Recycling of Waste Cooking Oils: variation of the chemical composition during water treatment

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Abstract

Samples of sunflower Waste Cooking Oils (WCOs) subjected to several cycles of frying were treated with water under four different combinations of temperature and pH. The variation of the chemical composition of the oil samples was monitored through headspace Solid-Phase Microextraction (HS-SPME) coupled with gas-chromatographic technique (GC), ^{1}H NMR spectroscopy and ESI[+] mass spectrometry measurements. The possibility to modify the chemical composition of the recycled vegetable oil by tuning the water treatment parameters was exploited for the designing of a mini-plant for the production of bio-lubricants. A full description of the proposed prototype is also reported.

Keywords: Waste Cooking Oil, volatiles, ^{1}H NMR, mass spectrometry, prototype.

1. Introduction

During the last decades, the efforts toward the developing of new sustainable green process has grown exponentially. One of the more recent examples of such tendency is represented by the Waste Cooking Oils (WCOs) management[1], which has been object of new international regulations and became of interest as raw material for several private companies. In Europe and in few other countries, WCOs are collected by the urban waste system[2] and delivered to an authorized recycling point. This by-product of the food chain, is currently considered an economic and green raw material for several industrial processes.[3] The possibility to easily transform the used vegetable oil in valuable goods combined with the necessity to avoid its dispersion in the environment[4] and with its availability in very large amounts,[5] pushed many local industries to invest in WCOs processing. The most common utilizations of recycled WCO include the bio-lubricants production,[6,7,8,9] the employment as animal feed,[10,11] and the energy production (direct burning[12,13] or as fuel ingredient[14,15,16,17]). In addition, some recent application of recycled WCOs involve the production of eco-friendly biodegradable solvents,[18] the use as additive for bio-asphalts and bio-concrete,[19,20] and its exploiting as non-aqueous gas sorbents devices.[21,22] Independently to the specific production, WCOs are usually pre-treated, sometimes by the same collectors, and transformed in regenerated low quality oleic derivative. This first stage of recycling gives a product with a low market values, which is sold to other industries for further transformations.

This first treatment usually includes washing the WCO with water and/or filtering it on cellulose papers or bentonite pads. The first step is also called degumming,[23] and is borrowed from the industry of edible oils, which are washed in order to remove wax, pigments and metal traces.[24,25,26] From the other side, the filtration procedure, also known as clarification step, was originally employed in the recycling of mineral oils and permits to decrease of the density and the viscosity and to enhance the color properties of the crude oil by removing selected polar compounds and by separating metal traces and other solids.[27,28,29] The variation of the chemical composition of WCOs depending on the degumming or filtration has been seldom studied.[30] It has been found that the volatile composition of crude WCOs is mainly composed by Free Fatty Acids (FFA) and degradation products with respect to the parent edible vegetable oils, and that such composition change depending on the kind of the bentonite employed for the filtering treatment.[31,32]

When WCOs are recycled for non-bio-diesel applications the treatment with water and the filtration represent the main steps in the vegetable oil regeneration process. In particular, the chemical-physical properties of the recycled oil are sensitive to the conditions of the water. For the best of our knowledge the recycling process of WCO for obtain bio-lubricant or bio-solvents has not been yet described and no report on the influence of the main parameters of the degumming on the chemical composition of the oil has been published so far.

Herein we present for the first time, a detailed description of the variation of the chemical composition of sunflower oils employed for frying[33] which have been subjected to four different type of water

treatment. Commercial, crude and refined oils were characterized by headspace Solid-Phase Microextraction (HS-SPME) coupled with gas-chromatographic technique, by ^{1}H NMR and by mass spectrometry (MS-ESI). The main differences between the samples were highlighted though multivariate statistical treatment of the data obtained. In addition, the design of a prototype based on the results of the present study for the production of regenerated vegetable oil is described and commented.

2. Materials and Methods

2.1. Starting materials

Sunflower oil was considered for the present study and samples of edible oil were purchased by ZUCCHI. Samples of commercial oil **M1** were subjected to several frying cycles involving different kind of foods and the corresponding Waste Cooking Oil **WCO1** was employed for the water treatments.

2.2. Degumming procedure

In a 200 mL flask, 50 g of **WCO1** and 50 g of water were mixed together and stirred for 3 hours at the selected temperature. Two sets of pH values and temperatures were considered: pH 3 and 9 and 30 °C and 80 °C. The water solutions at pH 3 were prepared by diluting a 33% HCl solution with distilled water, while the solutions at pH 9 were obtained by adding NaOH to deionized water. The pH was measured with a pH-meter XS Instruments.

