

Use of starch and actived tigernut by-product from the extraction of tigernut (*Cyperus esculentus*) milk for the purification of used cooking oils

Bou NDIAYE ^{1, 2, 3, *}, El Hadji Moussa DIOP ^{1, 3}, Khadim NIANE ^{1, 2}, Mohamed NDOYE ¹, Edouard Mbarick Ndiaye ^{1, 2}, Samba BALDE ^{1, 2} and Nicolas C. M. AYEISSOU ^{1, 2}

¹ Laboratory of Water Energy Environment and Industrial Processes (LE3PI), ESP-UCAD, ESP-UCAD, Cheikh Anta Diop University, BP 5085, Dakar, Senegal

² Center for Studies on Food Security and Functional Molecules (CESAM), Dakar, Senegal, (ESP-UCAD).

³ Higher School of Industrial and Biological Engineering (ESGIB), Dakar- Sénégal.

GSC Advanced Research and Reviews, 2024, 20(02), 119–127

Publication history: Received on 09 March 2024; revised on 11 August 2024; accepted on 14 August 2024

Article DOI: <https://doi.org/10.30574/gscarr.2024.20.2.0150>

Abstract

The management of used cooking oils represents a real economic and environmental challenges. The search for bioadsorbents allows for the pre-treatment of used oils suitable for reuse. Tigernuts starch and by-product from the extraction of tigernut milk are used as bioadsorbent in the purification of used oil. The objective of this study is to reduce the acid and peroxide values. Used oil is treated with 8 and 12% starch during 10, 20, 30 and 40 min heating. Activated by-product were used as adsorbent at 1 and 2% after adsorption with starch. The results show abatement rates ranging from 1.65 to 27.51% for the acid value and from 39.16 to 73.48% for the peroxide value for 8% starch. Reductions rate of 23.50 to 34.44% and 58.06 to 71.33% respectively for the acid and peroxide values during treatment with 12% starch. The oil pre-treated with 8% starch shows an acid number reduction from 28.58 to 38.40% with 1% residue. Peroxide value shows reductions of 75.74 to 80.15% with 1% residue and 77.37 to 80.66% with 2% residue. The pre-treatment with 12% starch shows an acid value reduction ranging from 27.88 to 49.01% and from 14.0 to 35.08% with 1 and 2% residues. The peroxide value abatement ranges from 60.26 to 85.12% and from 77.37 to 87.33% with 1 and 2% residues. Tigernut starch can be used to purify used frying oils. However, its effectiveness is seen more in reducing the peroxide value. The combination of activated by-product and starch is more effective.

Keywords: Used cooking oil; Tigernut by-product; Starch; Adsorption; Purification

1. Introduction

The food industry is a very important sector and one of the most dynamic in the world. However, it can generate a very large quantities of waste, such as used frying oil. These oils come mainly from catering companies and food processing industries [1]. It is one of the second generation wastes that are produced extensively in the world, with an estimated annual production of 190 million tonnes [1]. Oils kept at high temperatures for long periods during frying, combined with the release of water from the food, are subject to hydrolysis and oxidation reactions. Free fatty acids and peroxide compounds are among the most harmful products in used frying oil. These contain impurities, free fatty acids, carbonyl compounds and sulphur compounds [1], which can affect the quality and safety of fried food. This used oil can present risks to human health and the environment [2]. However, although they are waste products, they represent real resources and are used today in several areas[2], [3], [5]. As a result, the treatment of waste cooking oil has become an important topic of research to improve environmental and health quality [4], [3]. Different physical and chemical technic are used to reduce the level of contamination of waste oil. However, the search for effective and less toxic compounds is the major concern of some researchers [6],[4]. Biomass products are widely exploited in this sense [7]. This study is

* Corresponding author: Bou NDIAYE

in line with this search for adsorbents. Tiger nuts is a tuber rich in starch. However, very little work has been done to study the adsorption properties of Tiger Nut starch, especially in the context of the treatment of used frying oils. The aim of this study is to use tigernut starch and activated by-products from milk extraction to purify used cooking oil by analyzing the acid and peroxide indexes of the two components.

