. Secondly, it was continuously mixed on a magnetic stirrer for 2 hours. Then, the homogenous solution was exposed to ultrasound with a frequency of 37 kHz and 100% power to get rid of bubbles that formed during stirring. The beads were formed by dropping the 4N NaOH solution using a syringe. Lastly, hydrogels were left in NaOH solution at the same concentration for 2 hours before they were filtered and washed with distilled water.

2.2.1.2 Production of Chitosan Alcogel

Since water and carbon dioxide show low affinity, the water in the hydrogels was changed with ethanol and converted into alcogels. They were kept in an ethanol bath with concentrations of 10% 30%, 50%, 70%, 80%, and 90% for 1 hour for each concentration. To get rid of all water, they were kept in a 100% ethanol bath for 24 hours.

2.2.1.3 Production of Chitosan Aerogel with Supercritical Drying

Alcogels were made into aerogels by drying them with supercritical carbon dioxide. Supercritical drying with carbon dioxide was performed under 200 bar and 35 °C with a flow rate of 1 kg/h for about 4.5 hours.

2.2.2 Production of Used Frying Oil

For frying, the method used by Sahin Ozkan et al. (2019) was followed with some modifications. Frying was carried out with a double-chambered fryer (Model GN 1/2, Oztiryakiler, Türkiye) at the temperature of 180 °C. In total, 32 frying treatments were performed as 8 times a day for 4 days. For each treatment, 200 g of potatoes were fried in 3.75 L of SO for 5 min. Then, the oil was only heated for one week at 180 °C to reach the TPC at the level of 25% which is the maximum value set by most of the European countries (Kmiecik et al., 2018). The UFO samples were stored at -18 °C for further analysis.

2.2.3 Adsorbent Treatment of the Used Frying Oil

To perform the adsorption process, the parameters were decided by the justification of previous literature (Farag & Basuny, 2009; Yates, 2007)and common applications used in the industry. Firstly, 100 mL of UFO was heated to 90 °C, 135 °C, and 180 °C (which is frying temperature), and 0.5 g, 1 g, and 2 g of aerogels were added at each temperature. Then, they were stirred for 15 min and filtered with Whatman no. 1 paper. Since the industry mostly uses magnesium silicate as the adsorbent for the regeneration of frying oils, it was also used in the study to compare the results with aerogels. The optimum adsorbent concentration and process temperature were decided by obtaining the lowest % FFA value after regeneration and magnesium silicate was also used at that concentration and temperature. The samples were stored in dark amber bottles at -18 °C for further analysis.

2.2.4 Characterization of the Used Frying Oil and Chitosan Aerogels

2.2.4.1 Free Fatty Acids

FFA contents of the oil samples were determined after frying and after adsorbent treatment by following AOCS Official Method Ca 5a-40 with minor changes (AOCS, 1990). Firstly, a 5 g oil sample was mixed with 1% (v/v) phenolphthalein and 40 mL ethanol. After the oil is dissolved in the ethanol solution, the mixture was titrated with 0.1 N NaOH solution until the solution become pink color. The percentage of the free fatty acids was evaluated as oleic acid. % FFA calculated with the following equation;

$$Free\ Fatty\ Acid\ (\%) = \frac{V_{titrant} * N_{titrant} * 28.2}{m}$$

Where

$V_{titrant}$= Volume of used 0.1N NaOH (mL)

$N_{titrant}$= Normality of NaOH

m= Weight of oil (g)

2.2.4.2 Total Polar Compounds

Total polar compounds (TPC) were measured using a food oil monitor (FOM 310, Ebro, Germany) during frying. After the potatoes were fried, the measurement was performed by immersing the FOM in oil, read and recorded. The controlled frying was done until the TPC exceeds the value of 25%. All the results were recorded at 180 °C.

2.2.4.3 Smoke Point

To observe the smoke point, AOCS Official Methods Cc-9a-48 was followed. Oil was poured into a muslin kettle and heated. When a thin continuous stream of bluish smoke was seen with the help of a dark background, the temperature was recorded (Das et al., 2013).

2.2.4.4 *p*-Anisidine Value

Secondary oxidation products and unsaturated aldehydes were examined with *p*-AnV. *p*-AnV was determined according to AOCS Official method Cd 18-90 with minor changes. Firstly, a 0.1 g oil sample was dissolved in a 25 mL volumetric flask and diluted to volume with isooctane. Then, the absorbance (Ab) of the solution was measured in a cuvette at 350 nm with the A UV-1208 model spectrophotometer (Shimadzu, Kyoto, Japan). A reference cuvette was filled with solvent as a blank. After pipetting 5 mL of oil solution into one test tube and 5 mL of solvent into a second test tube, 1 mL of *p*-anisidine reagent was added to each tube and shaken. After incubating for 10 min in the dark, absorbance (As) of the solution in the first test tube was measured in a cuvette at 350 nm. The solution from the second tube was used as a blank in the reference cuvette. The *p*-anisidine value (p-Ans) was calculated using the following formula;

$p - Ans = \frac{25*(1.2As-Ab)}{m}$ where;

As= Absorbance of the oil solution after reacting with *p*-anisidine reagent

Ab= Absorbance of the oil solution

m= mass of the oil sample (g)

2.2.4.5 Color Measurement

The color measurements were done according to AOCS Official Methods Cc 13e-92. The color of the oil samples was estimated before and after the adsorption treatment using a Lovibond tintometer (PFXi-195/3 Spectro colorimeter, Amesbury, UK). The results were given as L*, a*, and b* values of the Hunter color system. L* means lightness with values varying from 0 (black) to 100 (white), a* means red (+a) or green (-a), and b* means yellow (+b) or blue (-b).

2.2.4.6 Fourier Transform Infrared Spectroscopy

The aerogels after the adsorption process were examined by FTIR (IR Affinity-1 Spectrometer with Attenuated Total Reflectance (ATR), Shimadzu Corporation, Japan) in the range of 4000-600 cm^{-1} with a resolution of 16 cm^{-1} and 32 scans.

2.2.4.7 Time Domain Nuclear Magnetic Resonance (TD-NMR) Relaxometry Analyses

Time Domain Nuclear Magnetic Resonance Relaxometry experiments were performed with a 0.5 Tesla NMR system (Spin Track, Resonance Systems GmbH, Kirchheim/unter Teck, Germany) equipped with a 10mm RF probe. Spin-spin (T_2) relaxation time measurements were done using CPMG (Carr-Purcell-Meiboom-Gill) sequence. Number of echoes was set to 2,000 with an echo time of 500 µs. Relaxation period was set to 1,500 ms. T_2 relaxation times of samples were measured after the adsorption treatments.

2.2.4.8 Statistical Analysis

All analyses replicated three times. Statistical analysis was carried out by analysis of variance (ANOVA) using Minitab (Minitab Inc., Coventry, UK) with means separation by Tukey’s comparison test performed with 95% confidence interval. The letters indicated significant difference among the samples ($p<0.05$). The assumptions of ANOVA were checked prior to analysis.

CHAPTER 3

RESULTS AND DISCUSSION

To obtain the UFO in control, potato sticks were fried 32 times for 5 min at 180 °C. Then, the UFO was filtered by using CA at different aerogel concentrations (0.5, 1 and 2% (w/w)) and adsorption temperatures (90, 135 and 180 °C). Then, the parameters such as FFA, TPM, smoke point, *p*-anisidine and color were measured before and after the filtration.

