RE-REFINING OF DEEP FRYING OIL

Kehkashan Nawaz[1], Ashraf Kamal[2], Syed Mumtaz Danish Naqvi[2], Sana Awan[2]

[1]Department of Chemical Engineering, University of Karachi, Karachi 75270, Pakistan
[2]Department of Applied Chemistry & Chemical Technology, University of Karachi, Karachi 75270, Pakistan

Abstract

A large amount of deep frying cooking oil is produced by a number of fast food restaurants containing a number of harmful compounds formed with food on its oxidation at frying temperature. It was made re-useable by adsorption column chromatographic technique and produced pale yellow colored oil with 90-95% yield having acceptable values of viscosity, conjugated dienes, free fatty acid, saponification and peroxide. Quality of the recovered oil was also analyzed by FTIR. Indigenous magnesite was proved as a better adsorbent than alumina and silica gel. It is cheap and available abundantly in nature. This process can save the human health from the horrible effects of hazardous components present in spent oil generated during deep frying which is used repeatedly without any treatment especially in third world.
Keywords: Deep frying oil, Magnesite, Alumina, Silica gel, FTIR

1. Introduction

Cooking oils are non-polar triglycerides [1]. They are good shelter for vitamins A, D, E and K, high caloric than carbohydrates and proteins and also hold essential fatty acids [2]. Anyhow theirs excessive ingestion and substandard grade cause nasty effects on health [2].

Deep frying is one of the common food processing techniques using worldwide. Foods ought to be tasty, crispy and more attractive after deep frying in cooking oil [3]. Uncooked food is thoroughly immersed in hot oil and can attained temperature up to 200^0C [4]. Simultaneous heat and mass transfer have been taken place in oil in aerobic environment, due to which oil is chemically and physically changed [5].

Oil is chemically transformed into hydroperoxides, free fatty acids, alcohols, acids, aldehydes, ketones, monoglycerides, diglycerides, cyclic compounds & polymers [6]. These products are also responsible for physical changes in oil i.e., odor, flavor, color, viscosity and etc. Moreover these substances are formed by process of auto-oxidation, oxidation, hydrolysis, isomer cyclization & polymerization [7].

A huge amount of waste oil has been used in animal feed. However, European and some other countries have rejected it to protect food chain [8]. Waste cooking oil could be turned into biofuel, soap, surfactants and lubricants but some pretreatments are needed to purify used oil [6]. Oil drainage would be an environmental issue due to rancidified oil components. Furthermore sewerage lines would be choked by carefree dumping of oil. Re-refining of oil could be a secure ditching routine to safe environment from the risky effects as well as to conserve state wealth.

It is considered to be after frying 40-70% triglycerides remain unreacted [4]. Though recycling or re-refining could be feasible. In literature survey, main techniques for re-refining have been collected are Supercritical extraction, Membrane processing and Adsorbent treatments [7,9-10]. In this research, adsorbent treatment is focused due to cheap and easy method.

Numerous studies have been done previously to compare the efficiency and effectiveness of a single adsorbent. Silica gel was discovered to be more effective as compare to magnesium oxide, activated clay and aluminum hydroxide gel [9]. Magnesium silicate possessed highest ability to adsorb polar components of oil while diatomaceous earth had least ability to adsorb it among various adsorbents [7]. By observing that; silica gel, alumina (active and neutral) and magnesite have been researched in present work.

Magnesite has low price and available locally as compare to other mentioned adsorbents. The performance of magnesite is judged by analyzing FTIR (Fourier Transform Infra-red spectroscopy), color index, viscosity, free fatty acids, conjugated dienes value, saponification value and peroxide value in particular investigation.

2. Experimental Procedure

2.1. Materials:

Sample of waste oil was taken from one well known restaurant of Karachi having dark brown color. Hexane was used as solvent supplied by E. Merck and it was chosen on the basis of highest solubility in oil. Silica gel, Alumina (active and neutral) and magnesite were investigated. Silica gel (70-230 mesh) and alumina (100-200 mesh) were of analytical grade and provided by E. Merck while magnesite was obtained locally. Magnesite was sieved to particle size of 50-100 mesh and 100-230 mesh and both were examined individually. Magnesite was activated at 500^0C for 2 hours while silica gel was activated at 650^0C for 2 hours.

2.2. Adsorbent treatment:

Column chromatographic technique was adopted to re-refine deep frying oil by using an adsorbent packed glass column of 1.5 cm diameter. Solvent mixed dark brown used oil (solvent to oil ratio was 3:1) was introduced into the column with respect to the mass of adsorbent present inside the column using a particular mass / mass ratio. After adsorption, a light colored solution was obtained from the bottom of column. Solvent was separated for reuse from the adsorbed oil using rotary evaporator under vacuum. Vacuum drying was also carried out to get solvent free oil.