2. Material and methods

2.1. Materials

2.1.1. Used frying oil

Frying oil was collected from fast food restaurants and large restaurants in Dakar. The oils obtained were mixed to form a homogeneous batch for analysis.



Figure 1 Used cooking oil

2.1.2. Tigernut tubers

Tigernut tubers of the brown variety are used in this study. They are an important source of starch, with a content of up to 30% by weight.



Figure 2 Tigernut tubers

2.2. Method

2.2.1. Extraction of starch from tigernut tubers.

The tigernut tubers are carefully cleaned to remove soil and impurities. They are then washed to remove residues. After washing, the tubers are placed in water for 24 hours. After the soaking time, the tubers are mixed with a blender and the resulting mixture is filtered (Figure 3).



Figure 3 Tigernut milk extraction processing

The resulting milk is decanted (Figure 4). The decantate was dried in an oven to obtain a solid final product (Figure 5). The dried starch was used as an adsorbent to purify the frying oil.



Figure 4 Starch decantation

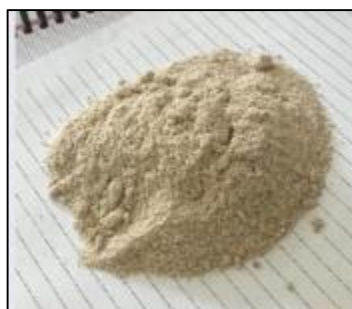


Figure 5 Dried starch

2.2.2. Bioadsorbant activation

The method described by Caleb MacCarthy and Stephen Adusei (2021) [8] and Wannahari and Mad Nordin (2012) [9] is used for bioadsorbant activation. The tigernut residues from the extraction of tigernut milk are used to produce a bioadsorbent. The co-product powder was heated to 200°C for 120 min. The heated coproduct was then mixed with 0.1 M NaOH and heated again for 90 min on a hot plate. The mixture was filtered. The filtrate was discarded, and the residue was heated to 200°C for 60 min. The dried residue was then ground and sieved (Figure 6).



Figure 6 Activated bagasse

2.2.3. Purification methods of used frying oil

Adsorption on starch

The used oil is first decanted for 48 hours in order to separate impurities such as solid particles and food remains. After settling, part of the oil is filtered through a fabric filter. The filtration is followed by adsorption with starch at 8% and 12%. After mixing the oil and starch, the mixture is heated on a hot plate for 10, 20, 30 and 40 minutes. The heated oil in the presence of starch is cooled and filtered and analysed. Each treatment gives 4 samples.

Adsorption with activated co-products

The used oil previously treated with starch is then treated with different proportions of adsorbent (1% and 2%) for each sample. The oil-coproduct mixtures are placed on a stirring tray at 500 RPM for 30 minutes. The samples from the 1 and 2% treatment are 16 samples. The processing method is described in the following diagram (Figure 7).

