Bentonite as refining agent in waste cooking oils recycling: flash point, density and color evaluation

Alberto Mannu*[a,b], Gina Vlahopoulou[a,b], Veronica Sireus,[c] Giacomo Luigi Petretto,[a] Gabriele Mulas[a] and Sebastiano Garroni[d,e]

[a]*Department of Chemistry and Pharmacy*, via Vienna 2, University of Sassari, Sassari, Italy
[b]*Leibniz-Institut für Katalyse e. V., Albert-Einstein-Straße 29, Rostock, Germany*
[c]*Departament de Física, Universitat Autònoma de Barcelona, 08193 Cerdanyola del Vallès, Spain*
[d]*International Research Centre in Critical Raw Materials-ICCRAM, University of Burgos, Plaza Misael Banuelos s/n, 09001 Burgos, Spain*
[e]*Advanced Materials, Nuclear Technology and Applied Bio/Nanotechnology. Consolidated Research Unit UIC-154. Castilla y Leon. Spain. University of Burgos. Hospital del Rey s/n, 09001 Burgos, Spain*

albertomannu@gmail.com

Clarification of waste cooking oil (WCO) is very important in order to refine the intermediate regenerated base resulting from the previous step during the recycling process. Bentonite has been historically employed as filling material for oil refining filters due to its easy availability and cheap price. In the present communication our early results from the filtration of degummed WCO through a pad of bentonite are presented. In particular, the variation of density, flash point and color have been monitored prior and after the filtration process and compared with samples of non-filtered WCO. An early classification of the bentonite employed has been achieved by FT-IR and XRD measurements.

Keywords: waste cooking oil; bentonite; flash point; FT-IR, XRD.

Introduction

Disposal of waste cooking oil (WCO) represents one of the main challenges in modern society [1a, 1b]. Currently the amount of collected WCO is about seven times less than the produced. The European Biomass Industry Association reveals that about 8L UCO/capita/year of waste vegetal oil could be collected only in EU, corresponding to a total capacity of 4 Mton of WCO per year [2]. Most of the collected WCO is originated from frying processes in which the food is treated with hot oil at temperature between 150 ºC and 190 ºC by immersion and contact with air. The main chemical transformations of the oil during the frying process are hydrolysis of triacylglycerols, lipid oxidation and polymerization therefore the main resulting products are free fatty acid, peroxides, acrolein and acrylamide [3]. These multiple transformations involving the oil matrix during the cooking strongly affect the oil composition making difficult its recycling for alimentary uses [4]. Moreover, WCO represents a high valued food by-product as can be used as raw materials for new non-food application [5] or for replace synthetic chemicals [6]. As reported by Lyn and coworkers, the economic impact of the recycling of WCO cannot be underestimated since the global consumption of vegetal oil exceeds the 160 Mton per year [7]. Once discarded, WCO can be a raw material for several industrial application, from bio-lubricant [8a, 8b], to cosmetics, as well as to eco-friendly solvents [9]. Waste cooking oil can be even used as energy source, through direct burning [10a, 10b] or as raw material for biodiesel production [11]. WCOs can be employed successfully also as bitumen binder [12], or as additives for mercury sorbents devices [13]. During the recycle process of WCO an important reduction of the amount of free fatty acids, waxes, metal ions and coloring pigments is usually achieved by water degumming [14a, 14b] or by distillation, while refining of the crude product is achieved through filtration on porous materials.

Clay minerals have been employed for oil clarification for many years, mainly for their effectiveness in removing grease and impurities and due to their cheap availability [15]. Some studies have been conducted on activation techniques of natural clays, most of the times applied to vegetal oil not exhausted [16, 17]. Filtration through membrane [18], Metal Organic Framework (MOF) [19] or Calcium-Silicate (CAS) [20] have been also proposed. Focusing on treatment of WCO for non-bio-diesel applications, small-scale local industrial plants currently employ commercial bentonite or cellulose filters. From the academic point of view, there is a general lack of information regarding the treatment of WCO of domestic origin for non-energy source applications. One of the aims of our recent research is to address a series of systematic studies on the currently employed techniques in small local micro-industries.

In the present communication, our preliminary findings on the bentonite mediated clarification step of some samples of degummed WCO are reported. The impact of such process on the density, the flash point and the color of the vegetal oil are studied. A classification of the bentonite employed by mean of the FT-IR profile and based on XRD measurements is also reported.

A collection of WCO from domestic origin was considered for the present study. A small scale replica of the current recycling process employed by small local industries was settled up: the raw oil samples were subjected to a degumming procedure at pH 5.5 and then filtered on a pad of bentonite. The degumming step was recently discussed by us in the terms of variation of density and flash point profiles [21]. During regeneration process, a consistent increasing of the quality of the color, in terms of de-coloration, is usually achieved by filtration through porous materials. Clays were the material of choice for clarification of crude oils, still employed in industry for oil regeneration. Also other methodologies as filtration through membranes [22a, 22b], CO_2 extraction [23], and cellulose based

adsorbent materials [24] have been proposed for frying oil regeneration.