2.3. Analytical methods for Used, Adsorbed and Fresh oils:

Color index, free fatty acid and Saponification values of different oils were found by ASTM methods. Conjugated diene and peroxide values were determined by JAOCS (Journal of American Oil and Chemists Society) methods. Viscosity was measured by Ubbelohde viscometer having 0.3 cst/sec viscosity coefficient. Bruker Vector 22 spectrophotometer was used to achieve FTIR spectra of various oil samples using KBr disk at 4 cm^{-1} resolution for 20 scans with the help of OPUS software.

3. Results and Discussions:

3.1. Adsorption by Magnesite:

Activated magnesite is highly porous having 100-150 m^2/g surface area and it has been proved as an effective adsorbent regarding decolourization of solvent extracted used lubricating oil [11]. Properties of magnesite have been presented elsewhere [12].

Two different particle sizes 50-100 and 100-230 mesh of magnesite were tested for adsorption of deep frying cooking oil after activation. It is clear from the Fig. 3.1 that smaller particle size (100-230 mesh) gave better yield of low color indexed oil than 50-100 mesh particles. It is due to the better column packing with smaller voids and larger surface area of particles. 1:0.8 adsorbent to oil ratio gives not only good yield but also produces a low color indexed adsorbed oil. At this ratio, 100-230 mesh particles of magnesite give about 90% yield of transparent pale yellow (color index 1.5) refined oil (Fig 3.1). This ratio is suitable for the adsorption of coloring matter present in waste oil. It means that impurities present in oil are trapped not only in pores of magnesite but also attached at the surface due to its affinity for these matters.

It may be concluded that 100-230 mesh magnesite particles may be better for refining of deep frying cooking oil.

3.2. Adsorption by Alumina:

Alumina is a good conventional adsorbent having larger surface area (300-350 m^2/g) than activated magnesite and has been used in various decolorizing processes. Decolorizing ability of alumina was checked to refine the deep frying cooking oil using three different adsorbent to oil ratio.

Fig. 3.3 shows that the highest yield (about 93.5%) was obtained at 1:1 adsorbent to used oil ratio with production of the same color index (1.5) oil like activated magnesite (Fig. 3.2). Perhaps it is due to the larger surface area and better affinity for coloring impurities than magnesite. By decreasing adsorbent to oil ratio, yield and color index both become inferior.

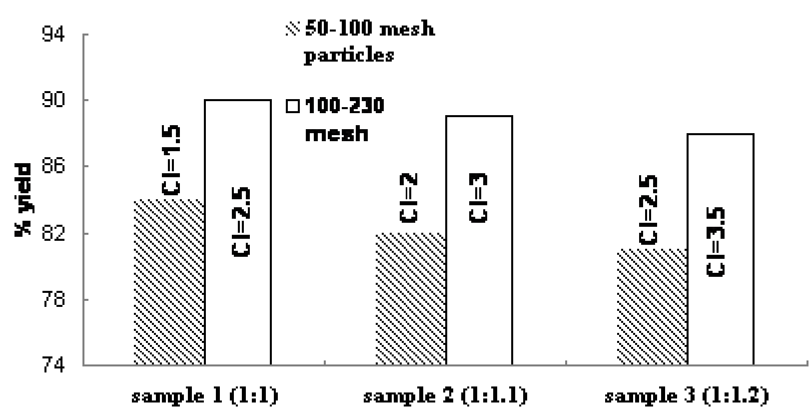
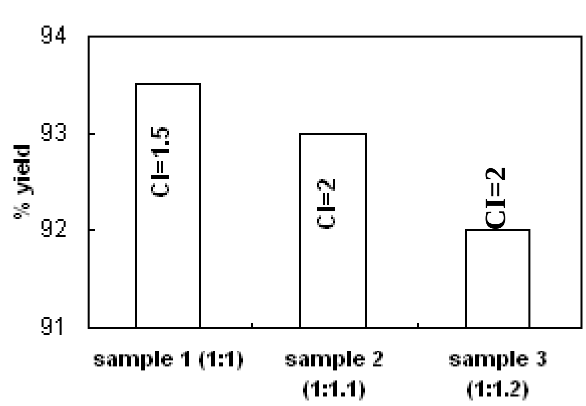


Fig. 3.1: Comparison of % yield of recovered oil obtained by 50-100 mesh and 100-230 mesh particles of manesite with color index (CI) of oil.