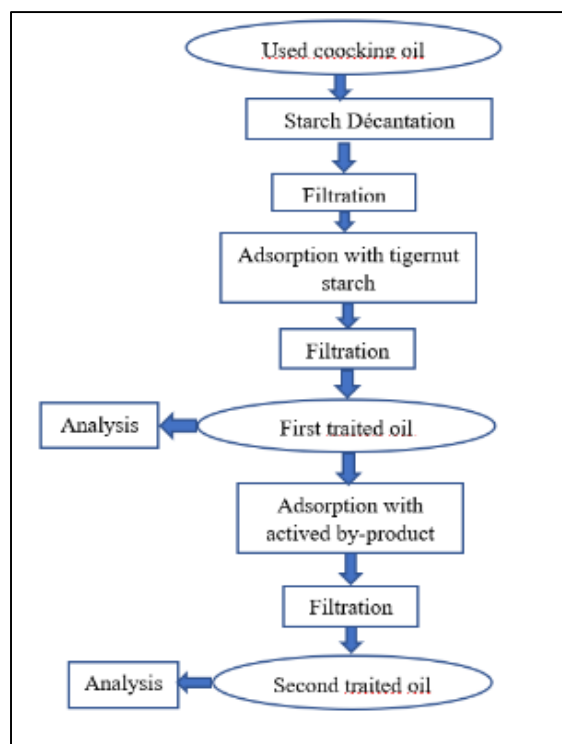


Figure 7 Processing diagram

The steps in the oil purification process are illustrated in figure 8.

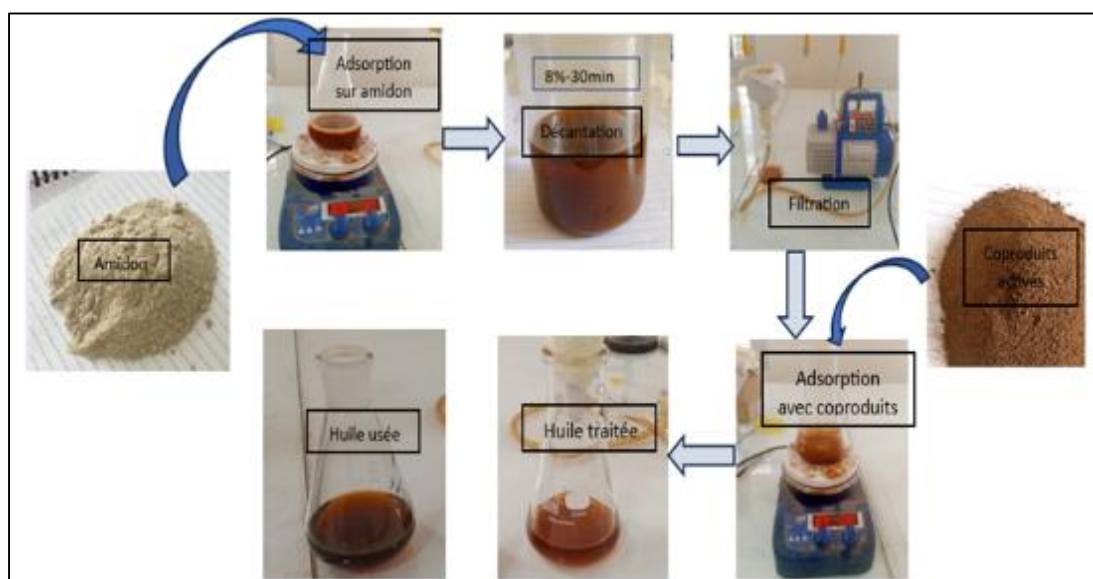


Figure 8 Steps in the oil purification process

2.3. Methods of analysis

The acid and peroxide indices are the parameters investigated in this study.

2.3.1. Determination of the acid number

The acid number determination is based on the steps described in the standard protocol of the AFNOR NFT 60-204. A weight of 1 g of samples were weighed and dissolved in 10 ml of ethanol in the presence of phenolphthalein. The mixture is then titrated with a 0.1 N ethanolic potash solution contained in a burette. The number of milligrams of potassium hydroxide required to neutralise the free acidity of the oil was then calculated using the following formula.

$$I_a = \frac{N \cdot V \cdot 56.1}{m} \text{ (mg KOH/g oil)}$$

N: normality of of KOH (0.1 N);

V: volume (ml) of KOH

Molar mass of KOH: 56.1g/mol.