2.3. Volatile determination

Headspace Solid-Phase Microextraction (HS-SPME) as well as GC-MS analysis were performed in agreement with a previous reported procedure.[34]

2.4. Retention indexes

A hydrocarbon mixture of n-alkanes (C9-C22) was analyzed separately under the same chromatographic conditions described in GC-MS section to calculate the retention indexes with the generalized equation by Van del Dool and Kartz,[35] $I_x=100[(t_x-t_n)/(t_{n+1}-t_n)+n]$.

2.5. NMR analysis

^{1}H NMR spectra were recorded on a Bruker AV500 spectrometer operating at 500 MHz for the proton nucleus. All the experiments were performed at 305 K with the following acquisition parameters: time domain 32K, relaxation delay 3s, 128 scans and a spectral width of 12 ppm. All the samples were analyzed in pure form, using a coaxial tube with deuterated DMSO for lock.

2.6. Mass spectrometry

The ESI-MS experiments were performed using a Bruker Esquire 3000 PLUS (ESI Ion Trap LC/MSn System), equipped with an ESI source and a quadrupole ion trap detector (QIT).

Acquisition parameters: needle: 4.5 kV, N_2 flow rate: 10 L h^{-1}, cone voltage: 40 V, Scan resolution and range: 13 000 (m/z) s^{-1} over the mass range m/z 35–500, by direct infusion of methanol solution of compounds at rate: 4 microliter min^{-1}.

2.7. Statistical analysis

The Principal Component Analysis (PCA) of the data relative to the chemical composition of the samples obtained by MS-ESI-IT spectrometry was conducted. Each sample was analyzed in triplicate to define a matrix m × n where m were the samples and n were the variables. The data were centered and autoscaled before the PCA. All PCA analyzes were performed with Metaboanalyst 4.0.[36]

3. Result and Discussion

In a previous paper, we studied through Design Of Experiments (DOE) and multivariate analysis the impact of acidic degumming of WCOs samples on their color, density and flash point, describing the influence of the temperature, stirring time, oil/water ratio, and pH.[30] We observed that the most influencing parameters during water treatment of WCOs are temperature and pH, while the oil/water ratio and the stirring time influence less the physical characteristics of the recycled oil. Taking into consideration our previous results, herein we investigate and report on the effect of pH and temperature on the chemical composition of sunflower waste oil. A temperature range from 30 °C to 80 °C and a pH window between 3 and 9 were considered. Samples of Waste Cooking Oil were treated with water at a specific pH and temperature[37], and the corresponding chemical compositions determined by GC/MS analysis, ^{1}H NMR spectroscopy and ESI$^+$ mass spectrometry were compared. In order to test the level of regeneration of the proposed procedure, the same analyses were performed on samples of the original matrix, the commercial sunflower oil **M1** (Table 1).

Table 1: nomenclature of the samples considered in the present study.

Sample	Condition[a]
M1	Sunflower commercial oil
WCO1	**M1** subjected to several frying cycles
O1	WCO1 after treatment at pH = 3 and T = 25 °C
O2	WCO1 after treatment at pH = 9 and T = 25 °C
O3	WCO1 after treatment at pH = 3 and T = 80 °C
O4	WCO1 after treatment at pH = 9 and T = 80 °C

[a]Ratio oil/water 70/30 in volume, time of stirring 3 hours.

3.1. Volatile Organic Compounds (VOCs)

All the samples indicated in Table 1 were analyzed by headspace Solid-Phase Microextraction (HS-SPME) coupled with gas-chromatographic technique in order to characterize the volatile fraction. Fifteen components were identified as reported in Table 2.[38]

Table 2: main components detected by Gas-Chromatography in samples of edible oil **M1**, fried oil **WCO1**, and treated samples **O1**, **O2**, **O3**, and **O4**. The values expressed are the result of the average value of three independent replicates ± SD of absolute TIC peak area (1E6).