3.1 Free Fatty Acids

The free fatty acids (FFA) content of oil gives information about the degree of hydrolysis of frying oil. Figure 3.1 shows the % FFA content before and after the treatment of the CA with different concentrations and adsorption temperatures (AdsT). The UFO had an FFA content of 0.44% ± 0.02 which exceeds the acceptable value of 0.3% (de ALMEIDA et al., 2019). According to the results, both aerogel concentration and temperature had a significant effect on the % FFA of the UFO ($p<0.05$), and an increase in both factors resulted in a decrease in the FFA content.

The results showed that the effect of 0.5% of aerogel concentration on the % FFA was insignificant at all the AdsT ($p>0.05$) except 180 °C. A possible explanation for this might be the well-known characteristics of the oil which is the decrease of viscosity of oil with the increase of the temperature (Diamante & Lan, 2014).

At the concentrations of 1% and 2%, it was observed that the % FFA declined significantly at all AdsT except for the adsorption performed at 90 °C with 1% of the CA. This reduction in the FFA content was expected since the chitosan can make a connection with the FFA due to its positively charged nature (Figure 3.2) (Bao et al., 2019; Goiri et al., 2010; Widiastuti et al., 2022)

Additionally, the high-temperature adsorption induced a significant decrease ($p<0.05$) in the FFA content of the UFO treated with 2% CA. This can be also explained by the rheological characteristics of the oil which means as the temperature increases the viscosity of the oil decreases, therefore the FFA could more easily interact with the CA (Diamante & Lan, 2014). According to Bhattacharya et. al. (2008), it is important to keep the level of FFA content below 0.4% to avoid the acceleration of the decomposition of the fats. Among all results, the lowest FFA content was achieved by the adsorption of 2% CA at the temperature of 180°C at which % FFA decreased from 0.44% to 0.18%. To compare the effectiveness of the CA with the MgSi, which is the most commonly used adsorbent for the regeneration of frying oil (Farag & Basuny, 2009), UFO was treated with 2% of the MgSi at 180°C. The MgSi affected FFA content insignificantly ($p>0.05$) which had a value of 0.41% ± 0.03. Our findings showed that the very low amounts of CA showed an immense adsorption capability due to its low density and high volume.

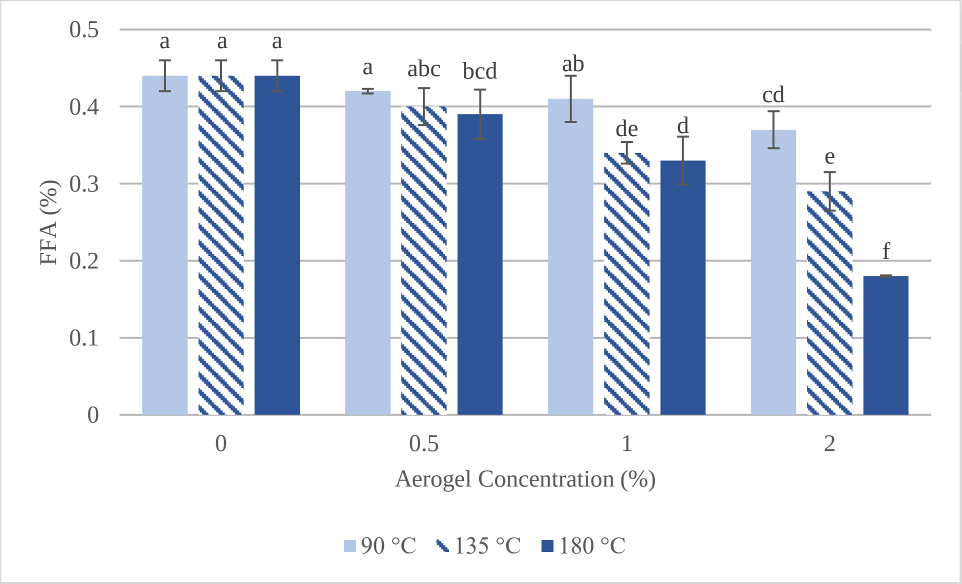

Figure 3. 1 Comparison of % FFA at different adsorption temperatures and aerogel amounts (g/g oil)

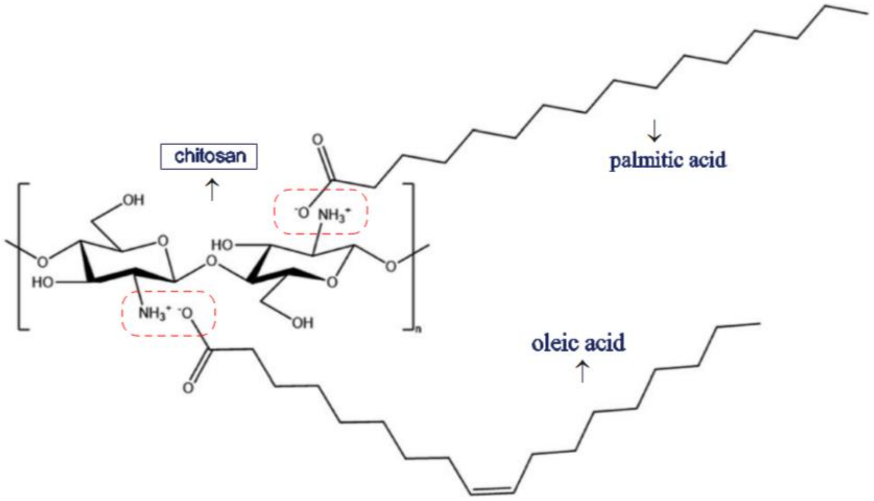

Figure 3. 2 Ionic interaction between chitosan and FFA (Widiastuti et al., 2022)

3.2 Total Polar Compounds

The total polar compounds (TPC) comprise a variety of polar components evolved during frying through hydrolysis, oxidation, and polymerization reactions (Elaine et al., 2022). The TPC is commonly divided into decomposed and polymerized products in terms of polarity and molecular weight. The polar fraction of the UFO includes non-volatile polar materials such as oxidized compounds (oxidized triglycerides and oligomeric triglycerides), monoglycerides, and the FFA (Bhattacharya et al., 2008; Elaine et al., 2022; Farag & Basuny, 2009).

In this study, the TPC of UFO were measured before and after adsorption at different AdsT and CA concentrations to estimate the oil quality (Figure 3.3). The untreated UFO had a TPC of 25.17% ± 0.03 which is slightly higher than the limit of 25% (Bhattacharya et al., 2008; Elaine et al., 2022). According to the results, both aerogel concentration and temperature had a significant effect on the TPC of UFO ($p<0.05$) The results revealed that the concentrations of 0.5% and 1% had an insignificant effect on TPC at all the AdsT except for 135°C ($p>0.05$). On the other hand, a significant increase of TPC was observed at 2% CA for all the AdsT, and the maximum was achieved at 180°C. The reason why CA could not achieve the reduction of TPC might be its aerogel network. The result of the MgSi treatment was 27.17% ± 0.03 which also increased TPC significantly ($p<0.05$). It seems possible that these results are due to the use of insufficient the MgSi since it is commonly used at a concentration of 10% (w/w) in the literature (Bhattacharya et al., 2008). As a result, the formation of the polar materials continued because of heating during the adsorption treatment.