2.3.2. Peroxide value determination

The European standard method NE 2658-91 is often used to determine the peroxide value of fats and oils. Total of 5 g of each sample of cooking oil was put into conical flask then added 30 ml of acetic acid - chloroform (3: 2), and 1ml of saturated potassium iodide solution. Then 75ml of distilled water and 0.5ml of starch indicator were mixed as indicator solution. The latter is titrated with 0.1 N sodium thiosulphate. The mixture was titrated with 0.1 N of $\text{Na}_2\text{S}_2\text{O}_3$ solution until the blue color began to disappear. The peroxide number expressed in milliequivalents of peroxide is calculated from every 1000 g of the sample.

N : represents the normality of the titrated sodium thiosulphate used ;

V_0 : represents the titration volume (ml) of the blank ;

V_s : represents the titration volume (ml) of sample ;

m: represents the mass of the test sample in grams ;

$$\frac{N * (V_s - V_0) * 1000}{m}$$

3. Results

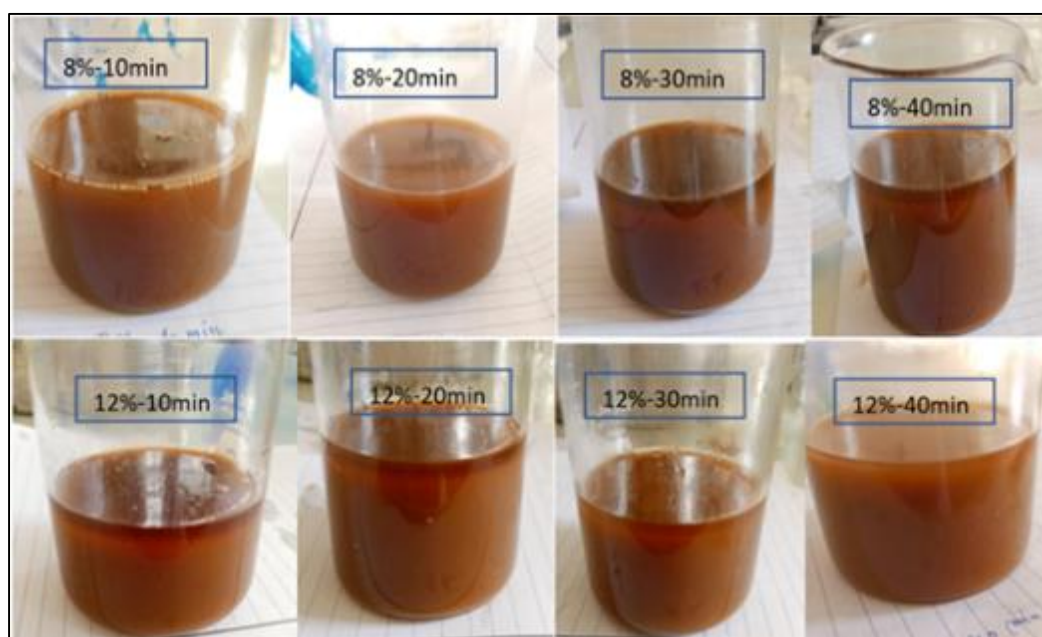


Figure 9 Treated oil with 8% et 12 % tiger nut starch (10, 20, 30 et 40 min)

The used oils are characterised by a deep colour degradation due to the presence of oxidation compounds. There is a clear difference between the oils treated with starch (Figure 9) and the untreated used oil. For the different treatments

taken individually, a significant difference was observed compared to the untreated sample. The results of the adsorption on starch show a significant improvement of the colour.

3.1. Effect of treatment with 8% and 12% starch

The acid number analysis is the quantity of free acids in the oil and is used to appreciate the oxidation state of an oil. The adsorption with 8% of starch shows acid values of 7.221; 5.61; 5.82 and 7.574 mg KOH/g for the 10; 20; 30 and 40 min treatments respectively (Figure 10). The adsorption abatement rates observed varie between 1,65 to 27.51%. However, it can be constated a litle decrease of acide value at 40 min of heating. For the treatment with 12% starch, the acid value varies between 5.049 and 5.891 mg KOH/g. The abatement rates are 27.15 ; 23.50 ; 33.83 and 34.44% during treatment times with 10; 20; 30 and 40 min respectively(Figure 10). The highest rate is observed at 40 min. However, a slight decrease in the acid value was observed at 20 min of treatment.