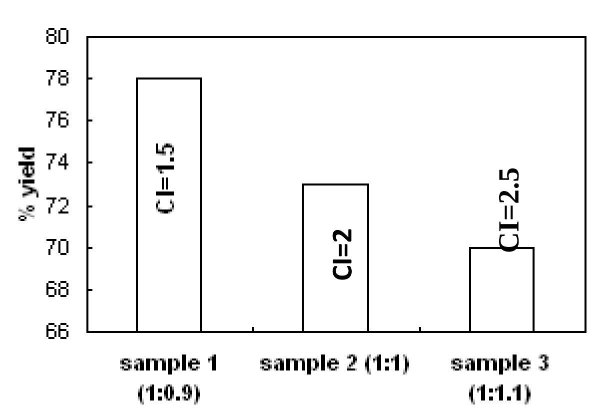


Fig. 3.2: Percent yield of recovered oil by alumina adsorption with color index (CI) of oil

Fig. 3.3: Percent yield of recovered oil by silica gel adsorption with color index (CI) of oil.

3.3. Adsorption by Silica:

Silica gel is another conventional adsorbent having the largest surface area (750-800 m^2/g) than the others two used in this study. It showed the least decolorizing capability for deep frying cooking oil at the same and the highest adsorbent to oil ratio (1:0.8). The recovered oil yield is only about 76% for the production of 1.5 color indexed oil (Fig. 3.3). Perhaps size of the coloring impurities present in used oil is larger than the pore entrance present at its particle surface hence most of the impurity particles are not able to enter then trapped into the pores. Moreover, surface affinity of silica particles may also be weak for impurity particles.

3.4. Effect on Conjugated Diene value:

A number of conjugated dienes are formed in cooking oil at deep frying temperature. A good adsorbent can minimize their amount during elution of oil. All the three adsorbents (magnesite, alumina and silica) reduce them during adsorption up to a certain level. In this regard, performance of magnesite is the best that separated the conjugated dienes up to the minimum level from 0.52 (used oil value) to 0.2 (Table 3.1). This value is almost equal to the conjugated diene value of fresh cooking oil.

3.5. Effect on Saponification value:

During deep frying of a food, a number of saponifiable triglycerides are also formed at high temperature of oil. In this study, magnesite has the best ability to reduce these matters from used oil during adsorption and produces the lowest Saponification value oil. This value (151.14) is near to the fresh canola oil value (150.42) shown in Tale 3.1. Other adsorbents did not reduce the Saponification value up to the significant level.

3.6. Effect on Peroxide value:

Deep frying process of cooking oil favors oxidation of not only triglycerides but also degraded components resulting a number of peroxide molecules formations [5]. These peroxide molecules can be removed by an effective adsorption process. Magnesite has been proved an efficient adsorbent by this study for the removal of such peroxide molecules that enhance peroxide value of deep frying oil at high temperature. It reduces peroxide value from 2.46 to 1.16 (Table 3.1) whereas alumina and silica were not found better adsorbent regarding for the reduction of this value.

3.7. Effect on Free Fatty Acids (FFA):

Significant amount of free fatty acids are found in all vegetable oils. Deep frying process develops more quantity of these shorter chain acids by breaking large triglycerides molecules [5]. These acids may also be incorporated from food. Magnesite minimized these acids efficiently during adsorption. FFA value of used oil was 2.24 that became 0.08 after adsorption by magnesite showing in Table 3.1. This FFA value obtained by magnesite adsorption showing compatibility between recovered and fresh canola oil. While in the other hand, other adsorbents could not remove the FFA sufficiently.

3.8. Effect on Viscosity:

Deep frying process forms a number of oil soluble degradation and oxidation products at high temperature causing increase in viscosity. This increase in viscosity may also be due to the formation of high molecular weight polymers, cyclic compounds, dimmers, trimers and epoxides [12]. Viscosity of adsorbed oil samples by magnesite, alumina and silica gel was determined at room temperature (32^0C). Comparison of viscosity of these samples with used deep frying and fresh canola oils is presented in Table 1. It shows that viscosity of magnesite adsorbed oil is compatible with fresh oil. It means that magnesite adsorbed almost all soluble matter present in degraded oil which were responsible to increase in viscosity.