Entry	Retention time	M1	WCO1	O1	O2	O3	O4	Analyte
1	15,489	n.d.	2,7287	1,9981	1,7933	0,8577	1.8302	Hexanal
2	19,009	n.d.	0,7503	0,2685	0,3263	-	0,6493	Heptanal
3	19,573	n.d.	0,7684	-	0,4901	-	0,4494	Limonene
4	20,354	n.d.	1,8623	1,0677	1,2202	-	0,4494	Furan, 2-pentyl-
5	25,183	n.d.	4,0382	3.8689	4.0172	2.8489	2.4767	Nonanal
6	26,086	n.d.	0,8284	0,6770	0,8705	0,4485	0,7353	1-octen-3-ol
7	27,052	n.d.	0,6783	-	0,5719	0,0791	0,1544	Furfural
8	29,158	n.d.	0,5625	0,4577	0,4587	0,1700	0,5569	Cyclohexanol,-dimethyl- (not identified isomer)
9	29,475	n.d.	0,4908	0,4230	0,4550	0,2407	0,2646	benzaldheyde
10	29,692	n.d.	0,6348	0,6042	0,5006	0,4925	0,7101	2-Nonenal
11	32,182	n.d.	-	-	-	-	-	2-Furan-methanol
12	32,423	n.d.	1,4988	1,4236	1,4708	1,3255	1,5066	2-Decenal
13	34,587	n.d.	1,0504	1,0649	1,0810	1,0060	0.6942	2-Undecenal
14	34,79	n.d.	1,2092	1,1551	1,1331	1,0718	1,0759	2,4-Decadienal, (not identified isomer)
15	35,929	n.d.	-	-	-	-	0,4468	2,4-Decadienal, (not identified isomer)

In the volatile fraction of edible oil **M1** cannot be detected any relevant analyte. This is in agreement with the fact that edible oils are usually subjected to a deodorization process, which remove most of the volatile compounds.[39,40]

Samples of fried **WCO1** resulted enriched in many classes of compounds, such as aldehydes, alcohols, dienes. These compounds result from the frying process and in particular from the oxidation of triacylglycerols and via the Maillard process (nitrogen-containing compounds). Some terpenes could also be found, probably arising from food leaching.[41,42] The presence of alkanes is a consequence of the pyrolysis process of the free fatty acids occurring during deep frying.[43] Also, some products resulting from the autoxidation of the linolenic acid were detected as dienals (e.g. 2,4-decadienal), and alkenals such as 2-undecenal, 2-decenal, 2-noenal, were also detected.[44]

The data reported in table 2 highlight two main trends. First, the treatment at room temperature, independently of the pH, is less effective with respect to the same procedure at 80 °C (**O1** vs **O3**, and **O2** vs **O4**). Second, the effect of pH is evident: the acidic treatment results to be more effective in reducing the amount of all the volatile compounds detected in comparison with the basic treatment. If we compare the two processes at 80 °C (**O3** vs **O4**), many compounds reduced with the basic washing are completed removed at pH 3 (heptanal, limonene, furan-2-pentyl, 2,4-decadienal).

Finally, all the four processes removed efficiently 2-furan-methanol, detected in the **WCO1** samples only.

3.2. NMR Spectroscopy

^{1}H NMR spectroscopy has been already exploited for the characterization of frying oils.[45,46,47] The technique represents a valid alternative to the commonly employed chromatographic methods as it allows the quick analysis of easily prepared samples and the identification of many compounds at the same time.[48] The application of ^{1}H NMR spectroscopy to the characterization of vegetable oil include: the assessment of the geographical origin of the olive oil,[49,50] the determination of the fatty acids profile,[51,52] and the estimation of the quality of waste cooking oils.[53]

