Biodiesel purification in one single stage using silica as adsorbent

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HIGHLIGHTS

- We report a dry biodiesel purification method of one single stage treatment.
- The methodology is a solution for biodiesel refining saving money and process time.
- The treatment is made under conditions of vacuum and temperature.
- The selected adsorbent is silica Trisyl 3000.
- Silica behaves as a non-selective adsorbent of high capacity.

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ABSTRACT

In this paper a simple biodiesel purification method consisting of one single stage treatment with silica as adsorbent is described. The presented method seems a solution for biodiesel refining saving water, money and process time. The treatment is made under conditions of vacuum (0.2 bar) and mild temperature (65–90 °C). The method allows for the removal of the excess of methanol and water (present in the crude biodiesel and adsorbed on the adsorbent material) simultaneously with the adsorption of the impurities.

Silica Trisyl 3000 retains 23% of its weight when the process is conducted at atmospheric pressure and nearly 235% when performed under vacuum conditions. This greatly improves the utilization of the adsorbent and reduces the cost of the process.

Under these conditions, the silica behaves as a non-selective adsorbent of high capacity that is able to adsorb different types of impurities, which makes it an excellent adsorbent to purify biodiesel. On the other hand, the adsorption phenomenon is not limited to the formation of a theoretical "monolayer" of adsorbed impurities; it is more complex and includes the formation of multiple layers.

1. Introduction

Biodiesel is obtained from the transesterification of vegetable oils or animal fats with a short-chain alcohol, with or without the use of catalyst. After the reaction glycerol (the main by-product) is separated by settling or centrifuging and a crude biodiesel phase is thus obtained. Many contaminants can still be present in the crude biodiesel depending on the technology of transesterification used. Impurities such as residual methanol and traces of glycerol, soaps, catalyst, phospholipids, water and unreacted glycerides can be found, that can produce harmful effects on engine performance if not removed [1,2]. The crude biodiesel requires a subsequent refining process in order to meet the strict international biodiesel standard specifications (ASTM D6751 and EN 14214 Standards) [3,4].

The process of crude biodiesel refining is complex and it is usually achieved via two techniques; wet and dry washings. Conventionally wet washing is the most widely employed technique to remove these impurities.

The wet washing method employs multiple successive washing steps with water in order to remove major impurities such as soaps, catalyst, glycerol and methanol from biodiesel. This technique is based on the affinity of polar compounds with water. There are some disadvantages in the use of this method such as: (i) high cost (representing 60–80% of the total processing cost [5]), (ii) a substantial increase of total production time, since water

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washing requires several cycles of washing and one stage of centrifugation and/or drying, which are time intensive processes, (iii) the difficulty of meeting normed specifications regarding final water content, (iv) product loss, because some of the biodiesel is lost with aqueous effluents, and, (v) the amount of waste water that is generated as process effluent, which must be treated before the final discharge, introducing an additional cost to the process.

In the wet washing process, for every 100 L of biodiesel produced some 20 L of wastewater are produced [5]. The water content of the biofuel after the washing step (mentioned in point iii), is around 0.15% [6,7]; this value is above the maximum set by the standards (0.05%) and it's therefore necessary to introduce a later stage of centrifugation and/or drying under vacuum conditions. The wastewater due to its physicochemical characteristics, should be treated before the final discharge in order to reduce the environmental impact. The washing water is characterized by high values of pH, COD (chemical oxygen demand), BOD (biological oxygen demand), fats and oils, needing a complicated and expensive biological treatment and thus increasing operating costs [5,8].

Problems associated with wet washing have led to the development of the dry washing process to purify crude biodiesel. This process involves the use of adsorbents such as carbon, silica, bleaching clay, and activated bleaching clay, zeolite, ion exchange resins (amberlite or purolite), cellulosics or sawdust, diatomaceous earth and magnesium silicate powder (magnesol) [9]. The process requires a mixing unit and the spent adsorbent must be generally discarded [10]. Cooke et al. [11] reported that water washing may be substituted in industrial plants by dry washing with Magnesol® (provided by Dallas Group of America, Inc.). However up to now the use of the dry washing technique has not spread much at industrial level, mainly due to the following disadvantages: (i) the cost of adsorbents, (ii) the difficulty of some adsorbents for adsorbing certain types of impurities such as glycerides and free fatty acids (FFA), and (iii) the difficulty of an adequate regeneration and reuse. For this reason the solid residue has to be disposed of in landfills or other applications (composting, use as a potential animal food additive) [2]. Therefore it is essential to find a cheap adsorbent, with high adsorption capacity and capable of adsorbing all biodiesel impurities.