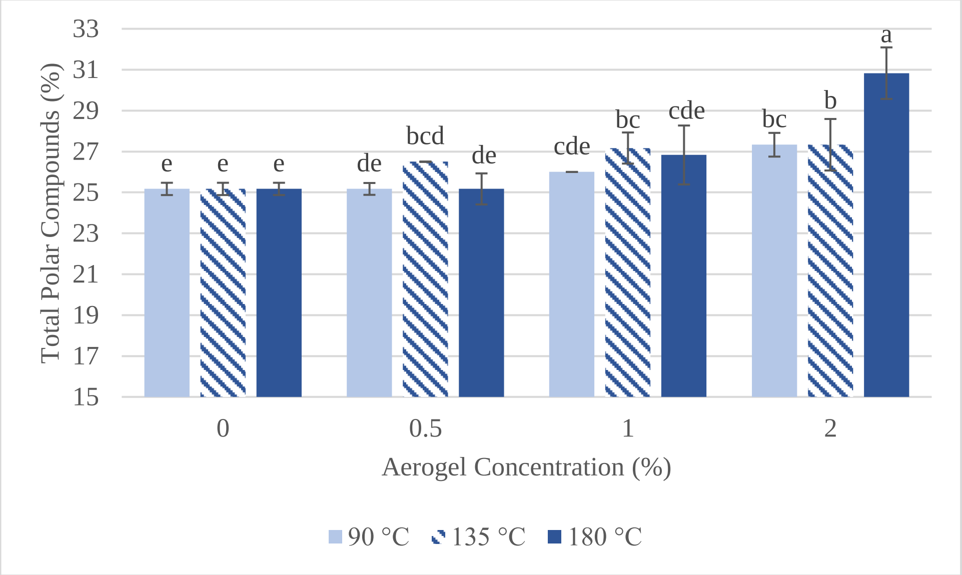

Figure 3. 3 Comparison of total polar compounds at different adsorption temperatures and aerogel amounts % (g/g oil)

3.3 Smoke Point

The temperature at which the oil begins to produce a continuous wisp of bluish smoke is known as the smoke point. Smoke point changes with respect to the FFA content of oil where the increase in FFA content leads to a decrease in smoke point.

This is because the amount of smoke spreading is related to the concentration of low-molecular-weight materials such as volatile compounds, monoglycerides, diglycerides, and FFA (Ahmad Tarmizi & Ismail, 2014).

Figure 3.4 shows the smoke points of the UFO before and after the CA treatment at different concentrations and AdsT. According to the results, both aerogel concentration and temperature had a significant effect on the smoke point of the UFO ($p<0.05$). Before the treatment of CA, the smoke point was 174.8°C ± 3.2 which was very close to the limit of 170°C (Matthäus, 2006). After adsorption, an increase in smoke point was expected but nevertheless, 0.5% CA concentration at both AdsT of 90°C and 180°C and 1% CA at 90°C had an insignificant effect on that ($p>0.05$). Other treatments achieved a significant increase in the smoke point ($p<0.05$). Even though the results demonstrated that CA was not sufficiently effective in raising the smoke point at low concentrations except for 135 °C, 2% CA improved it effectively. Moreover, the specific effect of concentration and temperature on the smoke point could not be determined, although the smoke point was increased for the rest of the treatments. This could be caused by the small pore size of the CA, which enabled the non-polar and low-molecular-weight decomposition products causing smoke to be adsorbed and absorbed when the CA is used in sufficient amounts.

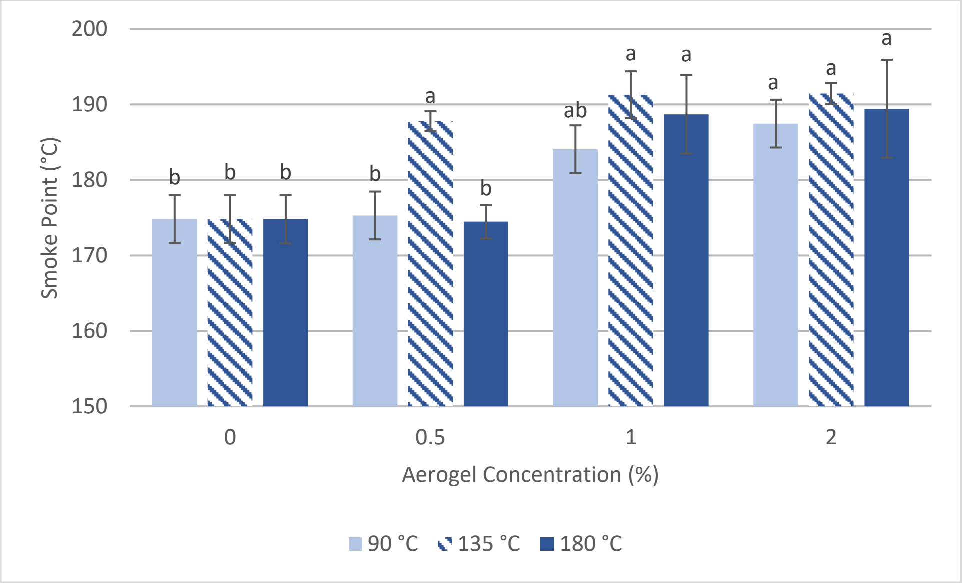

Figure 3. 4 Comparison of smoke point among adsorption temperatures across aerogel concentration% (g/g oil)

Additionally, the MgSi affected smoke point insignificantly with the result of 170.4°C ± 2.0 ($p>0.05$). When CA was compared with the MgSi, it was obvious that CA was more successful at increasing the smoke point.

3.4 *p*-Anisidine Value

The *p*-anisidine value (*p*-AnV) is a useful tool to determine the oxidative state of frying oil since it indicates the content of more stable aldehydes, while the peroxide value is unreliable because it is a measure of the content of hydroperoxides, which rapidly decompose at high frying temperatures (Ahmad Tarmizi et al., 2013; Ma et al., 2016).

Figure 3.5 provides an overview of the *p*-AnV of the UFO before and after the adsorption treatments with three aerogel concentrations and AdsTs. According to the results, aerogel concentration had a significant effect on the *p*-AnV of UFO ($p<0.05$). After the adsorption with the concentration of 0.5% CA, a significant increase in the *p*-AnV was observed ($p<0.05$), although it did not change significantly after the adsorption with the concentration of 1% CA ($p>0.05$). The observed increase in the *p*-AnV could be attributed to the further formation of the secondary oxidation products due to heating during the adsorption treatments, and the concentration of 0.5% CA was insufficient to adsorb these products. As the aerogel concentration increased, the *p*-AnV decreased significantly ($p<0.05$). This result demonstrated that the high concentration of the CA could adsorb the aldehyde compounds especially 2,4-dienals and 2-alkenals, which are the main products of the decomposition of hydroperoxides, reacting with the *p*-methoxy aniline (anisidine) (Alsufiani & Ashour, 2021). Aldehydes are polar molecules which may cause an increase in the polarity of the UFO. As previously discussed, TPC value of the UFO could not be reduced using CA effectively, although the specific aldehydes adsorbed by CA. An alternative explanation for this result might be that these aldehydes could be small part of TPC, therefore their adsorption was not causing an effective improvement in the value of TPC.

Different AdsT had a significant effect on the *p*-AnV ($p<0.05$). What is surprising is that although the adsorption at 180 °C resulted in the highest *p*-AnV in overall results, a 2% aerogel concentration could compensate it at that temperature. A possible explanation for this might be the increase in surface area, which enables it to interact with more secondary oxidation compounds.