In this communication, we present our preliminary results about the employment of the bentonite as decoloring agent.

Bentonites represent a class of naturally abundant raw materials which can be used for a widespread number of applications in industrial and civil sectors [25]. Montmorillonite, a clay mineral of Mg and Al, is the dominant component of the bentonite and its structural properties play a crucial role in the final applications of bentonite. Montmorillonite (Mt) is characterized by a layered structure consisting of a sandwich of one octahedral alumina sheet between two tetrahedral silica sheets (TOT) [26]. A small fraction of the tetrahedral Si atoms are substituted by Al and/or octahedral atoms (Al or Mg) are replaced by atoms with a lower oxidation number, resulting in a negatively charged surface, which is balanced by exchangeable inorganic cations (e.g. Na^+ and Ca^{2+}) located in the interlayer spaces. Typically, the interlayer space surfaces show a hydrophilic character due to the H_2O cluster which surrounding the inorganic cations. Furthermore, the interlayer spaces forms cavity or pores which fall into the micropore size domains [27]. By tuning pores dimensions and cations in the original structure of the starting Montmorillonite, is then possible to modulate its specific properties as, for example, the swelling behavior, adsorption and cation exchange capacity and surface area. All of these properties result, in fact, crucial for industrials applications such as foundries, cosmetic, enology, catalysis, etc. [28].

FT-IR measurements

A preliminary classification of the commercial bentonite has been done via FT-IR transmission spectroscopy (Figure X). The window of frequencies was considered between 4000 and 400 cm^{-1}, with a resolution of $2cm^{-1}$.
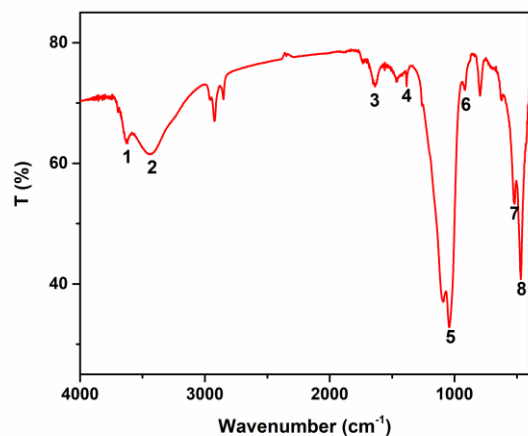

Figure 1: FT-IR profile of commercial bentonite.

The pattern observed in Figure 1 is quite characteristic of bentonites, constituted mainly by montmorillonite, responsible for the bending peak at 917 cm^{-1} (Al-Al-OH), 519 cm^{-1} (Si-O-Al) and 419 cm^{-1} (Si-O) [29]. The stretching of the –OH group of trapped and adsorbed water can be observed respectively at 3436 cm^{-1} and 1636 cm^{-1}. Table 1 reports a summary of the main FT-IR signals.

Table 1: FT-IR profile of commercial bentonite.

Band (cm^{-1})	Band (cm^{-1})	Functional group
1	3620	Stretching -OH (Al-OH)
2	3436	Stretching -OH (trapped water)
3	1636	Bending -OH (adsorbed water)
4	1384	Stretching CO_3^{2-} (calcite and dolomite)
5	1043	Bending Si-O
6	917	Bending Al-Al-OH
7	519	Bending Si-O-Al (Al in octahedral cationic form)
8	469	Bending Si-O

XRD

A structural and microstructural characterization of the bentonite has been conducted by XRPD technique. The diffractometric profile is in agreement with the commercial origin of the bentonite, which does not show any Bragg reflex related to impurities, typical of the crude material (Figure 2).
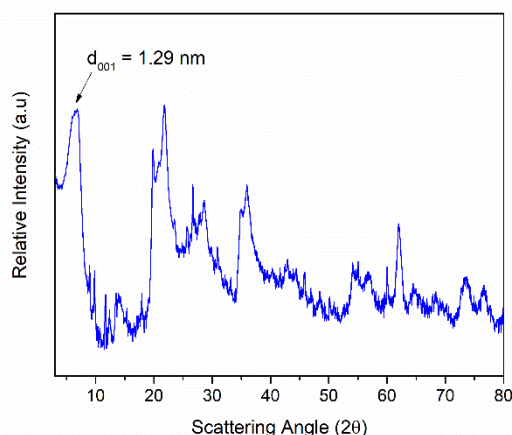

Figure 2: XRD analysis of commercial bentonite.

The distance between the layer of the bentonite can be measured from the peak d001 (Figure 2), related to the intrinsic cationic exchange capacity of natural clay. Calculation of the layer's distance was possible by applying the Bragg's equation (equation 1).

$$n\lambda = 2dsin\theta$$

The result, 1.29 nm, is characteristic of natural clay containing Na^+ between the layers [30].