Removal of glycerides from biodiesel is an important step of the process because key aspects of the quality of the fuel strongly depend on the content of bound glycerol. Main problem with these compounds is that when heated they tend to polymerize forming deposits. They also increase the cloud point of biodiesel and they complicate the operation of liquid–liquid phase splitting units due to their amphiphilic nature.

With respect to the ability to adsorb glycerides there are conflicting results in the literature. Berrios and Skelton [2] reported that magnesol and ion exchange resins do not retain glycerides (mono (MG), di (DG) and triglycerides (TG)) in a significant way; consequently, the refining process cannot comply with the limits set up in the EN 14214 standard. On the contrary, Faccini et al. [12] reported that Magnesol® and silica showed suitable results regarding free and bound glycerol removal.

It is known that silicas efficiently remove the main impurities of biodiesel, such as: methanol, residual metals, phospholipids and soaps [13]. It has been previously reported [14] that glycerol has a great affinity for the silica surface and is selectively adsorbed from biodiesel solutions. It was found that adsorption of glycerol is not influenced by the presence of small amounts of water and soaps. Conversely the presence of monoglycerides (MG) and/or methanol (MeOH) lowers the adsorption capacity of glycerol due to the competition for the adsorption sites on silica. Then, a necessary first step of methanol removal previous to the silica treatment is required.

The aim of this work was to develop a simple dry method for biodiesel refining, using silica as adsorbent material, involving the fewest possible steps in order to produce biodiesel that meets strict international quality standards. Refining operating conditions were sought to ensure: (i) adsorption of the main impurities of biodiesel, particularly glycerides, (ii) reduction of the refining costs, and (iii) optimization of the silica adsorption capacity.

2. Experimental section

2.1. Materials

The raw material employed to produce biodiesel was a degummed soy oil provided by a local producer. Methanol (99.9%) and pure glycerol (>99.5%) were supplied by Sintorgan SA. Sodium estearate (99%) was chosen as a model soap and was supplied by Serisa Química SRL. Glyceryl monoestearate (98%) was used as a model monoglyceride and was supplied by Cloretil SACIF. Silica samples were TriSyl 3000, 300B and 450 (provided by W.R. Grace Argentina SA).

2.2. Biodiesel preparation

Reference Methyl soyate was prepared according to the standard procedure (catalytic low-temperature method using NaOH as catalyst) described by Noureddini and Zhu [15].

Many batches of the solution of the biodiesel product and unreacted methanol were synthesized and mixed together in order to provide a common biodiesel stock. This biodiesel stock sample was spiked with contaminants such as monoglycerides and soaps, up to the values indicated in Table 1. Then it was kept in a dessicator for later use.

2.3. Bleaching experiments

The spiked biodiesel base sample was refined by performing bleaching tests at varying conditions and with different silica adsorbents. Bleaching was performed at different temperatures and contact times in a gas-tight stirred autoclave (stirring speed: 250 rpm). 100 cm³ of spiked biodiesel were put in contact with the silica (adsorbent weight: 1.0 and 3.0 g) at the selected temperature (50, 65, 80 and 90 °C) for a conveniently chosen contact time (15–100 min) The influence of vacuum and temperature was assessed by performing the bleaching procedure at normal pressure and in vacuum (0.2 bar) and by varying the bleaching reactor temperature. After the treatment the adsorbents were decanted, filtered and the liquid phase was sampled for analysis. All experiments were performed in triplicates.

Table 1
Main properties of the spiked biodiesel.

Properties	Spiked crude biodiesel (%)	Normal limits[a] (%)
Free glycerol, %	0.20	0.02
Bound glicerol, %	0.84	0.24
Monoglycerides, %	2.41	0.80
Diglycerides, %	0.08	0.20
Triglycerides, %	0.04	0.20
Acidity, %	0.27	0.50
Soaps, %	0.25	0.02
Water, %	0.10	0.05
Methanol, %	5.00	0.20

[a] As specified by the ASTM D 6751 and EN 14214 quality standards.

The amount of adsorbed impurity on the solid Q (%) was determined from a balance of the impurity in the liquid phase, measuring the variation in the concentration of the impurity in solution before and after the treatment.

$$Q(\%) = \frac{C^o - C^f \times 100}{W},$$

where:

Q (%): amount of adsorbed impurity on the solid (in g of adsorbed impurity per 100 g of adsorbent).

C^o: concentration of the impurity in the liquid phase before the treatment (in g of impurity per 100 g of biodiesel).

C^f: concentration of the impurity in the liquid phase after the treatment (in g of impurity per 100 g of biodiesel).w: adsorbent concentration (in g of adsorbent per 100 g of the biodiesel).

2.4. Biodiesel quality assessment

The characterization of the biodiesel stock solution and refined biodiesel was made according to the ASTM 6751 and EN 14214 norms [1,2].