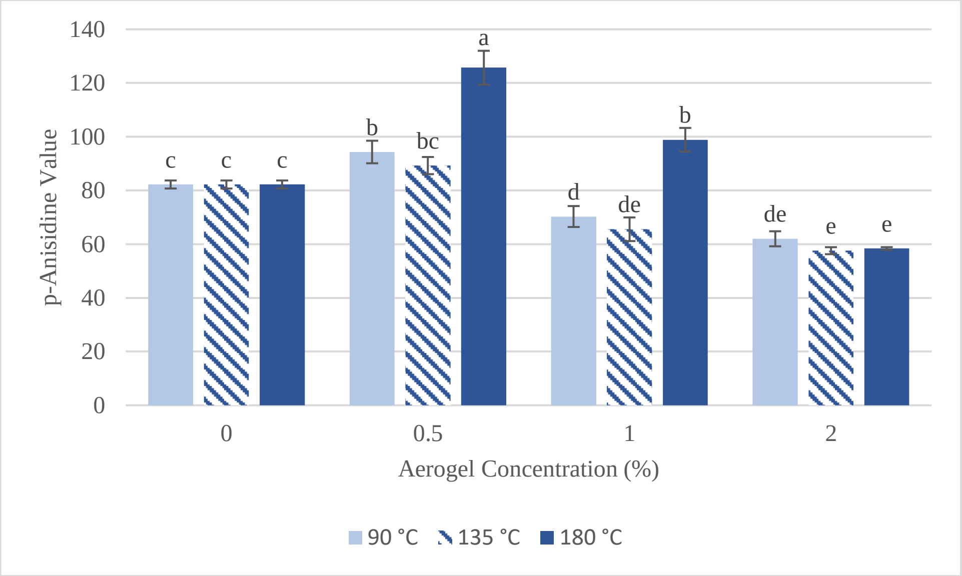

Figure 3. 5 Comparison of *p*-anisidine among adsorption temperatures across aerogel concentration% (g/g oil)

Additionally, the *p*-AnV of the MgSi was obtained as 80.22 ± 6.5 which is statistically the same as the value of the UFO (p>0.05). It is obvious that the CA at a concentration of 2% could adsorb the oxidation products successfully instead of the MgSi, which was used at the same concentration.

3.5 Color

Color change, particularly darkening, is a rapid determinant of the degree of deterioration and the quality of used oil. The fresh oil (FO) had 96.87 ± 0.19, -7.93 ± 0.03, and 30.23 ± 0.06 CIE values of L, a*, and b*, respectively. Table 3 provides the experimental data of CIE color values of the UFO before and after the adsorption treatments. Also, Figure 3.6 shows the CA produced using SC-CO_2. After the adsorption treatments, color change of CA and the UFO are shown in Figure 3.7, Figure 3.8, and Figure 3.9. In accordance with the present results, previous studies have demonstrated that the UFO was darker, more reddish, and yellowish in comparison with the color of the FO (Ahmad Tarmizi et al., 2013). The darkening is caused by the production of non-volatile degradation compounds involving hydroperoxides, oxidized triglycerides, and polymers (Ahmad Tarmizi et al., 2013; Serjouie et al., 2010). Additionally, the interactions of food nutrients and ingredients lead to the formation of browning products of the Maillard reaction, therefore the color of the UFO becomes darker (Ma et al., 2016).

According to the results, aerogel concentration and AdsT had a significant effect on the L values ($p<0.05$). An increase in both aerogel concentration and AdsT resulted in a decrease in the L values, which means that as concentration and AdsT increased, the UFO became darker. This finding was unexpected and suggests that the CA could not sufficiently adsorb the pigments formed during oxidation and thermal degradation of fatty acids. An alternative explanation for this result is that it is due to the adsorption of light-colored nonpolar pigments rather than dark ones and decrease in light colored compounds dominated the color of dark ones. This might have caused the UFO to seem darker (Figure 3.8). Also, it can be hypothesized that CA could be burned during the treatment at high temperatures and led to observe darker color. Further statistical tests revealed that aerogel concentration and AdsT had a significant effect on the a* values ($p<0.05$). As can be seen from the Table 3.1, an increase in both aerogel concentration and AdsT caused an increase in the a* values. The increase in the a* value indicated extreme browning, which turns the oil red (Sahin, 2000). It seems possible that these results are due to heating during the adsorption process which triggered the oxidation and thermal degradation, and the CA could not adsorb these red-colored pigments effectively. Further analysis of the data revealed that both aerogel concentration and AdsT affected the b* values significantly ($p<0.05$). It can be seen from the data in Table 3.1 that the b* values decreased with both increase in aerogel concentration and AdsT. The number of yellow pigments, such as carotenoids, contributes to the b* value (Wroniak et al., 2021).

Table 3. 1 CIE color values of the UFO before and after the adsorption treatments

Adsorption Temperature (°C)	Aerogel Concentration (%)	L	a*	b*

	0	74.76 ± 0.07^{b}	12.01 ± 0.12^{j}	98.61 ± 0.34^{b}
90	0.5	74.65 ± 0.05^{b}	13.10 ± 0.01^{g}	99.48 ± 0.02^{a}
	1	73.68 ± 0.26^{c}	12.59 ± 0.16$^{\imath}$	98.46 ± 0.34^{b}
	2	74.90 ± 0.17^{a}	13.01 ± 0.01^{h}	100.04 ± 0.28^{a}
135	0.5	71.62 ± 0.03^{d}	14.88 ± 0.02^{f}	98.49 ± 0.09^{b}
	1	70.52 ± 0.01^{e}	16.12 ± 0.02^{d}	97.06 ± 0.08^{c}
	2	69.85 ± 0.03^{f}	15.00 ±0.01^{e}	96.32 ± 0.22^{d}
180	0.5	65.01 ± 0.01^{g}	20.51 ± 0.01^{c}	96.64 ± 0.04^{cd}
	1	63.62 ± 0.09^{h}	21.69 ± 0.07^{b}	95.41 ± 0.23^{e}
	2	52.95 ± 0.12$^{\imath}$	23.42 ± 0.03^{a}	84.27 ± 0.08^{f}

These results supported the idea that the CA could adsorb the carotenoids successfully which declines the yellow color although it is not as low as fresh oil. Lastly, the comparative results of the L, a*, and b* obtained from the adsorption using the MgSi were 75.37 ± 0.03, 12.55 ± 0.08, and 100.00 ± 0.17, respectively. It is seen that the MgSi was also insufficient to improve the color of the UFO under the same conditions as the CA. Only the L value was increased significantly ($p<0.05$) but the value did not reach that of fresh oil.