Tigernut starch was used to study his efficacy in peroxid compounds removing. The treatment with 8% starch revealed values of 11.012 ; 7.293 ; 4.8 and 7.485 meq O₂/Kg respectively for the treatment times of 10, 20, 30 and 40 min (Figure 11). The observed peroxide values are 5.19; 5.456 ; 6.494 and 7.592 meq O₂/Kg respectively for the treatment times of 10; 20; 30 and 40 min with 12% starch (Figure 11). The results show an abatement rate ranging from 39.16 to 73.48% and 58.06 to 71.33% respectively for 8 and 12% of starch. The highest reduction rate was observed after at 10min and 30min treatment respectively for 8 and 12% of starch.

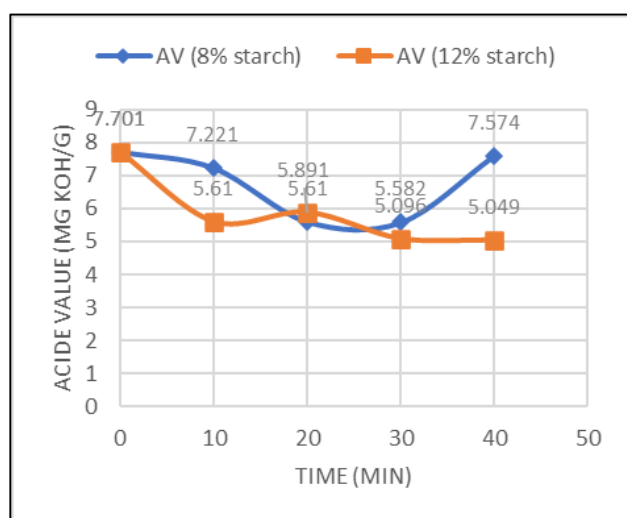


Figure 10 Acide value with starch (8 and 12%)

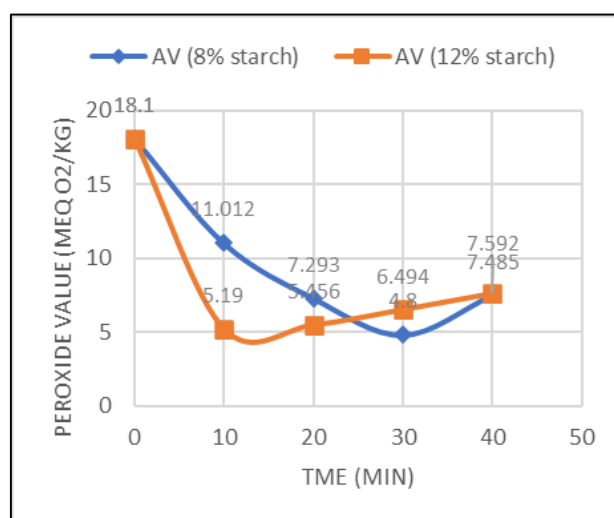


Figure 11 Peroxid value with starch (8 and 12%)

3.2. Effect of the treatment with combination of starch and in activated byproducts

3.2.1. Peroxide value

The analytical results obtained in the treatment of 8% of starch samples traited with 1% and 2% of co-product show respectively a peroxide value varying from 18.1 meq O₂/Kg in non traited oil to 3.593 meq O₂/Kg and from 18.1 meq O₂/Kg to 3.500 meq O₂/Kg (Figure 12). The maximum removal rate is 80.15% and 80.69% respectively for 1% and 2% of activated tigernut by-products (ATBp). These adsorption rates are observed at 40 min and 20 min respectively. The samples traited preverly with 12% of starch revel that peroxide value decreased from 18.1 meq O₂ /Kg to 2.694 meq O₂/Kg and from 18.1 meq O₂ /Kg to 2.293 meq O₂ /Kg of oil (Figure 13) for the treatments with 1% and 2% co-products respectively. A significant reduction was observed. The highest adsorption rates obtained with the 1% and 2% co-product treatments are 85.12% and 87.33%. These are observed at 20 min of treatments.