The data reported here are averages of duplicate determinations. Reproducibility was very good.

The water content of the samples was assessed by Karl-Fischer potentiometric titration, according to the EN ISO 12937 and ASTM D 2709 standards. The Karl-Fischer reagent was supplied by Merck and the titration was performed with an Altronix apparatus with a glass electrode. The soap content was indirectly assessed by means of the ASTM D874 test for sulfated ash content. The FFA (free fatty acid) content was determined by volumetric titration with a solution of NaOH as indicated in the ASTM D664 test.

The concentration of glycerol and glycerides was determined by means of the method indicated in the EN 14105 an ASTM D 6584. Pyridine (99.9%, Merck) was used as a solvent and as silylation catalyst for the derivatization of the samples. These were derivatized with N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA, Sigma Aldrich). 1,2,4-Butanetriol (>95%, Sigma Aldrich) and tricaprin (>99%, Sigma Aldrich) were added as internal standards. After 15 min at room temperature the silylated samples were dissolved in n-heptane (99.5%, Merck) and injected in the GC for their analysis. The analysis was performed with a Varian Star 3400 CX gas chromatograph equipped with an on-column Supelco injector and a FID detector.

The methanol content of the samples was assessed according to the EN 14110 standard, Methanol was determined using a Varian Star 3400 CX gas chromatograph equipped with a FID detector using the head space method with 2-propanol as the internal standard (>99%, Ciccarelli).

2.5. Adsorbents characterization

The composition of the silicas was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer, Optima 2100 DV) after digestion in an acid solution of hydrochloric acid and further dilution in water.

The adsorbents were characterized by means of nitrogen adsorption at $-194.6\,°C$. Before the adsorption, the samples were degassed in vacuo at $150\,°C$ for 2 h. Adsorption isotherms were measured in an automatic Accusorb Micromeritics equipment. The specific area and pore size distribution were estimated by the BET and the BJH methods, respectively [16]. TGA analysis of the adsorbents was performed with a Shimadzu TG-1000 equipment. The samples were tested without previous treatment and were considered to be in equilibrium with room humidity.

3. Results and discussion

3.1. Physicochemical characterization of silicas

The results of surface area, pore volume, mean pore diameter and pore size distribution are shown in Table 2 and Fig. 1. An adsorbent material must have high specific surface area to enable the adsorption of greater amounts of impurities and a suitable pore structure to allow the access of all impurities to its internal surface without difficulty. This latter topic is critical for large molecules (soaps, mono, di and triglycerides) with sizes similar to those of the pores of the adsorbent.

Isotherms obtained for the three silicas (not shown) can be classified as type IV, according to IUPAC nomenclature [17]. This type of isotherm is characteristic of mesoporous solids (pore diameters between 20 and 200 Å) [18]. Silicas have high specific surface area values (approximately 600 $m^2\,g^{-1}$) and silica Trisyl 3000 presents the highest value of surface area. The pore size distribution is unimodal for all samples (see Fig. 1) with pore diameters between 25 and 125 Å. Therefore the structures are purely mesoporous. The wide pore network of the silica was thought to present no problems for diffusion of the adsorbates. The approximate length of some molecules was included in Fig. 1. It can be seen that the sizes of soaps and TG are smaller than the average pore diameter of the network (Table 2). Then, it can be concluded that the silicas have high specific surface area and a suitable porous structure for use in biodiesel purification processes by selective adsorption.

The results of TGA are shown in Fig. 2. A significant mass loss can be seen in the three cases, which starts at temperatures near $40\,°C$ and ends at temperatures of $110-120\,°C$. The loss of mass is greater in samples 450 and 300B (40 and 50% respectively) and lower in sample Trisyl 3000 (10%). This loss is attributed to the release of water adsorbed on the surface. A subsequent

Table 2
Results of surface area (Sg BET), pore volume (Vp) and mean pore diameter (Dp Wheeler) of the silicas.

