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Adsorption in Biodiesel Refining - A Review

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1. Introduction

Biodiesel is a petrodiesel substitute composed of a mixture of fatty acid methyl esters obtained by the transesterification of plant oils or animal fats with short chain alcohols such as methanol or ethanol. Despite its natural origin biodiesel is technically fully compatible with petroleum diesel, requiring virtually no changes in the fuel distribution system or the Diesel motor. Its production and use have increased significantly in many countries and are in nascent status in many others. Other advantages of biodiesel compared to petrodiesel are reduction of most exhaust emissions, biodegradability, higher flash point, inherent lubricity and domestic origin (Chang et al., 1996; Romig & Spataru, 1996; Wang et al., 2000).

Literature on the refining of biodiesel is abundant but concentrates almost exclusively on the transesterification steps for transforming fats and oils into esters of short alcohols and fatty acids. In this sense in the last years the most important advances in the reaction technology have been the development of continuous heterogeneous transesterification reactors (Bournay et al., 2005; Portilho et al., 2008) and the design of new robust non-catalytic processes for multifeedstock operation (Saka & Kusdiana, 2001; Saka & Minami, 2009).

In the case of the refining operations downstream and upstream the transesterification reactors the biodiesel literature is however scarce. Two are the reasons for this: (i) Feedstock pretreatment in the case of biodiesel is a mature technology developed decades ago for the production of edible oil. (ii) After natural triglycerides are converted into fatty acid methyl esters, the product mixture needs little chemical adjustment since many properties of these esters are ideal for the functioning of Diesel motors.

Some reports on post-reactor biodiesel refining have dealt with classical and simple techniques of purification, e.g. water washing (Karaosmanoglu et al., 1996). Others have indicated that adsorption technologies are particularly suited for the refining of biodiesel (Yori et al. 2007; Mazzieri et al., 2008; Manuale et al. 2011). In order to elucidate the role of adsorption processes in the refining of biodiesel, this review studies some theoretical and practical aspects related to the functioning, design and operation of adsorbers and their application to the purification of biodiesel product and feedstocks.

2. The needs for refining of petrodiesel and biodiesel fuels

The objectives of Diesel fuel refining operations are aimed at improving the fuel combustion performance, maximizing the power delivered to the motor, increasing the engine life and reducing the emission of noxious compounds. The relevant properties involved are cetane

index, heat content, lubricity, viscosity, cold flow properties, oxidation stability and amount and kind of tailpipe emissions. Some properties are superior for biodiesel in comparison to petrodiesel and need no adjustment. This is the case of lubricity (93% film for biodiesel and 32% for petrodiesel), cetane index (45 for petrodiesel and 56 for biodiesel) and tailpipe emissions (Chang et al., 1996; Romig & Spataru, 1996). Other properties of biodiesel needing adjustment will be discussed in the next paragraphs.

Viscosity. Viscosity affects injector lubrication and atomization. Natural oils and fats (triglycerides) have excessive viscosity and cannot be easily injected; this is the main reason why they must be transformed into methyl esters. Even after transesterification the viscosity of biodiesel is higher than that of petrodiesel (5 cSt at 40 °C compared to 3 cSt), though it is considered enough low in international norms. A few reports have however indicated that additivations and chemical transformations could advantageously alter biodiesel viscosity. Nouredini et al. (1998) found that addition of GTBE in amounts as big as 22% could not only lower the pour and cloud points of biodiesel but also its viscosity by 8%. Yori et al. (2006) studied the acid-catalyzed isomerization of methyl soyate and found that isomerization decreased pour and cloud points but adversely increased the viscosity.

Oxidation stability. The stability of a diesel fuel is related to the occurrence of undesired reactions during storage. In the case of petrodiesel routine oxidation tests as performed by ASTM D2274 detect the formation of minor amounts of insolubles that are due to the precipitation of polar compounds, mainly polycyclic acids, after their reaction with iron particles or oxygen (Díaz & Miller, 1990). In the case of biodiesel the problem is worse because unsaturated fatty acid chains are main components of the fuel and they are active in oxidizing reactions. In contact with oxygen, peroxides are formed that promote the formation of organic acids, and then of polymers (gums) that plug fuel lines and filters. Oxidative degradation during storage can also compromise fuel quality with respect to effects on kinematic viscosity, acid value, cetane number, total ester content, and formation of hydroperoxides, soluble polymers, and other secondary products (Du Plessis et al., 1985; Bondioli et al., 2002; Thompson et al., 1998). The increased acidity and peroxide values as a result of oxidation reactions can also cause the corrosion of fuel system components, the hardening of rubber components and the erosion of moving parts (Tang et al., 2008). By now the only method for increasing the biodiesel resistance to oxidation is to add synthetic or natural oxidation inhibitors such as tocopherols and hydroquinones. Other alternative way is the hydrogenation of the unsaturated chains. Compared to untreated soybean oil methyl esters, partially hydrogenated products have shown superior oxidative stability and similar specific gravity, but inferior low-temperature performance, kinematic viscosity and lubricity (Moser et al., 2007). In order to raise the saturated fraction of biodiesel other efforts have been carried out by distillation and crystallization (Falk & Meyer-Pittroff, 2004) and it is conceivable that the same could be done by adsorption over suitable materials.

