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BLEACHING OF SUNFLOWER WASTE OIL BY ABSORPTION ON ACTIVATED CARBON AND IMPROVED BY OZONISATION

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Abstract*: The present investigation attempts to bleach the sunflower waste oil which can be reused for many industrial applications. A comprehensive bleaching technology developed with activated carbon and liquid ozone under laboratory condition. Laboratory bleaching was performed with different concentrations of activated carbon (w/v) in a round bottom flask under a vacuum. During the bleaching process, coloring pigments like carotenoids, chlorophylls, gossypol, peroxides and other impurities are removed from the edible oil using activated carbon. The bleached oil was retreated with different concentrations of liquid ozone and incubated at room temperature (27^0C) for 24 to 120 hrs. The retreated oil samples were drawn at every interval of 24 hrs, analyzed and the bleaching capacity were measured with UV-VIS Spectrometer to measure light absorbance in the visible region at 455 nm. The absorbance values decreased with respect to the increased mass of activated carbon (w/v in %) and liquid ozone. Bleaching of crude oil with activated carbon and liquid ozone are affordable method for sunflower waste oil management and recycling .*

Keywords*:Oil bleaching; Activated carbon; Liquid ozon; free fatty acid; Waste oil management.*

I. Introduction

In edible oil refining, both by chemical or physical process, the bleaching treatment is a critical step and the conditions for bleaching step depend on the type of crude oil and its quality. The main task of bleaching is the removal of color pigments and the decomposition of hydroperoxides. This increases the shelf life and aesthetic value of the product [1]. The sunflower oil is the edible oil produced in the world due to its favorable agronomic characteristics, high quality protein and valuable edible oil. Oil produced by mechanical pressing is termed crude soybean oil. The sunflower crude oil is a dark blackish brown color and has a strong characteristic flavor and odor. It contains free fatty acids, triglycerides, numerous minor components such as gossypol, phospholipids, tocopherols, sterols, carbohydrates, hydrocarbons and other pigments [2]. Oil bleaching, which is carried out in order to prepare a sufficient light-colored product of enhanced appearance and stability is improved, usually achieved by treating the crude or the refined oil with powdered absorbent. The principle of bleaching is based on several adsorption mechanisms including physical adsorption through van der Waals' forces, chemical bonding via covalent or ionic bonds, ion exchange, molecular trapping and chemical decomposition [3]. During the bleaching process, coloring pigments (primarily carotenoids, chlorophylls, gossypol), peroxides and other impurities are removed from the edible oil. Gallons of sunflower crude waste oil generated in India and it's used as fuels in various industrial applications, because the color of waste oil is blackish brown. This paper describes methods for color improvement of sunflower waste crude oil and it can be used for paints and resins industries etc.

II. Materials and Methods

The sunflower waste crude oil collected from five Edible oil extraction industries located in Bangalore, Karnataka, India. Each industry is generating approximately 30,000 liters of crude oil after filtration and extraction of valuable ingredients. The collected samples were collected and brought to the laboratory for the experiment.

A. Filtration

Crude oil was moderately heated upto 450C – 500C passed through the muslin cloths having the pore size of 5-6µm under the vacuum to remove the sunflower seed debris. The filtrate was collected and stored in a room temperature for further analysis.

B. Bleaching of oil using activated carbon

Laboratory bleaching was performed with different concentration of activated carbon (w/v) in a round bottom, three-necked flask of 500 ml equipped with a thermometer and attached to a vacuum pump. Bleaching was conducted using an electromagnetic mixer with adjustable heater. All bleaching parameters are given in Table 1. The filtered sunflower oil neutralized with suitable alkali. Weighed 250 g of oil into a round-bottom and the oil was stirred at 150 RPM under vacuum by using a vacuum pump and heated to 80°C in a mantel heater. Vacuum disconnected and the required amount of activated carbon as 0, 1, 2,3 per cent (w/w) was added to the hot oil. Then, vacuum was applied and the temperature was raised to a top bleaching temperature of 100°C (±1). These conditions were kept constant for the desired bleaching time 20, 30 or 40 min. At the end, the bleached oil was cooled to 70°C and allowed for settling, then filtered through filter paper (Whatman no. 541) under vacuum. Sample of bleached oil were stored at 50^0C for further color development.