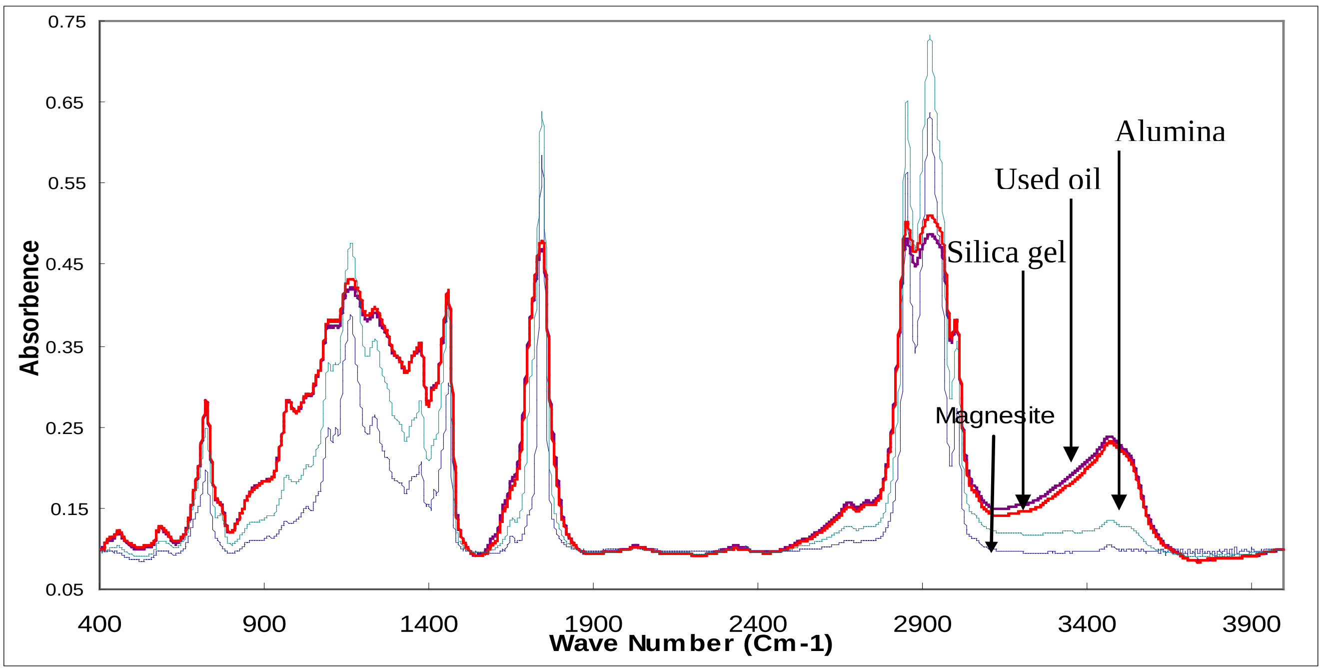
Table 1

Properties of deep frying used, fresh canola (for reference) and various recovered oils after treatment with different adsorbents (Magnesite, Alumina and Silica).

Parameters	Used oil	Magnesite	Alumina	Silica	Fresh oil
Conjugated diene value	0.52	0.2	0.24	0.3	0.19
Saponification value	197.22	151.14	155.24	159.01	150.42
Peroxide value (meq active oxygen/kg)	2.46	1.16	1.35	1.24	1.14
Free fatty acids	2.24	0.08	0.47	0.59	0.06
Viscosity (cst) at 32^oC	66.7	42.6	46.8	45.2	42.3
Color index	5	1.5	1.5	1.5	1.5

3.9. Analysis by FTIR:

The FTIR spectroscopy is a good tool to analyze the oxidation of cooking oils after deep frying of food. Typical FTIR specta of used deep frying, magnesite, alumina and silica gel treated oils are presented in Fig. 3.14. The most prominent peak in all spectra is at 1743 Cm-1 showing C = O aliphatic ester stretching [13, 14]. The strong bands at around 2922 and 2852 Cm−1 have been assaigned to asymmetrical and symmetrical C-H stretching of CH_2 group vibrations. A band at around 1157 Cm−1 has been assigned to C – O bond stretching of aliphatic esters [15-18]. On comparing the spectrum of used oil with treated oils, it may be observed that the region 996-983 cm-1 has the lowest value of absorbance for magnesite treated oil. This region has been assigned for conjugated double bonds present in cooking oils [19]. Similarly, no peak is present at around 3300 Cm-1 in the spectra of magnesite and alumina treated oils however absorbance of magnesited treated oil is the lowest at this point showing negligible concentration of hydroperoxide and free fatty acids [20] in magnesite treated oil. 1716 Cm-1 has also been assigned for free fatty acids [19]. At this point, the magnesite treated oil has also the least absorbence than other oils.



4. Conclusion:

Different porous adsorbents were used in this study to re-refine deep frying cooking oil. Magnesite is indigenous and cheap adsorbent that produced a good quality refined oil from deep frying cooking oil. It produced low color indexed transparent pale yellow oil. Properties of magnesite treated oil (color index, viscosity, saponification, peroxide, cojugated diene and free fatty acid values) are compatible with the properties of fresh cooking oil. FTIR spectrum of this oil is also showing its least absorbence regarding the presence of free fatty acids, hydroperoxides and conjugated diene. Alumina and Silica gel also produced low color indexed refined oils than the used oil however quality of these oil is inferior than the magnesite treated oil.

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