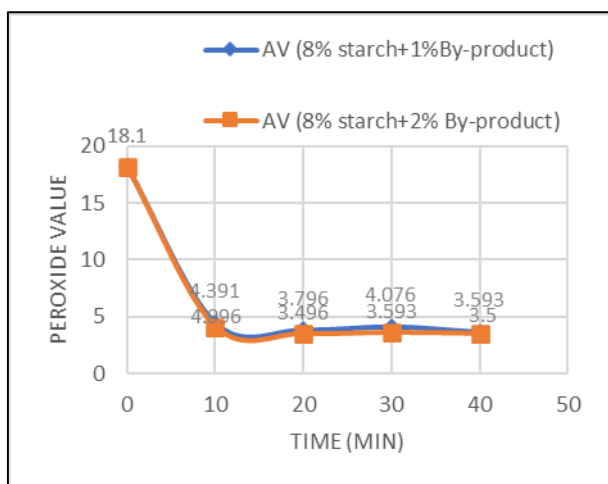


Figure 12 Peroxide value with starch (8%) and 1/2% ATBp)

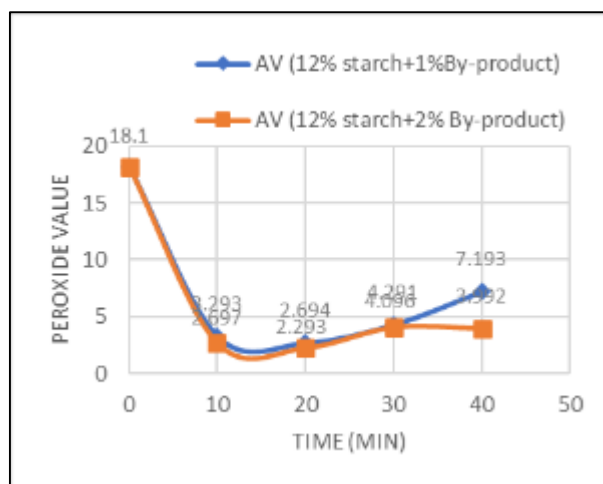


Figure 13 Peroxide value with starch (12%) and 1/2% ATBp)

3.2.2. Acid value

The results obtained after treatment with byproducts varied from 7.701 and 3.927 mg KOH/g with 1% and 7.01 and 3.61 mg KOH/g with 2% co-products respectively after first purification with 8% of starch (Figure 14). The high adsorption rates observed are 38.40% at 20 min and 53.12% at 40 min for the sample treated with 1% and 2% of byproduct respectively. For samples treated with 12% of starch, the acid values vary from 7.701 to 3.927 mg KOH/g and from 7.701 to 4.999 mg KOH/g for the treatment with 1% and 2% byproduct respectively (Figure 15). The high removal rate are 49.01% at 20 min for 1% byproduct treatment. The treatment with 2% co-product gives an abatement rate of 35.09% at 30 min.

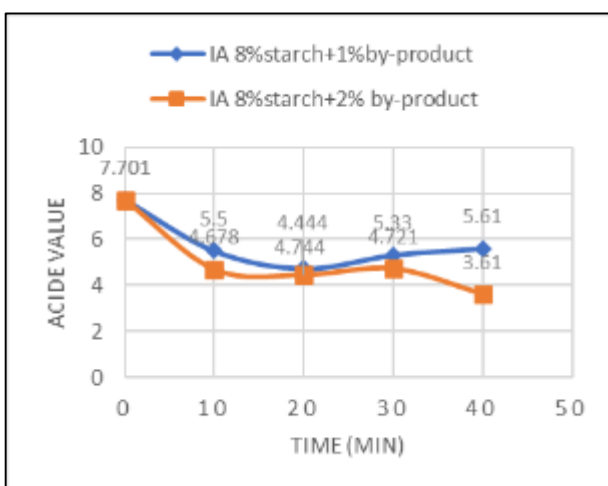


Figure 14 Acide value with starch (8%) and 1/2% ATBp)