C. Further color development with liquid Ozone

Ozone was generated by passing oxygen through an Ozone generator model TL03 at a fixed voltage (230 V), and a constant flow rate of 20 L h-1. The ozone initial concentration (55.2 mg/L) was determined modified Indigo method[4]. Bleached oil was treated with different volume/ concentration of liquid ozone. The whole content was stirred about 15mins and transferred into separate funnel for settling. Same experiments were repeated with different volume/concentration of liquid ozone (5,10, 15, 20,25ml) and incubated at room temperature for 5 days. Samples were drawn every 24hrs incubation for further analysis.

D. Estimation of Free-fatty Acid Content

The amount of free fatty acids was determined by simple titration using AOAC method, 1995 [5]. 1 ml of the sunflower crude oil and 2 ml phenolphthalein was added to 50ml alcohol in clean, dry flask. Then flask was placed in a water bath at 60-65°C until warm and titrated with 0.1N NaOH to produce faint permanent pink. 56.4g oil was weighed into the same flask and titrated again with 0.1N NaOH. The mixture was shaken until same faint permanent pink appears in separate alcohol. Reported as;

Free-fatty acid (as oleic acid) % = ml 0.1 N NaOH × 0.05

E. Color Determination

The color of bleached sunflower oil was measured by UV-VIS Spectrometer (Systronics, UV-VIS 118, India) to measure light absorbance in the visible region at 455 NM. This technique involves matching the color of light transmitted through a specified depth of oil with the color of light transmitted from the same source through a set of colored glass slides. Color reading is thus subjective and depends on the analytical skill judgment as well as on the type and model of colorimeter used.

III. Result and Discussion

A. Bleaching waste oil using Activated carbon

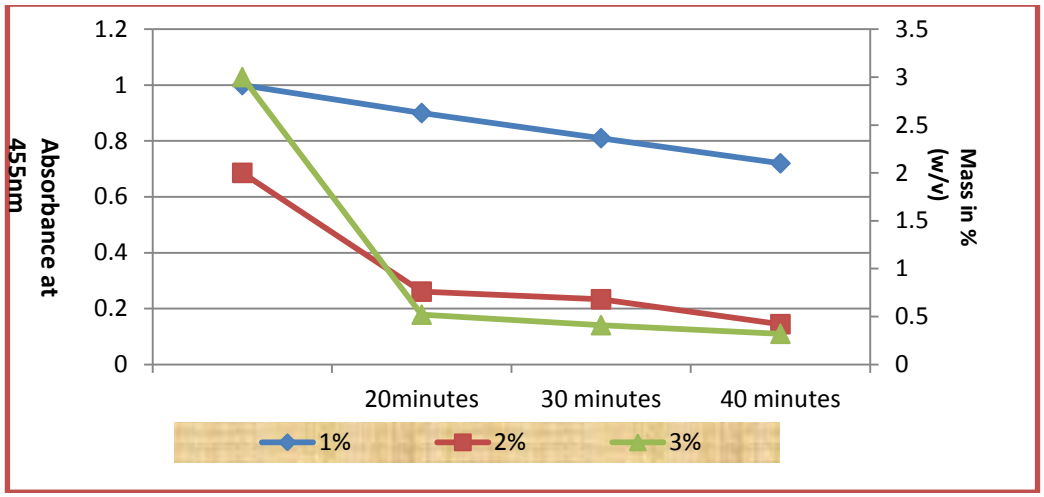
In this study, the bleaching experiments were conducted with different mass of activated carbon (0, 1,2,3,4, and 5 %) at different contact time (20mins, 30mins and 40 mins). Entire experiment was carried out at 100°C (±2) with continuous mechanical spinning. Bleaching level was measured by absorbance at 455nm. The results of bleaching process with activated carbon were reflected in table: I.

Table I: Shows Bleaching parameters of sunflower waste oil using activated carbon

Activated carbon in % (w/v)	Temperature (0C)	Time in Mins	Absorbance at 455nm
0	100	20	1.45
		30	1.45
		40	1.45
1	100	20	0.9
		30	0.81
		40	0.72
2	100	20	0.76
		30	0.68
		40	0.42
3	100	20	0.52
		30	0.4
		40	0.32