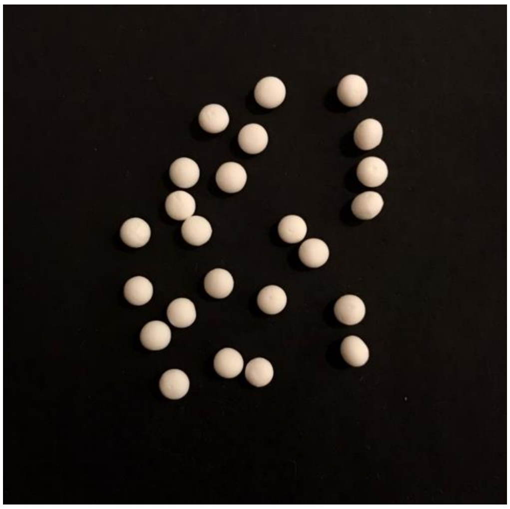

Figure 3. 6 Chitosan aerogels

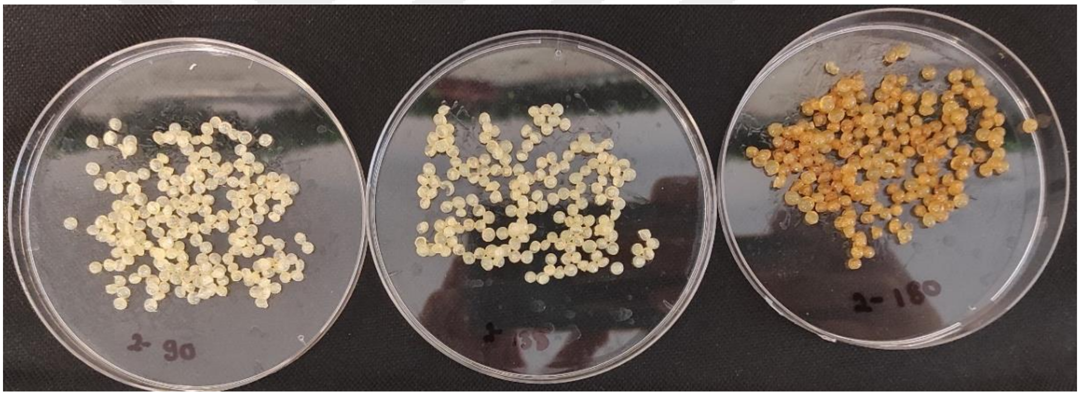

Figure 3. 7 Chitosan aerogels after the adsorption at 90, 135 and 180 °C (from left to right)

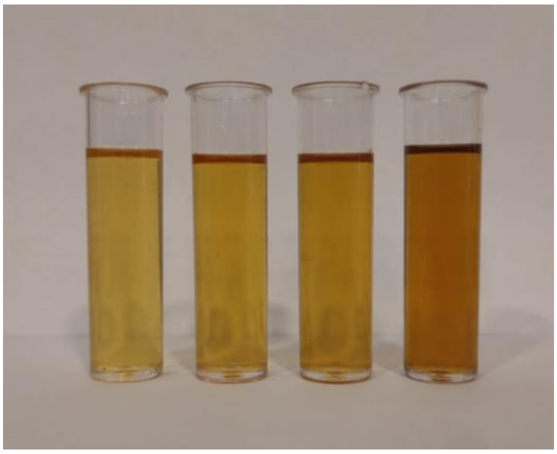

Figure 3. 8 Untreated and treated used frying oil samples with chitosan aerogels at 90, 135, 180 °C (from left to right)

Figure 3. 9 Untreated and treated used frying oil samples with MgSi at 180 °C (from left to right)

3.6 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra indicate changes in the chemical composition and functional groups of the aerogels before and after the adsorption. The appearance of new peaks or modifications in the peak intensity are indicators of changes in aerogel structure. Figure 3.6 compares the FTIR spectra of the aerogels (1), the concentration of 2% aerogels treated with FO at 180 °C (2), and the concentration of 2% aerogels used for regeneration of the UFO at 180 °C (3). The visual analysis of the FTIR spectra of the three different aerogel samples indicated that the peaks between 1250 and 600 cm^{-1} were the characteristic bands for CA which appears in all the samples. Additionally, new peaks belonging to the FFA were formed after the adsorption process performed with FO and the UFO.

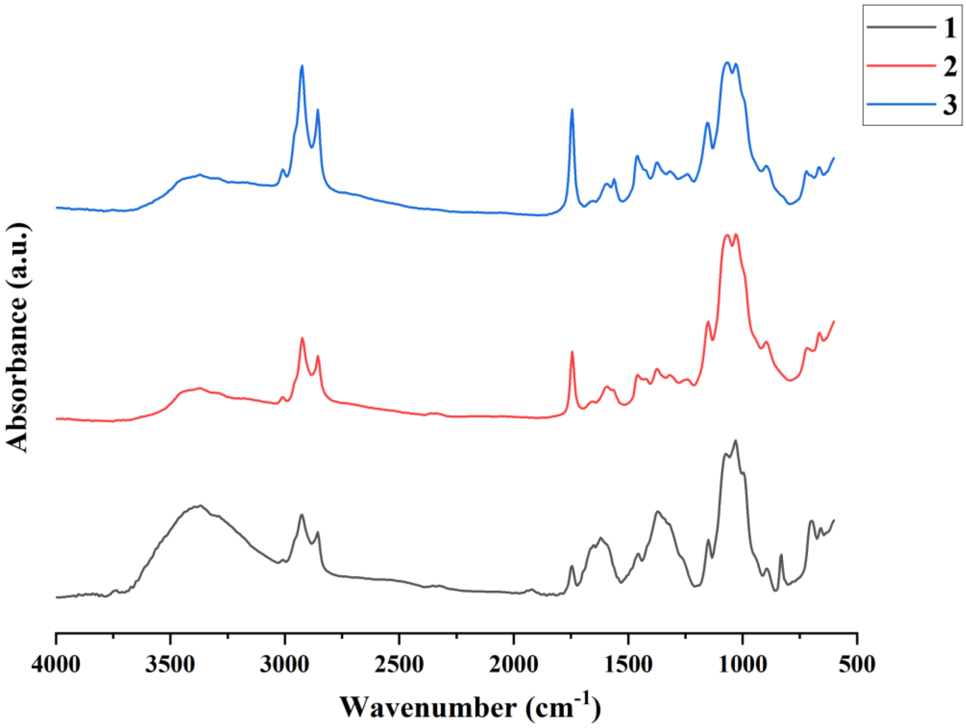

Figure 3. 10 FTIR analysis of the aerogels (1), treated with FO at 180 °C (2), treated with UFO at 180 °C (3)

At a closer look to the recorded spectra, the region of hydrogen's stretching vibrations between 2800 and 3050 cm^{-1}, and the region of carbonyl stretching vibrations between 1680 and 1780 cm^{-1} were the regions where the most significant changes were observed. Due to the significant number of CH_2, and CH_3 groups contained in the fatty acids of oil samples adsorbed by the aerogels, the hydrogen's stretching region was dominated by a series of aliphatic vibrations around 3000 cm^{-1}. The bands formed at 2922 and 2853 cm^{-1} showed asymmetric and symmetric stretching vibration of C–H bonds of the aliphatic CH_2 group of the fatty acid backbone. Additionally, the band at 3009 cm^{-1} was caused by the C–H stretching symmetric vibration of the *cis* double bonds of unsaturated fatty acids found in the oils adsorbed by the aerogels. When aerogels adsorbing the UFO were compared to the ones adsorbing fresh oil, it was observed that the absorbance of the bands in the hydrogen stretching region increased. Similarly, the intensity band formed at 1744 cm^{-1} due to the ester bonds between glycerol and fatty acids increased (Vlachos et al., 2006). This finding confirmed that the content of FFA present in the UFO was higher than the FO and the CA could adsorb the FFA successfully.

3.7 Time Domain Nuclear Magnetic Resonance Analysis

Time-domain nuclear magnetic resonance (TD-NMR) gives fundamental information about the chemical, structural, and molecular properties of food samples. It has gained popularity in the field of food research since it is non-destructive, non-invasive, and provides both qualitative and quantitative data on food systems without the need for any preparation before analysis. Certain nuclei, such as hydrogen in food, are excited using electromagnetic radiation in the radio frequency (RF) range. Examining the relaxation of this excited signal reveals information about the studied sample through longitudinal (T_1) and transverse (T_2) relaxation times. T_2 is the time constant that measures how long it takes for a transverse magnetization to decay (Ozel & Oztop, 2021). Table 1 shows the T_2 results of CA treated with FO at 25 and 180 °C and UFO at 180 °C. In order to observe the effect of treatment of CA on the quality of UFO, CA was firstly treated with FO at room temperature since it could not be obtained any signal from unused CA. According to the results, aerogel concentration and AdsT had a significant effect on T2 relaxation times ($p<0.05$). The table below illustrates that the CA which adsorbed UFO resulted in a significantly short T_2 relaxation times that the ones adsorbed FO. This might be caused by the increased viscosity and polarity during the frying process. Another words, increase in the viscosity may cause a decrease in the mobility of the oil protons. As a result, the relaxation time of T_2 was shortened (C. Wang et al., 2019). In this study, TPC value of FO was measured as 16.17% ± 0.3 and the TPC value was also increased with the treatment of CA as discussed in the previous parts. These T_2 results are in agreement with those obtained by Wang et. al. (2019) who support the idea that increase in the viscosity and TPC value of frying oil led to a decrease in T_2 relaxation time.