Adsorbent	Dp wheeler (Å)	Sg BET ($m^2\,g^{-1}$)	Vg ($cm^3\,g^{-1}$)
Trisyl 3000	71	631	1.1
Trisyl 450	67	598	1.0
Trisyl 300B	74	592	1.1
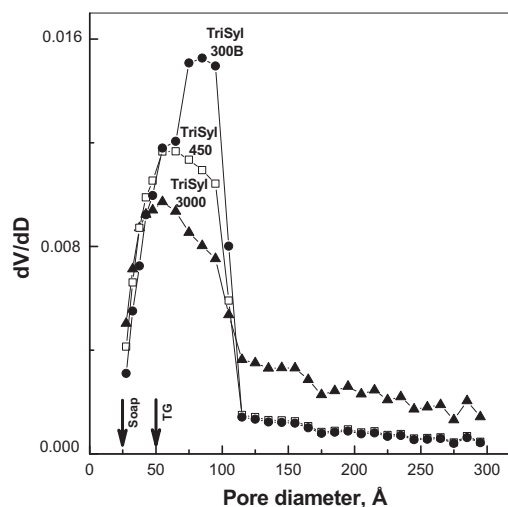
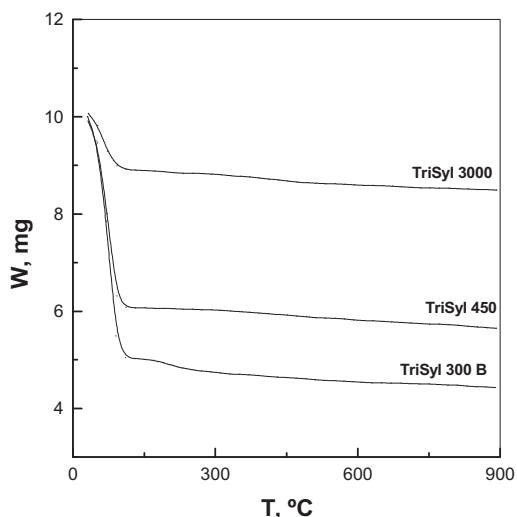**Fig. 1.** Pore size distributions of the silicas: (▲) TriSyl 300B, (●) TriSyl 450, (■) TriSyl 3000.

Fig. 2. TGA traces of the silicas.

Table 3
Adsorption capacity of impurities. Conditions: contact time = 90 min., P = 1 bar, adsorbent concentration = 3.6 wt%.

Adsorbent	T (°C)	Q_{FG} (%)	Q_{MG} (%)	Q_{DG} (%)	Q_{TG} (%)	Q_{soap} (%)
TriSyl 3000	50	8.0	16.4	n,d.	n.d.	0.99
TriSyl 450		7.0	12.1	2.3	1.1	0.90
TriSyl 300B		8.5	17.9	2.3	1.1	0.5
TriSyl 3000	65	8.4	13.6	n.d.	1.0	0.79
TriSyl 450		7.6	14.7	n.d.	0.7	0.58
TriSyl 300B		8.1	14.7	n.d.	1.0	0.44
TriSyl 3000	80	8.0	12.3	n.d.	0.2	0.54
TriSyl 450		8.6	18.0	n.d.	1.1	0.45
TriSyl 300B		7.1	13.3	1.5	1.0	0.32

n.d.: not detectable.

evolution of structural water or decomposition processes at higher temperatures were not observed.

Adsorbed water can affect the adsorption process in several ways: (i) blocking the access of impurities to the adsorption sites, (ii) preventing the diffusion of these impurities by increasing the intraparticle resistance, and (iii) changing the surface affinity of the adsorption sites. Feng et al. [19] studied the rate of adsorption and desorption of water on silica and they concluded that the silica surface becomes hydrophobic after heating in vacuo but it becomes hydrophilic immediately after contact with water at low temperature.

Moreover the presence of impurities in significant amounts in the materials used as adsorbents may affect the adsorption sites and consequently their adsorption capacity, therefore is very important to know the chemical composition of the adsorbents. The results of the chemical analysis by ICP of the three silica samples indicated that all of them had essentially the same composition. Silica samples were composed of SiO_2 of high purity (>99.0%) containing impurities such as Mg, Al and Na, in contents lower than 0.2%.

3.2. Influence of bleaching conditions

Preliminary experiments were performed at three different adsorption temperatures (50, 65 and 80 °C) under atmospheric pressure and using the untreated adsorbent in order to choose the best silica for the next exhaustive study. Prior to the adsorption tests, the spiked biodiesel was subjected to a treatment under vacuum at 90 °C for 1 h in order to remove residual methanol. This step is necessary since the presence of significant quantities of polar compounds, such as methanol, affects the affinity of the most hydrophilic compounds (glycerol) for the adsorbent, reducing its adsorption [13]. After this treatment the methanol content in the spiked biodiesel was less than 0.01% while the water content was reduced to 0.04%.

Table 3 shows the results of adsorption capacity: free glycerol (Q_{FG}), monoglycerides (Q_{MG}), diglycerides (Q_{DG}), triglycerides (Q_{TG}) and soaps (Q_S) for the different samples at three operating temperatures. The results indicate that:

(i) The three silicas adsorb glycerides.
(ii) The silica samples adsorb similar amounts of impurities despite having different water contents. The order of affinity for the impurities is: MG > FG ≫ Soaps, DG, TG. The greater

affinity for adsorption of FG and MG can be explained considering the presence of surface OH groups on the silicas, capable of adsorbing and retaining polar groups.
(iii) The treatment temperature does not appear to have a significant effect on the adsorption capacities of the different adsorbents for the analyzed impurities.