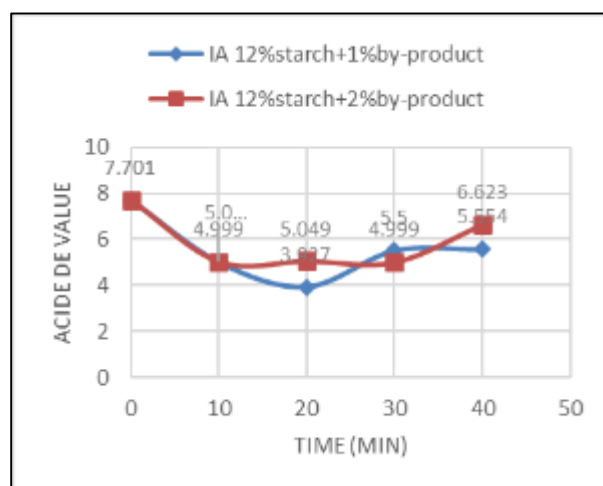


Figure 15 Acide value with starch (12%) and 1/2% ATBp)

4. Discussion

The treatment process reduces the level of oil oxidation. It can be observed in this study, a reduction in the peroxide and acid values. The tigernut starch acts in the process as an adsorbent for the acid and peroxide compounds. The technical treatment applied in the adsorption process with starch is thought to increase the solubility of fatty acids and peroxide compounds in the oil, making them more accessible to the adsorbent. Starch known for its adsorption properties [10]. Starch is believed to have adsorption properties for polar compounds. Plasticization of the starch during heat treatment could be at the origin of adsorption. However, it was found that adsorption with starch was greater on peroxidised compounds than on acidic compounds.

The highest abatement rates obtained with starch were 34.44% (12% starch) and 73.48% (8% starch) for acid and peroxide values respectively. Under the effect of heat, the starch adsorbs the residues and impurities in the oil and reduces the free fatty acids and peroxides. The products of the Maillard reaction are powerful antioxidants that could be associated with the reduction of peroxide compounds [11]. Slight increases in acid and peroxide values were observed in both processes, which could be explained by desorption of the compounds due to saturation. Similar results were obtained by Yazid in their study [7]. The combination of starch and co-products activated by NaOH showed the best adsorptions. The rate of adsorption remained virtually constant regardless of the duration of the heat treatment for samples treated with the starch-coproduct combination (8% starch + (1% or 2%) coproducts) for peroxides. However, slight desorption was observed with the 12% starch-coproduct combination from 30min onwards. The best abatements observed were 53.12% and 87.33% for the acid and peroxide indices respectively. A deacidification rate of around 77.11% was obtained using NaOH in the work of Ding et al., (2012) [12]. The work of C. MacCarthy and S. Adusei (2021) [8] showed a reduction of around 82% for a mass to volume ratio of 2.5 g per 50 ml of oil with activated sugarcane bagasse. This study showed an increase in the percentage of adsorption as a function of the increase in adsorbent mass. According to C. MacCarthy and S. Adusei (2021), heating could contribute to the reduction of peroxidised compounds [8]. The study of Wannahari and Mad Nordin revealed a highest percentage reduction of FFA (82.144%) is obtained at 60-min contact time and 7.5 gr adsorbent used [9]. Functional groups in tigernut by-product adsorbents, such as hydroxyl, carboxyl and amide groups, could be responsible for enhancing the adsorption potential.