Table 3. 2 T_2 relaxation times of chitosan aerogels used for the treatment of fresh oil (FO) at 25 °C, FO at 180 °C and with used frying oil (UFO) at 180 °C

Adsorption Temperature (°C)	**Aerogel concentration (%)**	**T_2 (ms)**
25 (FO)	0.5	108.72 ± 2.51^{bc}
	2	102.83 ± 0.38^{c}
180 (FO)	0.5	115.67 ± 4.66^{a}
	2	109.79 ± 0.46^{ab}
180 (UFO)	0.5	92.77 ± 2.56^{d}
	2	95.45 ± 0.28^{d}

CHAPTER 4

CONCLUSION AND RECOMMENDATION

In the presented study, a novel method for the regeneration of the UFO with different concentrations of CA (0.5%, 1%, and 2%), and the different AdsT (90, 135, and 180 °C) was investigated. Adsorption with Magnesium silicate was also studied with the concentration and AdsT which gave the optimum % FFA result for the CA (2% and 180 °C, respectively) for comparison.

In order to determine the quality of the UFO, it was analyzed before and after the adsorption treatments. The quality parameters of frying oil which are the FFA content, TPC, smoke point, *p*-AnV, and color measurements were examined. Additionally, the used aerogels were investigated by using FTIR analysis.

This study has found that the UFO could be successfully regenerated using the CA rather than the MgSi which is the most used synthetic adsorbent in the industry. The most obvious finding that emerges from this study is that the CA reduced the FFA content of the UFO significantly due to its positively charged nature. Additionally, the increase in the aerogel concentration and AdsT decreased significantly the FFA content of the UFO. The optimum reduction of the % FFA in the UFO was achieved using 2% of the CA at 180 °C.

The TPC results revealed that the CA did not affect the adsorption of the polar materials in the UFO. The TPC value of the UFO increased during the adsorption treatments because of heating. It was also observed that the treatment with the MgSi could not decrease the TPC of the UFO in the same conditions as the treatment of CA.

Smoke point results showed that treatment of the CA improved the quality of the UFO by increasing the smoke point. Although the CA could not adsorb the polar molecules overall, the results showed that it could keep the nonpolar and a small part of the polar molecules which cause smoke. On the other hand, the MgSi did not affect the smoke point of the UFO significantly ($p>0.05$).

The p-AnV demonstrated that the secondary oxidation products formed during the frying process could be compensated with 2% of the CA concentration treated at 180 °C. Moreover, the MgSi treatment in the same conditions did not change the p-AnV significantly ($p>0.05$).

Color measurements were found lower the L and b* values and higher a* values after treatment with the CA at the optimum combinations of the parameters (2%, 180 °C). This means the CA treatment causes darker and more reddish color and less yellow pigments in the UFO. When the results were compared with the MgSi treatment, it was seen that it could improve significantly only the L values of the UFO ($p<0.05$).

The finding of the FTIR analysis of the aerogels revealed that there are new peaks related to the FFA which are at the wavelengths of 1744, 2853, 2922, and 3009 cm^{-1} were observed after adsorption treatment. The adsorbed the FFA molecules could also be observed in these FTIR results of aerogels in addition to examinations of the UFO.

To conclude, this is the first study that uses the CA for the regeneration of the UFO and examines the quality parameters of the frying oil before and after the adsorption. The evidence from this study suggests that the CA could improve the UFO quality by reducing the FFA content, secondary oxidation products, and the b* value, which is the yellow color indication. Also, it enhances the quality of the UFO by increasing the smoke point. The major limitation of this study is that the treatment of CA could not decrease the polar compounds formed due to frying and could not lighten the color of the UFO. Further experimental investigations are needed to estimate the reason behind the darker color and increase in the TPC values. Moreover, new aerogel formulations like hybrid aerogels combined with chitosan can be developed and used to recover the polar material adsorption of the UFO for future research.

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APPENDICES

A. Statistical Analysis

Table A. 1 ANOVA Results of FFA of the UFO

General Linear Model: FFA versus Temperature; Concentration

Factor Information

Factor	Type	Levels	Values
Temperature	Fixed	3	90; 135; 180
Concentration	Fixed	4	0.0; 0.5; 1.0; 2.0

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Temperature	2	0.031403	0.015702	73.37	0.000
Concentration	3	0.120382	0.040127	187.52	0.000
Temperature*Concentration	6	0.030784	0.005131	23.98	0.000
Error	21	0.004494	0.000214		
Total	32	0.190976			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0146285	97.65%	96.41%	94.70%

Comparisons for FFA

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping		
90	11	0.413134	A		
135	12	0.368229		B	
180	10	0.334881			C

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping			
0.0	9	0.440000	A			
0.5	8	0.399131		B		
1.0	7	0.367225			C	
2.0	9	0.281971				D

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature*Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Temperature*Concentration	N	Mean	Grouping					
180 0.0	3	0.440000	A					
90 0.0	3	0.440000	A					
135 0.0	3	0.440000	A					
90 0.5	3	0.423333	A					
90 1.0	2	0.422279	A	B				
135 0.5	3	0.403108	A	B	C			
180 0.5	2	0.370951		B	C	D		
90 2.0	3	0.366925			C	D		
180 1.0	2	0.343870				D		
135 1.0	3	0.335526				D	E	
135 2.0	3	0.294281					E	
180 2.0	3	0.184705						F

Means that do not share a letter are significantly different.

Table A. 2 ANOVA Results of TPC of the UFO

General Linear Model: Total Polar Compounds versus ... ; Temperature

Factor Information

Factor	Type	Levels	Values
Concentration	Fixed	4	0.0; 0.5; 1.0; 2.0
Temperature	Fixed	3	90; 135; 180

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Concentration	3	68.953	22.9843	94.81	0.000
Temperature	2	5.370	2.6852	11.08	0.000
Concentration*Temperature	6	19.751	3.2918	13.58	0.000
Error	22	5.333	0.2424		
Total	33	105.765			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.492366	94.96%	92.44%	87.83%

Comparisons for Total Polar Compounds

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping			
2.0	8	28.7222	A			
1.0	8	26.3889		B		
0.5	9	25.6111			C	
0.0	9	24.8333				D

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping	
180	11	26.7083	A	
135	11	26.6250	A	
90	12	25.8333		B

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration*Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Concentration*Temperature	N	Mean	Grouping		
2.0 180	3	30.8333	A		
2.0 135	2	28.0000		B	
2.0 90	3	27.3333		B	C

1.0 135	3	27.1667	B	C		
0.5 135	3	26.5000	B	C	D	
1.0 90	3	26.0000		C	D	E
1.0 180	2	26.0000		C	D	E
0.5 90	3	25.1667			D	E
0.5 180	3	25.1667			D	E
0.0 90	3	24.8333				E
0.0 135	3	24.8333				E
0.0 180	3	24.8333				E

Means that do not share a letter are significantly different.