^{1}H NMR experiments were performed in order to confirm the differences in the composition of sunflower commercial oil **M1**, the derived waste **WCO1**, and the four treated samples **O1**, **O2**, **O3** and **O4**. As expected, the main composition of all the samples analyzed was a mixture of fatty acids (linolenic, linoleic and saturated fatty acids) and unsaturated acids (Figure 1 and Table 1).
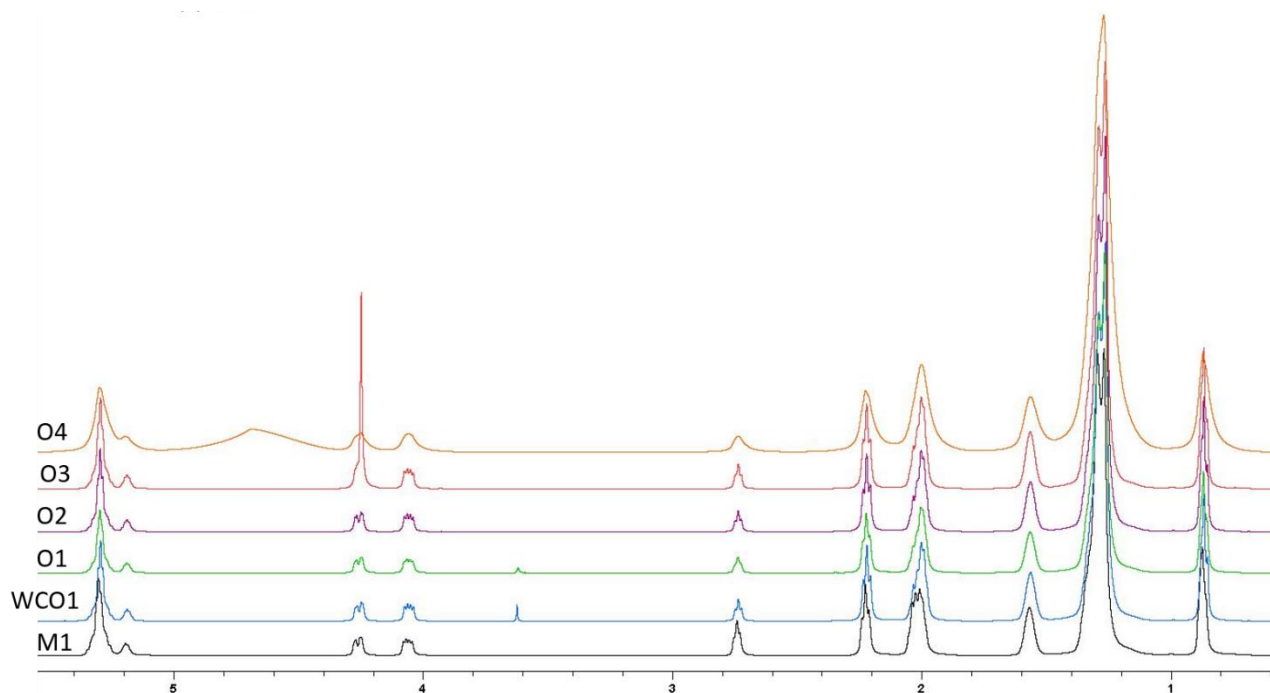
Figure 1: ^{1}H NMR spectra of oil samples edible oil **M1**, fried oil **WCO1**, and treated samples **O1**, **O2**, **O3**, and **O4**.

^{1}H NMR spectra of samples **M1**, **WCO1**, **O1**, **O2**, **O3** and **O4** are reported in Figure 1. The characteristic signals of fatty acids and unsaturated acids are present: $-CH_3$ signals at 0.9 ppm, $-CH_2$ group of the acyl chains at 1.3 ppm, 1.6 ppm and 2.3 ppm, and the methylenic signals of the unsaturated fatty acids, linolenyl acid and glycerol at 2.0 ppm, 2.2 ppm and between 4.0 and 4.4

ppm, respectively. The triacylglicerols and unsaturated fatty acids can be detected at 5.2 ppm and 5.3 ppm.

According to the methodology proposed by Popescu and coworkers,[54] it was possible to determine the main composition of the samples analyzed as reported in Table 3.

Table 3: main composition of samples edible oil **M1**, fried oil **WCO1**, and treated samples **O1**, **O2**, **O3**, and **O4** observed by ^{1}H NMR spectroscopy. The relative normalized percentage are reported.

Entry		Linolenic acid	Linoleic acid	Oleic acid	SFA	IV
1	M1	1.9%	35.7%	46.4%	14.0%	106
2	WCO1	1.7%	19.1%	62.2%	15.4%	91
3	O1	1.8%	17.0%	63.7%	15.7%	88
4	O2	1.7%	17.6%	63.6%	15.4%	89
5	O3	1.9%	18.4%	62.1%	15.8%	90
6	O4	3.7%	14.7%	63.4%	14.1%	85

The relative concentration of the main acids presents in sunflower vegetal oil showed considerable changes after frying: the concentration of linoleic acid drops from 35.7% of the M1 samples to 19.1% of **WCO1**. On the other hand, the relative concentration of oleic acid increases from 46.4% of the edible oil to more than 60% in **WCO1** and in all the treated samples. Treatment of **WCO1** at 80 °C and pH 9 (**O4**) results in an increasing of the relative amount of linolenic acid (entry 6 versus 2-5) and a reducing of the linoleic acid (14.7% versus 17-19% of the others). The change in the composition of the oil and in particular of the ration between linoleic and oleic acids as consequence of the frying are reflected in a change of the iodine number, related to the global insaturation (**IV**).