As the silicas have a high initial surface water content the possibility of needing a drying treatment prior to refining in order to increase the adsorption capacity is therefore raised. Nock postulated that the high moisture content trapped within the silica structure is beneficial and creates the ideal environment for attracting polar impurities [20]. In this sense a drying pretreatment of silicas before refining could be detrimental and affect their adsorption capacity. Anyway it is necessary to assess the adsorbed water effect. Thus, a previous conditioning step of the adsorbent would be required in addition to removing the methanol excess from the crude biodiesel. If the refining treatment were performed under conditions of vacuum and temperature, it would be possible to reduce the number of process stages, removing the excess of methanol and water (present in the crude biodiesel and also adsorbed on the adsorbent material) simultaneously with the impurities adsorption. This would eliminate the need to add previous stages of removal of excess methanol and dehydration of the adsorbent.

In this research study a single refining step was performed by treating the crude biodiesel directly with the adsorbent, without a previous drying step and under temperature and vacuum conditions.

It is necessary to adjust the operating conditions in order to remove water and methanol fast enough so that they do not interfere with the adsorption of other impurities, thus lengthening the required process time. It is intended that in one step most of the impurities present in the crude biodiesel are removed in a reasonable short contact times, if possible similar to that used in dry refining processes which employ other adsorbents. The treatment conditions (pressure, temperature, mass of adsorbent) to be selected as optimal should ensure both adsorption of FG, DG, TG and soaps, as well as the elimination of methanol and water. In this way a product that meets quality specifications would be obtained.

Table 4 shows the results of tests carried using silica Trisyl 3000 as adsorbent. The choice between silicas was made considering that silica Trisyl 3000 has the highest surface area and contains the lowest amount of adsorbed surface water.

The temperatures evaluated were 65, 80 and 90 °C. Assays were performed at the absolute pressure of 0.2 bar. The concentration of adsorbent used was 1.1%. Contents of soaps, water, methanol, FG, MG, DG and TG, flash point and FFA were then measured on the refined biodiesel.

Table 4
Bleaching treatment. Content of impurities. Conditions: adsorbent = silica Trisyl 3000, pressure = 0.2 bar, adsorbent concentration = 1.1%.

T (°C)	Time (min)	Soaps (%)	Water (%)	MeOH (%)	FG (%)	MG (%)	DG (%)	TG (%)	FP (°C)	FFA (%)
Norm values		0.07	0.050	0.2	0.02	0.8	0.2	0.2	>101	0.5
Spiked biodiesel	0	0.25	0.100	5	0.2	2.41	0.08	0.04	45	0.27
65	15	0.25	0.050	0.002	0.03	2.41	n.d.	n.d.	163	0.23
	30	0.13	0.044	0.001	0.027	2.41	n.d.	n.d.	186	0.20
	45	0.009	0.042	n.d.	0.027	2.41	n.d.	n.d.	190	–
	90	0.004	0.040	n.d.	0.023	0.78	n.d.	n.d.	–	–
80	15	0.25	0.050	0.0034	0.03	2.41	n.d.	n.d.	155	0.17
	30	n.d.	0.048	0.003	0.025	0.81	n.d.	n.d.	153	–
	45	n.d.	0.045	0.0025	0.02	0.8	n.d.	n.d.	–	0.16
	90	n.d.	0.040	n.d.	0.02	0.672	n.d.	n.d.	–	–
90	15	0.001	0.040	0.005	0.03	0.47	n.d.	n.d.	152	–
	30	0.001	0.038	n.d.	0.028	0.45	n.d.	n.d.	–	–
	45	n.d.	0.030	n.d.	0.02	0.4	n.d.	n.d.	–	0.16
	90	n.d.	0.030	n.d.	0.019	0.32	n.d.	n.d.	–	0.16

FP: flash point.
n.d.: not detectable.

Based on the results shown in Table 4, the following issues arise:

(i) It is possible to remove methanol and water from the reaction medium in acceptable treatment times, reaching values complying with the quality standards.
(ii) Contrary to our expectations water elimination does not affect the adsorption of polar impurities on silica.
(iii) It is possible to achieve the limit values prescribed by the regulations for the impurities analyzed, in a one-step treatment under vacuum (0.2 bars) and mild temperature (90 °C), with contact times longer than 45 min and low concentrations of adsorbent (1.1%). The proposed treatment under vacuum conditions is effective for removing methanol, water, FG, glycerides (particularly MG), FFA and soaps.
(iv) Flash point values confirm the low residual methanol contents obtained.