Table A. 3 ANOVA Results of Smoke Point of the UFO

General Linear Model: Smoke Point versus ... concentration; Temperature

Factor Information

Factor	Type	Levels	Values
Concentration	Fixed	4	0.0; 0.5; 1.0; 2.0
Temperature	Fixed	3	90; 135; 180

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Concentration	3	1332.5	444.16	33.78	0.000
Temperature	2	229.8	114.92	8.74	0.001
Concentration*Temperature	6	209.4	34.91	2.65	0.040
Error	24	315.6	13.15		
Total	35	2087.3			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
3.62625	84.88%	77.95%	65.98%

Comparisons for Smoke Point

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping	
2.0	9	189.456	A	
1.0	9	188.022	A	
0.5	9	179.189		B
0.0	9	174.833		B

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping	
135	12	186.350	A	
180	12	181.858		B
90	12	180.417		B

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration*Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Concentration*Temperature	N	Mean	Grouping	
2.0 135	3	191.467	A	
1.0 135	3	191.300	A	
2.0 180	3	189.433	A	
1.0 180	3	188.700	A	
0.5 135	3	187.800	A	
2.0 90	3	187.467	A	
1.0 90	3	184.067	A	B
0.5 90	3	175.300		B
0.0 90	3	174.833		B
0.0 135	3	174.833		B
0.0 180	3	174.833		B
0.5 180	3	174.467		B

Means that do not share a letter are significantly different.

Table A. 4 ANOVA Results of p-AnV of the UFO

General Linear Model: p-Anisidine versus Concentration; Temperature

Factor Information

Factor	Type	Levels	Values
Concentration	Fixed	4	0.0; 0.5; 1.0; 2.0
Temperature	Fixed	3	90; 135; 180

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Concentration	3	8718.6	2906.20	244.84	0.000
Temperature	2	2027.8	1013.92	85.42	0.000
Concentration*Temperature	6	2173.8	362.30	30.52	0.000
Error	24	284.9	11.87		
Total	35	13205.1			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
3.44526	97.84%	96.85%	95.15%

Comparisons for p-Anisidine

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping		
0.5	9	103.093	A		
0.0	9	82.223		B	
1.0	9	77.904		B	
2.0	9	59.319			C

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping	
180	12	91.0483	A	
90	12	77.2075		B

135	12	73.6492	C

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration*Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Concentration*Temperature	N	Mean	Grouping
0.5 180	3	125.707	A
1.0 180	3	97.877	B
0.5 90	3	94.317	B
0.5 135	3	89.257	B C
0.0 90	3	82.223	C
0.0 135	3	82.223	C
0.0 180	3	82.223	C
1.0 90	3	70.290	D
1.0 135	3	65.547	D E
2.0 90	3	62.000	D E
2.0 180	3	58.387	E
2.0 135	3	57.570	E

Means that do not share a letter are significantly different.

Table A. 5 ANOVA Results of L value of the UFO

General Linear Model: L versus Temperature; Concentration

Factor Information

Factor	Type	Levels	Values
Temperature	Fixed	3	90; 135; 180
Concentration	Fixed	4	0.0; 0.5; 1.0; 2.0

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Temperature	2	645.45	322.723	74696.51	0.000
Concentration	3	335.19	111.729	25860.37	0.000
Temperature*Concentration	6	377.69	62.949	14569.89	0.000
Error	22	0.10	0.004		
Total	33	1420.67			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0657302	99.99%	99.99%	99.98%

Comparisons for L

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping
90	10	74.4904	A
135	12	71.6883	B
180	12	64.0883	C

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping
0.0	9	74.7633	A
0.5	9	70.4278	B
1.0	8	69.2289	C
2.0	8	65.9361	D

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature*Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Temperature*Concentration	N	Mean	Grouping
90 2.0	2	75.0050	A
90 0.0	3	74.7633	B
135 0.0	3	74.7633	B
180 0.0	3	74.7633	B
90 0.5	3	74.6533	B
90 1.0	2	73.5400	C
135 0.5	3	71.6167	D
135 1.0	3	70.5233	E
135 2.0	3	69.8500	F
180 0.5	3	65.0133	G

180 1.0	3	63.6233	H
180 2.0	3	52.9533	I

Means that do not share a letter are significantly different.

Table A. 6 ANOVA Results of a* value of the UFO

General Linear Model: a versus Temperature; Concentration

Factor Information

Factor	Type	Levels	Values
Temperature	Fixed	3	90; 135; 180
Concentration	Fixed	4	0.0; 0.5; 1.0; 2.0

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Temperature	2	233.840	116.920	401472.30	0.000
Concentration	3	113.718	37.906	130159.22	0.000
Temperature*Concentration	6	80.183	13.364	45887.90	0.000
Error	19	0.006	0.000		
Total	30	470.194			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0170654	100.00%	100.00%	100.00%

Comparisons for a

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping
180	10	19.4012	A
135	11	14.4871	B
90	10	12.6717	C

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping

2.0	9	17.1456	A
1.0	7	16.8239	B
0.5	9	16.1656	C
0.0	6	11.9450	D

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature*Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Temperature*Concentration	N	Mean	Grouping
180 2.0	3	23.4200	A
180 1.0	2	21.7300	B
180 0.5	3	20.5100	C
135 1.0	3	16.1167	D
135 2.0	3	15.0033	E
135 0.5	3	14.8833	F
90 0.5	3	13.1033	G
90 2.0	3	13.0133	H
90 1.0	2	12.6250	I
180 0.0	2	11.9450	J
135 0.0	2	11.9450	J
90 0.0	2	11.9450	J

Means that do not share a letter are significantly different.

Table A. 7 ANOVA Results of b* value of the UFO

General Linear Model: b versus Concentration; Temperature

Factor Information

Factor	Type	Levels	Values
Concentration	Fixed	4	0.0; 0.5; 1.0; 2.0
Temperature	Fixed	3	90; 135; 180

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Concentration	3	143.127	47.7091	856.58	0.000
Temperature	2	187.259	93.6293	1681.04	0.000

Concentration*Temperature	6	247.130	41.1884	739.50	0.000
Error	24	1.337	0.0557		
Total	35	578.853			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.236003	99.77%	99.66%	99.48%

Comparisons for b

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping
0.0	9	98.6133	A
0.5	9	98.2056	B
1.0	9	96.9756	C
2.0	9	93.5422	D

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping
90	12	99.1492	A
135	12	97.6217	B
180	12	93.7317	C

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration*Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Concentration*Temperature	N	Mean	Grouping
2.0 90	3	100.037	A
0.5 90	3	99.483	A
0.0 90	3	98.613	B
0.0 135	3	98.613	B
0.0 180	3	98.613	B
0.5 135	3	98.493	B
1.0 90	3	98.463	B

1.0 135	3	97.057	C
0.5 180	3	96.640	C D
2.0 135	3	96.323	D
1.0 180	3	95.407	E
2.0 180	3	84.267	F

Means that do not share a letter are significantly different.