The absorbance values were decreased with respect to increased mass of activated carbon (w/v in %) . The absorbance value of bleached oil decreased A=0.90 to A= 0.32 at 455nm. 1% (w/v) of activated carbon improved the crude oil color resulted with absorbance value of 0.9 within the contact time of 20 mins. Further, the absorbance value was decreased to A= 0.81 and A= 0.72 within the contact time of 30 and 40 minutes. 2% (w/v) of activated carbon gives result of the absorbance value A= 0.76, A=0.68 and A= 0.42 within the contact time of 20 mins, 30mins and 40mins. Similarly, 3% (w/v) mass of activated carbon bleached the crude oil resulted with the absorbance value of A= 0.52, A= 0.40 and A= 0.32 with contact time of 20mins, 30mins and 40 mins respectively (Figure I). The result of crude oil treating with activated carbons indicates that bleaching efficiency of activated carbon increased with contact time and mass of absorbent. The absorbance results directly proves that activated carbon removes the unwanted plant pigments like carotenoids, chlorophylls etc. Similar finding by Toro Vazquez [6] that Carotenoids are efficiently removed by adsorption with activated carbon in soybean, cottonseed, corn, and squash seed oil. Similarly, groundnut oil has been decolorized by activated carbon from coconut shells. The adsorption of color bodies increased rapidly with an increase of temperature and mass of absorbents [7]. Besides, there were no obvious changes for free-fatty acid contents in activated carbon bleached oil. These values approximately estimated around 0.065 % .

Figure 1: Bleaching efficiency of activated carbon at different contact time



B. Bleaching with Liquid Ozone

Bleached crude oil was re-treated with liquid ozone in different concentration and incubated at room temperature for five days. The samples were drawn at every 24hrs incubation period and bleaching rate was studied at 455nm and the results were reflected in Table 2. Experimental results of bleaching with liquid ozone reveals that absorbance value of bleached oil decreased with increasing concentration of liquid ozone and incubation time. Initially, the absorbance was A= 0.850 (5ml of Liquid Ozone at 24hrs contact time) and decreased to A= 0.462 at 120 hrs. Similarly, 10ml of liquid ozone significantly developed the oil color at incubation period of 120hrs. The recorded absorbance was A= 0.463 at 24hrs and absorbance was decreased to A= 0.174 at 120hrs ie.5days (Figure II). However, high concentration of liquid ozone i.e 15 (w/v) to 25(w/v) did not produce any significant results in bleaching the sunflower oil. Beside, free fatty acid content increased after treating with ozone. Initially, 0.0657% of free fatty acid was estimated after treating with activated carbon and the values gradually increased to 0.0698% (Figure III). Sunflower oil is a monounsaturated (MUFA)/polyunsaturated (PUFA) mixture of mostly oleic acid (omega-9)-linoleic acid (omega-6) group of oils. Excess of free fatty acid is attributed by linoleic acid, Oleic acid hydrolyzed by ozone and liberated the free fatty acid. Ozone has distinct mechanisms of action depending on the environment in which it is applied, being subject to different classifications according to their predominant behavior. Humidity, oxygenation and temperature have a great effect on the action of ozone, being directly proportional to its effectiveness[8][9]. Ozone is a highly reactive gas and its main characteristic is to react with molecules that have double bond between carbon atoms (> C = C <), breaking the connection with the introduction of an oxygen atom at each end of the link (2> C = O) and thus forming two new compounds[10]. Several of the formulations described as ozone stabilized liquid solutions use vegetable oils such as olive oil. Molecules that composes the vegetable oils have double bond > C = C < in its structure. Therefore, it can be expected that the contact of ozone with these substances generate new compounds by the reaction of breaking the double bonds. The ozone present in oily vehicles could have advantages over gaseous or aqueous media , since the oil remains in contact with the surface for a longer period of time, exercising its functions for a longer period [11].

Figure II: Decreasing tendency of absorbance indicates that further bleaching has improved by liquid ozone