The values of the adsorption capacities for some impurities at different temperatures are shown in Fig. 3. The comparison of the values obtained under vacuum conditions with those obtained under atmospheric pressure (Table 3) suggests that the adsorption capacity of the silica increases greatly in vacuum. When working at 90 °C and a contact time of 90 min the adsorption capacity of FG increases from 7–9% to 15–17%. For soaps it increases from less than 1% to 20–22% and for MG from 13–18% to more than 180%.

The results largely exceeded our expectations. The rise observed cannot be attributed only to an increase in the number of sites available for adsorption after the removal of surface water. On the other hand these results are very promising because the adsorbent retains approximately 23% of its weight when the process takes place at atmospheric pressure and nearly 235% when carried out under vacuum (these values are obtained by adding the values of Q (%) obtained for each impurity). This greatly improves the utilization of the adsorbent, reducing the cost of the process.

Another important observation is that the retention of soap is greatly improved under vacuum, equating the amount of glycerol retained. The order of affinity observed was: MG > FG ~ soaps > FFA, DG, TG. This leads us to affirm that the silica after treatment in conditions of mild temperature and vacuum, behaves as a non-selective adsorbent with a high capacity of adsorption of different types of impurities. It therefore presents affinity for all impurities in different degrees, which makes it an excellent adsorbent to purify biodiesel.

Under the conditions used, the methanol and water are removed from the medium without interference on the adsorption of the other impurities. In fact, it cannot be ruled out that part of the methanol and water remain adsorbed on the silica surface.

It is possible to achieve impurities concentration values that comply with the quality standards, in one-step under vacuum (0.2 bars) and temperature (90 °C) and at contact times of 45 min. These contact times are common in the industrial practice of oil bleaching.

A clear effect of temperature on the adsorption rate of MG is noticed, which is larger at higher temperatures. If a sample presents a greater adsorption rate at higher temperatures, this fact could be associated to high values of resistance to the diffusion of the impurities within the pores at lower temperatures. Although to a lesser degree this also happens with soaps. As to FG the treatment temperature does not have a major effect, since it is irreversibly adsorbed at low treatment times. Then we can conclude that despite that silica has a suitable porous structure, at the conditions of treatment there exists a steric hindrance to the free movement of the molecules of bigger size (glycerides). In a recent paper [21] we reported that during refining with silica powders the mass-transfer mechanism of FFA is controlled by intraparticle diffusion.

The free acid content in the crude biodiesel was low because of the characteristics of the feedstock used to prepare the biodiesel and the process itself in which FFAs react with the alkaline catalyst to form soaps. Therefore the impurities concentration values after the treatment are adjusted to the specified quality standards. On the other hand the production of biodiesel using alkaline catalysts provides a high biodiesel yield (>98%) and the main subproducts of the transesterification are FG and MG. The concentration of DG and TG is much lower than that of MG and generally meets the quality standards.

Table 5 compares the values of adsorption capacities experimentally obtained for FG, soaps, MG and FFA, with the maximum theoretical values calculated for each of these impurities, assuming that adsorption is reduced to the formation of a "monolayer" on the adsorbent. For the calculation of the theoretical values the postulates of Langmuir were considered valid [22]. The assumptions were:

(i) The concentration of adsorption sites of silica was 4 OH/nm² [23].
(ii) The adsorption stoichiometry was 1:1 for all impurities.
(iii) Each impurity is alone in the liquid medium.
(iv) All sites are the same for the purpose of adsorption.