Table A. 8 ANOVA Results of % FFA value of Untreated UFO (0), UFO Treated with 2% CA (1), and UFO Treated with 2% MgSi (2)

One-way ANOVA: FFA versus Adsorbent Type

Factor Information

Factor	Levels	Values
Adsorbent Type	3	0; 1; 2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Type	2	0.113689	0.056844	124.78	0.000
Error	6	0.002733	0.000456		
Total	8	0.116422			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0213437	97.65%	96.87%	94.72%

Means

Adsorbent Type	N	Mean	StDev	95% CI
0	3	0.4400	0.0173	(0.4098; 0.4702)
1	3	0.18667	0.00577	(0.15651; 0.21682)
2	3	0.4067	0.0321	(0.3765; 0.4368)

Pooled StDev = 0.0213437

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent Type	N	Mean	Grouping
0	3	0.4400	A

2	3	0.4067	A
1	3	0.18667	B

Means that do not share a letter are significantly different.

Table A. 9 ANOVA Results of TPC of Untreated UFO (0), UFO Treated with 2% CA (1), and UFO Treated with 2% MgSi (2)

One-way ANOVA: Total Polar Compounds versus Adsorbent Type

Factor Information

Factor	Levels	Values
Adsorbent Type	3	0; 1; 2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Type	2	49.556	24.7778	99.11	0.000
Error	6	1.500	0.2500		
Total	8	51.056			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.5	97.06%	96.08%	93.39%

Means

Adsorbent Type	N	Mean	StDev	95% CI
0	3	25.167	0.289	(24.460; 25.873)
1	3	30.833	0.764	(30.127; 31.540)
2	3	27.167	0.289	(26.460; 27.873)

Pooled StDev = 0.5

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent Type	N	Mean	Grouping		
1	3	30.833	A		
2	3	27.167		B	
0	3	25.167			C

Means that do not share a letter are significantly different.

Table A. 10 ANOVA Results of Smoke Point of Untreated UFO (0), UFO Treated with 2% CA (1), and UFO Treated with 2% MgSi (2)

One-way ANOVA: smoke versus Adsorbent Type

Factor Information

Factor	Levels	Values
Adsorbent Type	3	0; 1; 2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Type	2	595.1	297.54	15.83	0.004
Error	6	112.8	18.79		
Total	8	707.8			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
4.33500	84.07%	78.76%	64.16%

Means

Adsorbent Type	N	Mean	StDev	95% CI
0	3	174.83	3.23	(168.71; 180.96)
1	3	189.43	6.49	(183.31; 195.56)
2	3	170.40	1.95	(164.28; 176.52)

Pooled StDev = 4.33500

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent Type	N	Mean	Grouping	
1	3	189.43	A	
0	3	174.83		B
2	3	170.40		B

Means that do not share a letter are significantly different.

Table A. 11 ANOVA Results of p-AnV of Untreated UFO (0), UFO Treated with 2% CA (1), and UFO Treated with 2% MgSi (2)

One-way ANOVA: p-ans versus Adsorbent Type

Factor Information

Factor	Levels	Values
Adsorbent Type	3	0; 1; 2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Type	2	1048.99	524.50	35.27	0.000
Error	6	89.22	14.87		
Total	8	1138.21			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
3.85620	92.16%	89.55%	82.36%

Means

Adsorbent Type	N	Mean	StDev	95% CI
0	3	82.223	1.546	(76.776; 87.671)
1	3	58.384	0.531	(52.936; 63.832)
2	3	80.22	6.48	(74.77; 85.66)

Pooled StDev = 3.85620

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent Type	N	Mean	Grouping	
0	3	82.223	A	
2	3	80.22	A	
1	3	58.384		B

Means that do not share a letter are significantly different.

Table A. 12 ANOVA Results of L value of Untreated UFO (0), UFO Treated with 2% CA (1), and UFO Treated with 2% MgSi (2)

One-way ANOVA: L versus Adsorbent Type

Factor Information

Factor	Levels	Values
Adsorbent Type	3	0; 1; 2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Type	2	978.551	489.276	75791.39	0.000
Error	6	0.039	0.006		
Total	8	978.590			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0803465	100.00%	99.99%	99.99%

Means

Adsorbent Type	N	Mean	StDev	95% CI
0	3	74.7633	0.0666	(74.6498; 74.8768)
1	3	52.9533	0.1193	(52.8398; 53.0668)
2	3	75.3700	0.0265	(75.2565; 75.4835)

Pooled StDev = 0.0803465

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent Type	N	Mean	Grouping		
2	3	75.3700	A		
0	3	74.7633		B	
1	3	52.9533			C

Means that do not share a letter are significantly different.

Table A. 13 ANOVA Results of a* value of Untreated UFO (0), UFO Treated with 2% CA (1), and UFO Treated with 2% MgSi (2)

One-way ANOVA: a versus Adsorbent Type

Factor Information

Factor	Levels	Values
Adsorbent Type	3	0; 1; 2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Type	2	248.488	124.244	17282.79	0.000
Error	6	0.043	0.007		
Total	8	248.531			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0847873	99.98%	99.98%	99.96%

Means

Adsorbent Type	N	Mean	StDev	95% CI
0	3	12.0133	0.1185	(11.8936; 12.1331)
1	3	23.4200	0.0300	(23.3002; 23.5398)
2	3	12.5533	0.0814	(12.4336; 12.6731)

Pooled StDev = 0.0847873

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent Type	N	Mean	Grouping		
1	3	23.4200	A		
2	3	12.5533		B	
0	3	12.0133			C

Means that do not share a letter are significantly different.

Table A. 14 ANOVA Results of b* value of Untreated UFO (0), UFO Treated with 2% CA (1), and UFO Treated with 2% MgSi (2)

One-way ANOVA: b versus Adsorbent Type

Factor Information

Factor	Levels	Values
Adsorbent Type	3	0; 1; 2

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Adsorbent Type	2	455.516	227.758	4468.76	0.000
Error	6	0.306	0.051		

Total	8	455.822

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.225758	99.93%	99.91%	99.85%

Means

Adsorbent Type	N	Mean	StDev	95% CI
0	3	98.613	0.342	(98.294; 98.932)
1	3	84.2667	0.0814	(83.9477; 84.5856)
2	3	100.007	0.171	(99.688; 100.326)

Pooled StDev = 0.225758

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Adsorbent Type	N	Mean	Grouping
2	3	100.007	A
0	3	98.613	B
1	3	84.2667	C

Means that do not share a letter are significantly different.

Table A. 15 ANOVA Results of T2 times of CA treated with oil

General Linear Model: T2 versus Concentration; Temperature

Factor Information

Factor	Type	Levels	Values
Concentration	Fixed	2	0.5; 2.0
Temperature	Fixed	3	25; 180; 181

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Concentration	1	41.28	41.284	7.07	0.021
Temperature	2	1062.70	531.351	91.01	0.000

Concentration*Temperature	2	73.42	36.708	6.29	0.014
Error	12	70.06	5.838		
Total	17	1247.46			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
2.41627	94.38%	92.04%	87.36%

Comparisons for T2

Tukey Pairwise Comparisons: Concentration

Grouping Information Using the Tukey Method and 95% Confidence

Concentration	N	Mean	Grouping
0.5	9	105.720	A
2.0	9	102.691	B

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Temperature	N	Mean	Grouping
180	6	112.732	A
25	6	105.777	B
181	6	94.108	C

Means that do not share a letter are significantly different.

Tukey Pairwise Comparisons: Concentration*Temperature

Grouping Information Using the Tukey Method and 95% Confidence

Concentration*Temperature	N	Mean	Grouping
0.5 180	3	115.673	A

2.0 180	3	109.790	A	B		
0.5 25	3	108.720		B	C	
2.0 25	3	102.833			C	
2.0 181	3	95.450				D
0.5 181	3	92.767				D

Means that do not share a letter are significantly different.