Storage stability. Also related to the stability of biodiesel, some other minor components of biodiesel, the monoglycerides (MGs) and diglycerides (DGs) can form crystals during storage at low temperatures and precipitate. These crystals not only can clog fuel lines and fuel filters but due to their amphiphilic nature, their absence in the solution causes the precipitation of other unstable solvatable impurities such as glycerol.

Acidity. Acidity in petrodiesel is mainly related to the presence of naphthenic acids in the crudes. Acidity of biodiesel depends on a wider variety of factors and is influenced by the type of feedstock used and on its degree of refinement. Acidity can also be generated during the production process, e.g. by mineral acids introduced as catalysts or by free fatty acids

resulting from hydrolysis of soaps and esters. Biodiesel acidity also reflects the degree of fuel ageing during storage, as it gradually increases due to hydrolytic cleavage of ester bonds. High fuel acidity of biodiesel has been discussed in the context of corrosion and the formation of deposits within the engine, particularly in fuel injectors, by catalyzing polymerization in hot recycling fuel loops (Refaat, 2009). However the main problem associated with acids is the formation of soaps as it will be discussed later.

Carbonization properties. Formation of carbon deposits in the injectors of a Diesel engine is undesired; the tendency of a fuel to form these deposits being measured by the Conradson Carbon Residue (CCR) test (ASTM D189). In the case of petrodiesel CCR is related to the presence of aromatic and polyaromatic compounds, and is favorably reduced by hydrotreatment. In the case of biodiesel deposits formed in the injectors are related to polymerization of glycerol and glycerides. These polymers undergo further decomposition to carbon deposits and tarnishes over injectors and cylinders. In this sense the needed biodiesel refining step is the removal of free and bound glycerol to minimum values. ASTM D6751 constrains the iodine number of biodiesel to less than 112 on the same basis because olefinic chains are also reactive for polymerization. However this is not an issue in european norms (EN 14214).

Cold flow properties. In raw biodiesel the presence of wax-like, long acyl chains, poses the problem of crystallization when temperature is too low. Crystal nucleation is enhanced by the presence of MGs and DGs, mainly affecting the cloud point (van Gerpen et al., 1996). A first solution is to eliminate glycerides to negligible values. Other solutions for waxy FAMES are not without drawbacks: (i) Catalytic dewaxing (Yori et al., 2006) decreases the cetane number and increases the viscosity. (ii) Winterization for removing the waxy saturated fraction also removes the fraction with higher cetane and oxidizing stability. (iii) Commercial pour point depressants are reported to reduce the pour point of biodiesel but usually do not reduce its cloud point nor improve its filterability at low temperatures (Dunn et al., 1996). Fortunately, biodiesel-petrodiesel blends have cloud and pour points closer to those of petrodiesel. The saturated portion eliminated by winterization can also be used as a “summer fuel” if massive storage is available.

Refinery operation issues. Some specifications for feedstocks and intermediate streams in refineries are related to the correct functioning of process units. Sulfur reduction in the case of petroleum fuels is necessary not only to improve the quality of the final product but also to prevent the poisoning of catalysts in some hydroprocessing units (Ito and van Veen, 2006). In the case of biodiesel many undesired components are responsible for the malfunctioning of reactors and phase separators:

- Phosphorous, calcium, and magnesium are minor components typically associated with phospholipids and gums that act as emulsifiers or cause sediments, lowering yields during the transesterification process. Phosphorus typically leads to an increased difficulty in the separation of the biodiesel and glycerol phases (Anderson et al., 2003).

Component	Crown Iron Works (USA)	Lurgi GmbH (Germany)
Moisture and volatiles	0.05% max	0.1% max
Acidity	0.5% max	0.1% max
Phosphorus total	20 ppm max	10 ppm max
Soap	50 ppm max	n.a.
Unaponifiables	1% max	0.8% max

Table 1. Quality requirements for the feedstock of two alkali homogeneous catalyst biodiesel production technologies (Anderson et al., 2003; Lurgi, 2011).