Based on the analysis of Table 4 it can be concluded that for the silica Trisyl 3000 (under vacuum conditions) the adsorption
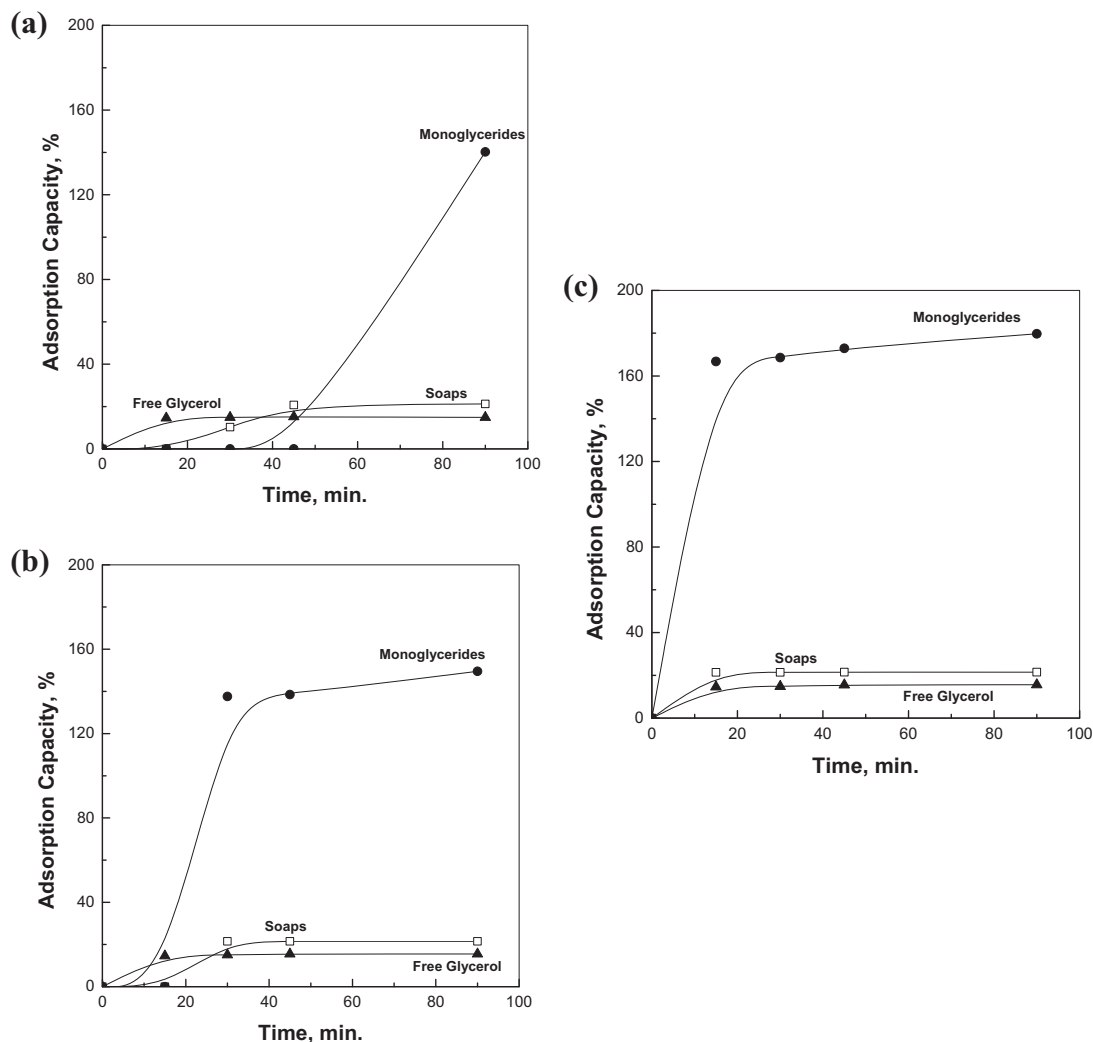
Fig. 3. Evolution of the adsorption capacity as a function of time. (a) $T = 65\ °C$. (b) $T = 80\ °C$. (c) $T = 90\ °C$.

Table 5
Comparison between the theoretically calculated and experimentally determined adsorption capacities ($P = 0.2$ bar, $T = 90\ °C$, contact time = 90 min., adsorbent concentration = 1.1 wt%.).

Compound	$Q_{\text{theoretical monolayer}}$ (%)	$Q_{\text{experimental}}$ (%)
FG	36.0	15.6
MG	140.0	180.1
DG	244.0	6.9
TG	348.0	3.4
Soaps	120.0	21.6
FFA	113.0	7.8

phenomenon is not limited to the formation of a theoretical "monolayer" of the adsorbed impurities. This is clear when considering that the adsorption of MG alone exceeds the monolayer value (without taking into account the adsorption of the other impurities). Then the adsorption phenomenon is more complex and must include multilayer formation.

The chemistry on the silica surface depends on the nature of attractive forces existing between the adsorbate and the adsorbent. This interaction may be due to chemical bonding, hydrogen bonding, hydrophobic bonding or van der Waals forces. Hydroxyl groups play an important role on the silica surface because hydrogen bonding is the most common mechanism of adsorption. Parida et al. [24] postulated that due to the presence of silanol groups at

the surface silica is mostly embedded with water in a multilayer. The authors found differences between the characteristics of the first layer of adsorbed water and the subsequent layers. Yamauchi and Hondo [25] suggested that water would settle only on part of the silanols at first as $SiOH–OH_2$ complexes by an H-bonding mechanism. A second water molecule would be added on the previous silanol water complexes in the form of $SiOH–OH_2–OH_2$.