Some undesired products arising from the frying can be detected by NMR. From the expansion of the[1]H NMR spectra between 10.5 and 11.8 ppm reported in figure 2 is possible to observe the presence of alkenals, which result from the oxidation of the fatty acids promoted by heat and oxygen (Figure 2, **M1** versus **WCO1**).**Errore. Il segnalibro non è definito.** All the four treatments reduce the amount of detectable aldehydes, even if they are not effective in completely removing them from the crude substrate (Figure 2, spectra **O1**, **O2**, **O3**, and **O4**).
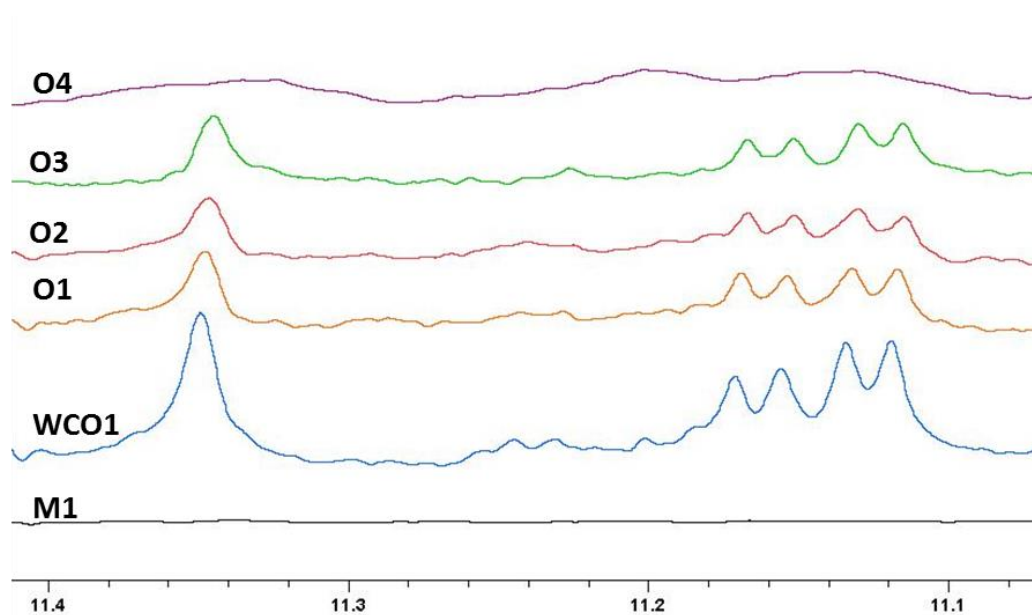
Figure 2: Zoom of ¹H NMR spectra of edible oil **M1**, fried oil **WCO1**, and treated samples **O1**, **O2**, **O3**, and **O4**. Spectral region between 10.5 and 11.8 ppm.

3.3. Mass spectrometry analysis (MS-ESI)

Samples of edible oil **M1**, fried oil **WCO1**, and treated oils **O1**, **O2**, **O3** and **O4** were analyzed by MS-ESI⁺ measurements. The MS-ESI spectra of the different samples are very different and complex as they have a huge amount of signals in the observed region. This makes the visual inspection and comparison of the samples difficult. For this reason, multivariate analysis was used in order to discriminate the samples on the bases on their chemical fingerprint.

From the GC-MS and ¹H NMR data we observed that the main differences in composition between untreated, fried and treated samples were related to the presence of degradation products which are low molecular weight molecules (**Figures 3 and 4**). Taking this into account and with the aim to verify which treatment is more suitable for the regeneration of the fried oil in terms of removing the decomposition products, the spectral region between *m/z* 100 and 500 was subjected to Principal Component Analysis (PCA) (Figures 3 and 4).
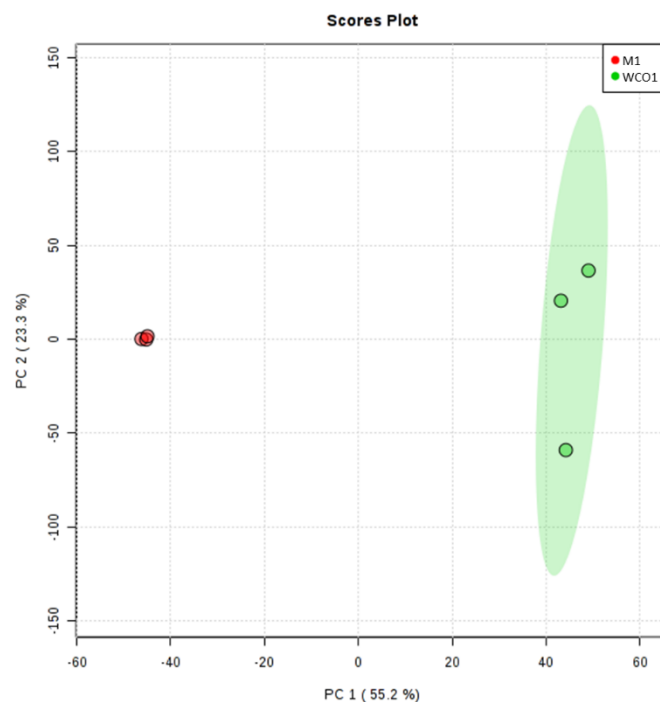
Figure 3: PCA score plot for samples of edible oil **M1** (red) and fried oil **WCO1** (green).