5. Conclusion

Pre-treatment of used frying oils is an important step that must precede subsequent uses. The search for good quality natural adsorbents has always been the subject of research. The residues from the extraction of Tiger Nut milk and its starch have been used to reduce free fatty acids and peroxidised compounds. Adsorption of used frying oil onto starch may be a very promising technique for treating good quality used oil. The results show that adsorption of frying oil onto starch can be used to reduce the acid value and peroxide value of frying oil. However, the combination of tigernut starch and residues from the extraction of tigernut milk appears to be more effective for the purification of used frying oils. Adsorption rates are higher with this combination. It follows from this work that tigernut residues would be good materials for purifying used frying oils.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References

- [1] A. Mannu et al., « Variation of the Chemical Composition of Waste Cooking Oils upon Bentonite Filtration », Resources, vol. 8, no 2, Art. no 2, juin 2019, doi: 10.3390/resources8020108.
- [2] R. Marchetti, C. Vasmara, L. Bertin, et F. Fiume, « Conversion of waste cooking oil into biogas: perspectives and limits », Appl. Microbiol. Biotechnol., vol. 104, no 7, p. 2833-2856, avr. 2020, doi: 10.1007/s00253-020-10431-3.
- [3] Sahar et al., « Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel », Sustain. Cities Soc., vol. 41, p. 220-226, août 2018, doi: 10.1016/j.scs.2018.05.037.
- [4] E. Girsang, A. A. Kiswandono, R. Ikhtiari, H. Aziz, Z. Chaidir, et R. Zein, « The purification of waste cooking oil based on lipid profiles measurements by using skin of Salacca zalacca », J. Chem. Pharm. Res., vol. 7, no 9S, p. 59-65, 2015.
- [5] A. Achylov et B. KAYGIN, « RECYCLING WASTE VEGETABLE OILS », Bartın Univ. Int. J. Nat. Appl. Sci., vol. 5, no 2, p. 95-100.
- [6] I. Aziz, R. C. Sulistina, Hendrawati, et L. Adhani, « Purification of Crude Glycerol from Acidification Using Tea Waste », IOP Conf. Ser. Earth Environ. Sci., vol. 175, no 1, p. 012010, juill. 2018, doi: 10.1088/1755-1315/175/1/012010.
- [7] E. A. Yazid, A. Wafi, et S. Maryaningsih, « Determination of peroxide by spectrophotometry in waste cooking oil using adsorbents from banana midrib and water hyacinth », Nat. Sci. J. Sci. Technol., vol. 10, no 02, p. 36-41, 2021.

- [8] C. MacCarthy et S. Adusei, « Reduction of Free Fatty Acids in Palm Kernel Oil Using Bagasse Adsorbent of Varying Masses », IPTEK J. Technol. Sci., vol. 32, no 2, p. 74-80, 2021.
- [9] Rizki Wannahari et M. F. M. Nordin, « The Recovery of Used Palm Cooking Oil Using Bagasse as Adsorbent », Am. J. Eng. Appl. Sci., vol. 5, no 1, p. 59-62, janv. 2012, doi: 10.3844/ajeassp.2012.59.62.
- [10] P. S. Khoo et al., « Starch-Based Polymer Materials as Advanced Adsorbents for Sustainable Water Treatment: Current Status, Challenges, and Future Perspectives », Polymers, vol. 15, no 14, Art. no 14, janv. 2023, doi: 10.3390/polym15143114.
- [11] B. E. Elizalde, M. D. Rosa, et C. R. Lericci, « Effect of Maillard reaction volatile products on lipid oxidation », J. Am. Oil Chem. Soc., vol. 68, no 10, p. 758-762, 1991.
- [12] J. Ding, Z. Xia, et J. Lu, « Esterification and deacidification of a waste cooking oil (TAN 68.81 mg KOH/g) for biodiesel production », Energies, vol. 5, no 8, p. 2683-2691, 2012.