Clarification of WCO

Four degummed oil samples were considered for de-coloration with bentonite: a gravity filter was assembled with a 800 mL funnel filled, 500 g commercial bentonite and 500 g of oil were than filtered. New bentonite was used for every oil sample; no further studies on the saturation capacity of the filter were performed.

The density, the flash point and the color of the filtered oils were then measured and compared with four samples of non-treated oil (Table 2).

Table 2: Density, flash point and color of degummed and filtered waste cooking oil (WCO).

Sample	Density	Flash Point	Color (CIE)[a]		
			L[b]	**a**[c]	**b**[d]
F[e]	0.922	271	26.04	3.67	12.97
NF[e]	0.927	284	21.50	1.57	5.70

[a]Commission Internationale de l'Eclairage; [b] L, lightness; [c], green–red; [d], blue–yellow;. [e]F, filtered samples; NF, not filtered samples.

Comparing filtered and crude oil samples we can notice that treatment with bentonite reduce the flash point of about 13 °C, while the density does not seem to be significantly affected from the filtration procedure. The most important difference is related to the color. The chromatic CIE L*, a and b coordinates were determined by means of spectrophotometric transmittance method. As expected filtered samples show higher lightness (L*) values, as for the color components (from 21.50 to 26.04 for green-red and from 1.57 to 3.67 for blue-yellow) resulting light yellow-orange colored after bleaching.

Darkness color in fried oils is mainly due to several oxidative reactions, polymerization, to the presence of dissolved chemicals arising from the food [31] the latter substances mainly derived as the result of the Maillard process [32]. A comparison with literature data is not easy to perform due to the different methods (absorbance or transmittance) applied for the determination of the CIE coordinates [33]. Rossi and coworkers associated the color changes in crude palm oil subjected to bentonite treatment, to the variation of the carotenoid content [34]. In the case reported the trend was the same of in our case. An opposite variation of parameters *a* and *b* has been observed by Maskan in the case of sunflower seed oil after frying process [35]. In that case, the crude oil was subjected to treatment with adsorbent materials without any previous degumming.

It is not easy to establish the exact relation between the changes observed in flash point and color and the chemical composition of the waste cooking oil after bleaching. The bentonite acts as refining agent by removing pigments (as chlorophyll), residual gums, trace of metals, and some oxidation products through chemical and physical adsorption, absorption and filtration. In addition, bentonite-catalyzed degradation of some components of the oil can take place [36]. A more exhaustive chemical characterization of degummed oil prior and post filtration and a correlation between the quality of the refined oil and the type of bentonite are objects of our current research.

Experimental

Waste oil samples

Waste cooking oil samples were collected from domestic supplier in the geographic area of north Sardinia. Deionized Water was used for all the experiments.

Degumming procedure

1 kg of waste cooking oil and 400 mL of water (pH 5.5) were mixed and vigorously stirred for 3 hours and then decanted during 2 hours in a separatory funnel. The organic fraction was then collected and submitted to filtration.

Filtration procedure

A filter was settled up in a laboratory scale filling a 800 mL funnel with 500 g of bentonite sifted with a metallic 3 mm sieves. Then 500 g of washed waste cooking oil were filtered by gravity and collected in a flask.

Determination of the flash point

The flash point, defined as "the lowest temperature at which application of an ignition source causes the vapours of a specimen of the sample to ignite under specified conditions of test", was determined employing a Pensky-Martens - SDM 750/E instrument according to standard method ASTM D93-13 with minor modifications. Briefly: 10 g of oil were heated at constant rate of 5 °C/min. A natural gas flame was directed towards the oil sample at constant intervals of 10 s, until a flame occurred over the entire surface of the sample.

Determination of the density

The density, defined as "the mass of liquid per unit volume at 15°C with the standard unit of measurement being kilograms per cubic metre", was determined according standard method ASTM 1298-12b with minor modification.

Briefly: 15 g of oil were transferred in a hydrometer cylinder and the sample was homogenized by manual stirring with a glass rod. The densimeter was then lowered into the test portion and allowed to settle until the temperature equilibrium has been reached.

Determination of CIE L*ab coordinates Color analysis was carried out according to, ASTM D 6045 – 02, briefly: the measurements of chromatic coordinates were performed with a UV/VIS spectrophotometer and obtained data were processed using Cary Win UV Color Application V. 2.00 software. Transmittances in a wavelength interval between 380 and 780 nm were measured using D65 illuminate with a 10° observation angle. The analysis was performed without any dilution, in a 10 mm polystyrene cuvettes (Kartell 01937) [33].

FT-IR

FT-IR spectrum of bentonite powders has been recorded using a Spettrofotometro FT-IR Jasco 480 Plus. For the analysis the powders have been mixed with anhydrous KBr and pressed into a disk by a hydraulic press.

XRD

X-ray-diffraction (XRD) pattern of the commercial bentonite was acquired by a Rigaku D-Max powder diffractometer, operating in Bragg-Brentano geometry equipped with a Cu-anode source (Kα, λ =1.5418 Å) and a graphite monochromator mounted on the diffracted beam.

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