The MS-ESI normalized data were analyzed using MetaboAnalyst 4.0, an online tool for Multivariate statistical Analysis. The PCA score plot reported in figure 3 shows differences in the chemical composition between the edible oil **M1** and the fried one **WCO1**. The plot reported in Figure 3 confirms that MS/ESI combined with statistical analysis can be used to underline differences and similarity in chemical composition of edible and fried oils. The two principal components PC1 and PC2 explain the 78,5% of the total variance, respectively for the 55,2% and 23,3%. The data relative to the edible oil **M1** form a small cluster while the fried oil **WCO1** points are more separated, thus indicating a greater inhomogeneity of the sample.

In order to measure the degree of purification of every process studied, the data relative to all the samples (including the treated oils **O1**, **O2**, **O3** and **O4**) were introduced in the statistical system.

The 2D and 3D PCA score plots for the comparison of edible oil **M1**, fried oil **WCO1** and the treated samples **O1**, **O2**, **O3** and **O4** are reported in figure 4.
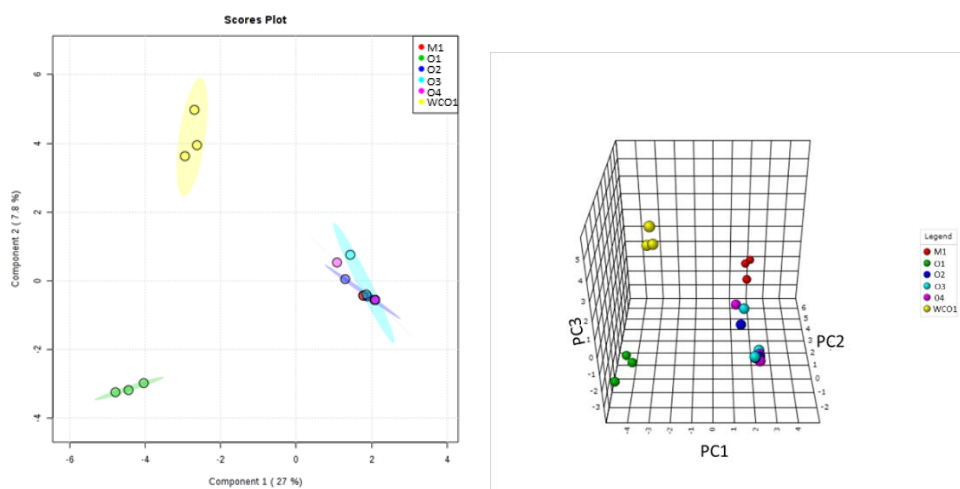
Figure 4: 2D (left) and 3D (right) PCA score plot for comparison of samples **M1** (red), **WCO1** (yellow), **O1** (green), **O2** (dark blue), **O3** (light blue), and **O4** (pink).