Garrone et al. [26] compared the adsorption of water on the silica surface with that of other molecules of similar size (CO, H_2O, N_2O and NH_3). They found evidences indicating that the main interactions of silanol groups (SiOH) with the O end of CO, with the O end of N_2O, with the O atom in H_2O, and with the N atom in NH_3, are due to H-bonding. This H-bonding could be extended in the pore space involving more adsorbate molecules. Mizukami et al. [27] proposed the formation of surface molecular macroclusters for adsorption of ethanol on the silica surface and proposed that the H-bonding between the silanol group and the OH group of ethanol is responsible for adsorption.

The H-bonding adsorption model would allow obtaining adsorbed amounts of the impurities higher than the monolayer value. On the other hand it would explain the results obtained in the tests at atmospheric pressure and under vacuum. When the refining treatment is performed at atmospheric pressure the surface of silica is covered by one or more layers of adsorbed water so that in principle there would no free silanol groups capable of

Table 6
Comparison of the adsorption capacity of different adsorbents.

Adsorbent	C_{ads} (%)	Adsorption capacity (%)						Q_{total} (%)
		FG	MG	DG	TG	Soaps	FFA	
Magnesol[a]	1	24.0	5.0	6.0	8.0	16.0	5.9	64.9
Silica[a]	2	11.5	2.0	2.5	4.5	8.0	4.7	33.2
Amberlite resin[a]	1	–	–	–	–	15.2	8.5	23.7
	2	–	–	–	–	2.0	4.7	6.7
Purolite resin[a]	1	–	–	–	–	14.5	9.0	23.5
	2	–	–	–	–	1.0	3.0	4
Trysil 3000[b]	1.1	15.6	180.1	6.9	3.4	21.6	7.8	235.4

C_{ads}: adsorbent concentration.
Q_{total} (%): total adsorption capacity (%).
  [a] Ref. [12]. Pretreatment: (i) the crude biodiesel was heated at 90 °C for 10 min to remove the excess of methanol, (ii) adsorbent: none. Treatment: T = 65 °C, P = atm, contact time = 20 min, stirring.
  [b] Our results. Pretreatment: none. Treatment: T = 90 °C, P = 0.2 bar, contact time = 90 min, stirring.

retaining impurities. However this retention indeed happens. The impurities are linked by H-bonding to adsorbed water molecules. When the treatment is performed under vacuum and mild temperature conditions the water is removed from the surface sites of adsorption, which are then occupied by impurities. An additional adsorption by this mechanism is seen making it possible to obtain values of adsorption greater than the monolayer one.

In Table 6 our biodiesel refining results and those reported by Faccini et al. [12], are compared. These authors used different adsorbent materials (silica, Magnesol® and ion exchange resins) for biodiesel dry refining. It can be seen that:

(i) Unlike our methodology, which is of one single stage treatment, that used in reference [12] involves two steps of treatment since it is necessary to remove excess methanol before refining.
(ii) The values of total adsorption capacity obtained with our methodology far exceed those reported by Faccini et al. With our methodology silica Trysil 3000 retains 2.35 times its weight of impurities while silica and Magnesol® retain 0.33 and 0.65 times its weight, respectively.

It can be concluded that the proposed method has the following advantages: (i) simplicity, and (ii) it greatly improves the utilization of the adsorbent, reducing the cost of the process.

At this point, one last consideration can be made regarding the regenerability of the silicas. Our group is working on this topic using selective solvents. At present we have managed to recover 80% of the adsorption capacity of the silicas. The procedure and the main conclusions will be presented in a next contribution.

4. Conclusions

The conventional biodiesel refining downstream transesterification reactors, currently performed by decanting/washing or centrifugation/washing, can be conveniently replaced by a simple biodiesel purification method consisting of one single stage treatment with silica as adsorbent. The method seems a solution for biodiesel refining, saving water, money and process time.

With the proposed method it is possible to achieve a biodiesel composition complying the regulations on the analyzed impurities without a preliminary step to remove residual methanol, as it is the case with other adsorbents, and loading the adsorbent without a previous drying treatment. Optimum operating conditions are 0.2 bar, 90 °C, contact times longer than 45 min and 1.1% charge of adsorbent. Working under these conditions makes it possible

to totally eliminate the methanol and water from the medium without affecting the adsorption of other impurities. Water elimination does not affect the adsorption of polar impurities.

Silica Trisyl 3000 retains 23% of its weight when the process is performed at atmospheric pressure and nearly 235% when performed under vacuum conditions. This greatly improves the utilization of the adsorbent and reduces the cost of the process.

At the optimal process conditions silica behaves as a non-selective adsorbent with a high capacity of adsorption of the different types of impurities, which makes it an excellent adsorbent to purify biodiesel. The adsorption phenomenon is not limited to the formation of a theoretical "monolayer" of adsorbed impurities. The phenomenon is more complex and includes the formation of multiple layers.

Acknowledgements

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