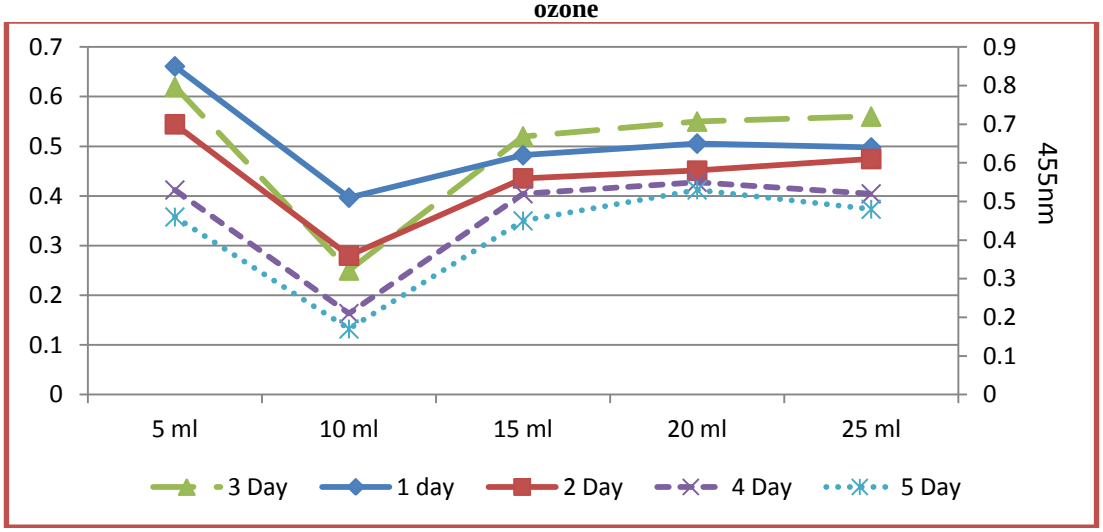
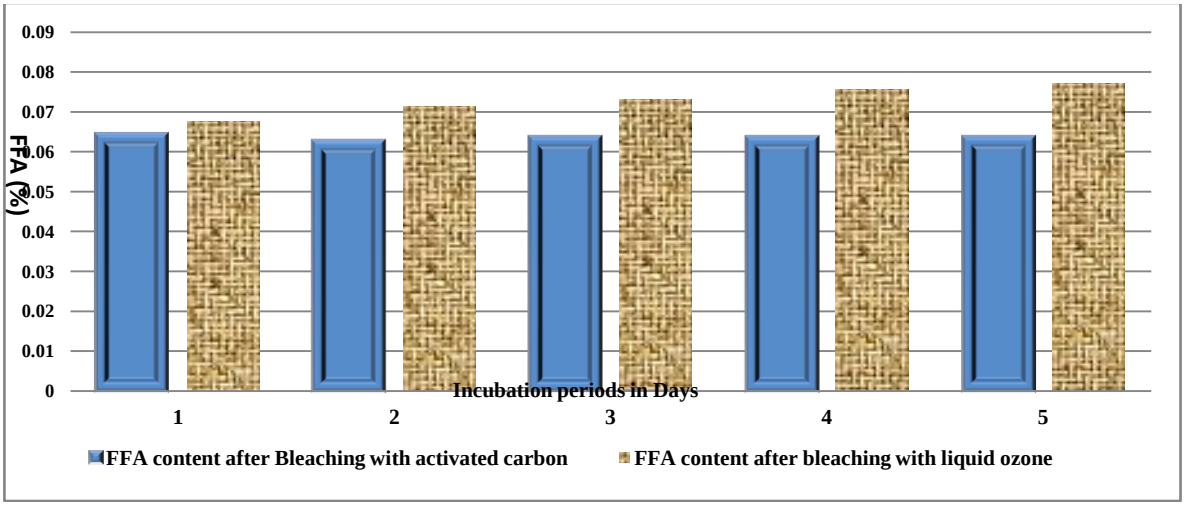


Table II. Color Improvement parameters using Liquid Ozone

Volume of Liquid Ozone (ml) (Ozone Con=55.2mg/L)	Temperature (°C)	Incubation period (Days)	Absorbance at 455nm
5	27-37	1	0.85
		2	0.7
		3	0.62
		4	0.53
		5	0.46
10	27-37	1	0.46
		2	0.36
		3	0.25
		4	0.21
		5	0.17
15	27-37	1	0.62
		2	0.56
		3	0.52
		4	0.52
		5	0.45
20	27-37	1	0.65
		2	0.58
		3	0.55
		4	0.55
		5	0.53
25	27-37	1	0.64
		2	0.61
		3	0.56
		4	0.52
		5	0.48

Figure III: Shows percentage of Free fatty acid (FFA) content of bleached oil



IV. Conclusion

The study indicates that the efficiency of activated carbon on sunflower crude oil bleaching were determined by the type of absorbent used and contact time. Bleaching efficiency of activated carbon gradually increased with contact time and mass of absorbent used. The percentage of free fatty acid (FFA) contents remains constant throughout the study. The treated crude oil color was subjected to ozone treatment. Color of carbon treated crude oil further improved when treated with ozone 10mg/L with contact time of 120hrs (5days) at constant temperature 27- 37^0C is most suitable for bleaching sunflower crude oil. Besides, the percentage of free fatty acid contents increased by reactive ozone present with longer exposure time. Bleaching is only a part of oil refining process and certain negative effects can be corrected during ozonisation. The proposed method for bleaching crude sunflower oil can be applied for industrial application. The bleached sunflower oil is not suitable for edible purpose but it can be used by paint and lubricant industries. The proposed method may be appropriate for management and recycling of sunflower waste oil.

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