Samples **O1** form a cluster far from **M1** samples and from **O2**, **O3** and **O4**, clearly indicating that the treatment at pH 3 and room temperature is not as effective as the others in regenerating the frying oil. Conversely, samples **O2**, **O3** and **O4** form a cluster partially overlapped to **M1** samples confirming a similarity of these samples and revealing the partial regeneration of the oil. This suggests that pH 3 and 80 °C and pH 9, at both 25°C and 80 °C are the ideal conditions to clean the **WCO1** by restoring the original chemical composition of **M1**. These data are particularly useful if combined with some practical observations. In fact, alkaline treatment of **WCO1** leads to the formation of an emulsion due to the saponification of the fatty acids present in the vegetable oil, making any further separation procedures complex. On the contrary, the treatment at pH 3 does not show any evident side-reaction (as saponification), thus allowing an easier separation of the treated oil from the wastewater than the alkaline processes. A careful analysis of the plots reported in figure 4 points out some subtle differences among samples **O2**, **O3** and **O4**. Oils arising from alkaline treatments (**O2** and **O4**) are almost superimposed in both the components which contribute to the variance (figure 4 left, 2D plot), while the oil resulting from the acidic process at 80 °C (**O3**) shows more variability in the component 2 with respect to the other **O2** and **O4**. In general, alkaline treated oils are more similar than **O3** to the original edible oil **M1**, but the differences are indeed small leading to the conclusion that, considering the collateral saponification process occurring in alkaline media, the ideal conditions for waste cooking oils regeneration are pH=3 and 80 °C.

3.4. Prototype

From the data collected in the present study and during our previous investigations,[27] a proper recycling of WCO should allow to obtain specific characteristics in the recycled material by tuning some process parameters. In particular, the water treatment led to different outcome depending mainly on the temperature and on the pH, while the filtration step improves the color of the

regenerated oil and helps removing residual aldehydes.^{Errore. Il segnalibro non è definito.} Taking in consideration these findings, we designed a modular mini-plant for the recycling of WCOs.

The overall process has been partitioned in three main steps, each one related to a specific working module: the storing and washing module, the filtering module, and the product storing module (**Figure 5**).
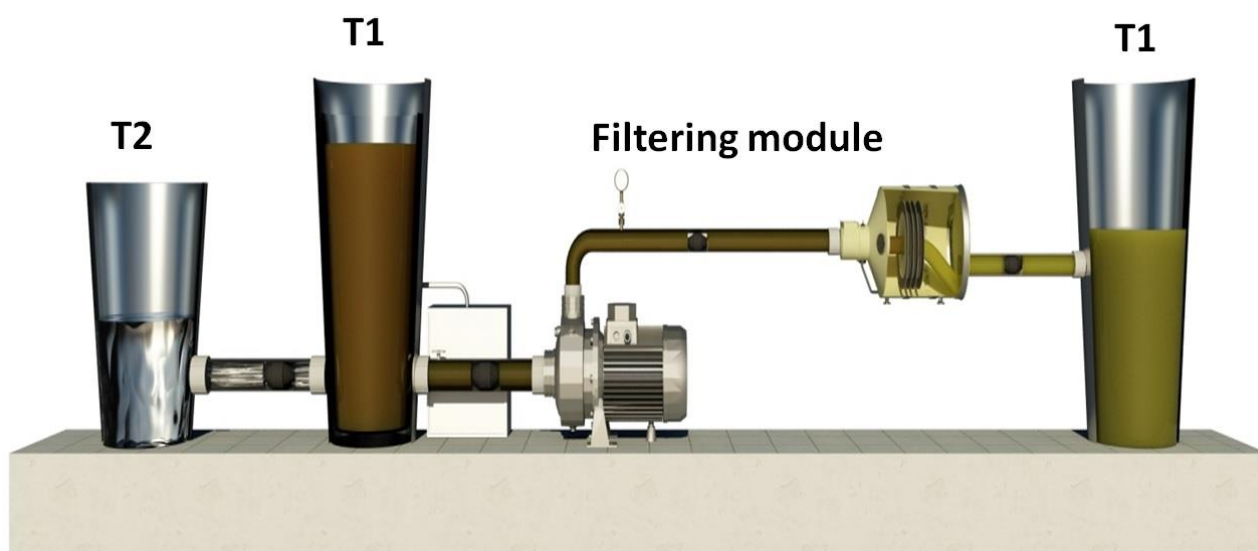
Figure 5: Overview of the mini-plant designed: washing tank (**T1**), wastewaters decantation tank (**T2**), filtering module, and storing tank **T3**.

3.4.1. Storing and washing module

The WCO is introduced inside the tank **T1** (AISI 304) with a capacity of 50 L of oil. A first gross filtration (≥ 100 μm) take place at this stage thanks to an electronic controlled self-cleaning filter connected to the inlet nozzle. A bag filtering system steel AISI 316 with an integrated electric pump is used. The maximum flow of 100 L/min. obtaining a laminar motion-based flux (Normal flow filtration), and allowing the oil to pass through the filter perpendicularly to the surface of the septum. The process is monitored by an electronic control every 10 filtering cycles. Once the oil has been introduced in **T1**, the suitable amount of water is added.

A system of level probes would be necessary in order to establish the water presence on the bottom of the tank. Two solenoid valves are installed: one for the water discharge and a second one on the opposite side for the washed oil transport to the next module. An additional tap is present for occasional sampling or for emptying the system (e.g. for maintenance).

The temperature of the tank is controlled by a hydraulic system constituted by a serpentine filled with a process fluid passing inside a suitable interspace.

3.4.2. Separation module

Once concluded the water treatment, the oil is separated by the water through gravity decantation in the separation module.

The separation module includes a second tank (**T2**) for the decantation of the wastewater and the connecting pipe. The pipe is made by DN = 15 mm steel, while the connections between the two tanks **T1** and **T2** are governed by automatic release systems. This is mandatory for the easy replacing of the tanks. The tank **T2** is of AISI 304 type with a total capacity of 30 L. Also, as in the case of **T1**, a tap is installed for sampling or for the controlled emptying.

3.4.3. Filtering module

Washed oil is then filtered with clays in order to remove pigments, metal traces improving its color and the density characteristics.

The filtering module includes one hydraulic pump, a filter filled with porous materials,**Errore. Il segnalibro non è definito.** and all the corresponding connections (DN 15 mm). The pump pushes the oil from the **T1** to the filter unit with a maximum pressure of 4 bar. An automatic control which include a shutdown system in the case of excessive pressure will be also installed.

The filtering unit is made by a fiberglass container with a maximum capacity of 3 liters of solid material, connected to the rest of the system by flanged joints. The type of filtration proposed is the "Deep bed filtration", where the oil pass through all the length of the filter. Once exhausted the filtering unit can be easily substituted. The difference between the upstream and the downstream pressure is monitored in order to detect any load loss. As the load losses are related to the grain size of the filtering material, the system also allow to tune the flow pressure depending on the kind of clay employed. The optimization of the filtering procedure has been made considering the equation **$\Phi = \Delta P / R$** which describes the flux of a fluid that pass through a porous bed.[55]

3.4.4. Storing module

The storing area is constituted by the connecting steel pipe (DN 15 mm) between the filtering unit and the storing tank **T3**. The connections between the pipe and the tanks are controlled by a gate sludge system, in order to make easier the disassembly of the module. The **T3** steel AISI 304 tank have a maximum capacity of 30 liters and are used for the storing of the regenerated vegetable oils. As for **T1** and **T2**, a pipe allow sampling and emptying.

The overall mini-plant is assembled on a wheeled structure with the possibility to remove every single module at the need. The frame of the support structure is constituted by tubular steel cables DN 30 mm on 4 full rubber wheels. The upper part of the frame has a multilayer base of the type "*Okumè*" 40 mm, with a flexural strength of 48 MPa (longitudinal) and 16 MPa (transversal).[56]

The modular prototype described is able to treat about 35 liters of WCOs every three hours. In fact, the possibility to change the tank **T1** once the water treatment is concluded allows to treat new oil while the previous washed is stored for decantation. The condition defined through the tests reported above (pH 3 and 80 °C) reduce the decantation time from days (in the case of alkaline processes, where saponification occurs) to 4-5 hours. In addition, as these conditions avoid the saponification,

there is no need of adding undesired salts of other additives the emulsion brake down.. The possibility to easily tune the temperature, the stirring time, the oil/water ratio and the water pH, also permits to change the treatment depending on the specific target without any time loss. For instance, waste oils destined to biodiesel can be washed at pH=3 at 25 °C, while waste oils for biolubricants should be regenerated at pH=3 and 80 °C.

4. Conclusions

The regeneration of waste cooking oils (WCOs) through water treatment has been discussed and described. The analysis of the variation of the chemical composition of samples of WCOs degummed under different conditions by headspace Solid-Phase Microextraction (HS-SPME) coupled with gas-chromatographic technique, ^{1}H NMR and ESI-MS revealed the possibility to tune the characteristics of the recycled oil by changing the temperature and the pH of the process. From the analysis of the data obtained was evident that working at pH 3 and 80 °C ensures a good regeneration level of WCO samples avoiding the formation of emulsions which make difficult the subsequent water removal. Also, the possibility to employ the fast ESI-MS technique coupled with PCA analysis for determining a fingerprint of vegetable oils has been revealed, opening to a new industrial application of such procedure (e.g. in the production of biolubricants). A prototype of a mini plant for WCOs recycling, based on the finding described, has been also presented and described. The process optimized allows to fast regenerating waste cooking oils for different applications.

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