- FFAs and soaps. In the case of the alkali-catalyzed process, the dominant biodiesel technology, the presence of free fatty acids (FFAs) leads to the use of an increased amount of catalyst and other chemicals. It also increases the concentration of salt and water in the crude glycerol phase. Aside from the increased cost of chemicals, the presence of FFA causes a larger potential for soap formation and all the production issues associated with soap, including more difficult phase separations and more frequent cleaning of process vessels. Although FFA can be reacted in an acid-catalyzed reaction with methanol to form methyl esters, the amount of acid required is much higher than the amount of catalyst used in the transesterification of neutral oil. The reaction also does not go as far to completion as transesterification, which may lead to the resulting biodiesel product to be out of specification on FFA. Acid catalysis of FFA to methyl esters also results in higher salt and water formation. For all these reasons feedstock specifications for FFA have low limits.
- Unsaponifiable matter (UM) consists of plant sterols, tocopherols and hydrocarbons, with very small quantities of pigments and minerals. UM is limited in the feedstock of biodiesel processes mainly on the basis of its foaming properties that make separations difficult (see Table 1). The unsaponifiable matter is not affected by ester preparation, so it is likely to be present in similar amounts in biodiesel to its level in the crude feedstock. UM has no harmful effects except possibly for a change in the crystallization onset temperature (van Gerpen et al., 1996). For this reason UM is not limited in biodiesel norms. Some unsaponifiable compounds, such as the phytosterols, have antioxidizing capacities and they are useful for prolonging the storage life of biodiesel (Rabiei et al., 2007). A possible challenge for adsorption operations in this case could be the selective removal of impurities while not affecting these antioxidizing compounds.
- Water. Alkaline catalysts (NaOH, KOH, MeONa) react with water and oil to produce soaps. Acid catalysts (e.g. H_2SO_4) when hydrated reduce their effective acid strength and their catalytic activity. Water thus leads to deactivation and higher catalyst usage.

3. Refining of biodiesel feedstocks

Depending on their degree of refining, biodiesel feedstocks might need some or all the refining steps common to the refining of edible oils: (i) Degumming, that is necessary if large amounts of phosphatides are present in the feedstock, phosphoric acid and steam being used to swell the gums for further removal. (ii) Deodorization, that is used with feedstocks up to 30% FFA. It is basically a vacuum distillation at 240-270 °C and 2-5 mmHg, that removes aldehydes, ketones and smelly products, pesticides, fungicides, herbicides, etc. It also lightens up the product by destroying carotenoids. (iii) FFA reduction by many means, steam stripping, caustic stripping, solvent extraction, glycerolysis, acid esterification, etc. (iv) Bleaching, that is normally used to remove remaining impurities such as pigments, soaps, insolubles, peroxides, phospholipids and metals.

It must be noted however that biodiesel and edible oil have different quality specifications. This is especially true for color and odor, that are not an indication of technical quality of biodiesel. ASTM quality biodiesel can range from clear to black and have an unpleasant smell. This is more a consumer issue because it raises uncertainties. Color removal may need carbon filtration and bleaching while odor removal may need deodorization.

The degree of FFA reduction in biodiesel feedstocks needs special attention because it has a high dependence on the technology of biodiesel production used: (i) In the case of the non-

catalytic method that uses supercritical methanol at high temperatures and pressures, FFA content is not an issue, because triglycerides and FFAs react to form methyl esters with similar rates (Warabi et al., 2004). (ii) In the acid-catalyzed method feedstocks with up to 20% acidity can be completely reacted by acid catalysis with mineral acids though the kinetics are much slower (Lotero et al., 2005; Freedman, 1986). (iii) The alkali-catalyzed method (dissolved NaOH, KOH, MeONa, etc. catalysts) tolerates only 0.5% FFA in the feedstock (Table 1). However some producers accept feedstocks of up to 4% FFA and then use caustic stripping by the same catalyst in the reactor or caustic washing before the reactor to eliminate them from the reaction medium. The soap that goes into the glycerol phase or the wash water is hydrolyzed and reacted to biodiesel by acid-catalyzed transesterification in a separate reactor. (iv) In the acid-base method feedstocks with up to 20% acidity are first esterified in acid catalysis and then the reaction is continued with alkaline catalysis.

The use of adsorbents for the pretreatment of biodiesel raw materials is related to known techniques for edible oil refining. After pressing of oil seeds, and after degumming and caustic refining of the virgin oil, a step of bleaching is commonplace in order to improve the colour by adsorbing chlorophylls, carotenoids and other pigments, and the removal of other undesired components such as metals and free fatty acids, that contribute to the instability of the oil under oxidizing conditions. Bleaching of oils can be done with natural clays such as bentonite, smectite, montmorillonite, etc., or activated clays produced by acid treatment (Foletto et al., 2011). Clays are mainly used for removing high molecular weight organic compounds but their affinity for polar compounds and metals is low. In this sense most part of the metals is eliminated during the caustic refining of edible oils and in the subsequent water washing steps, while bleaching with clays does not practically modify the metal content (van Dalen & van Putte, 1992; Farhan et al., 1988).

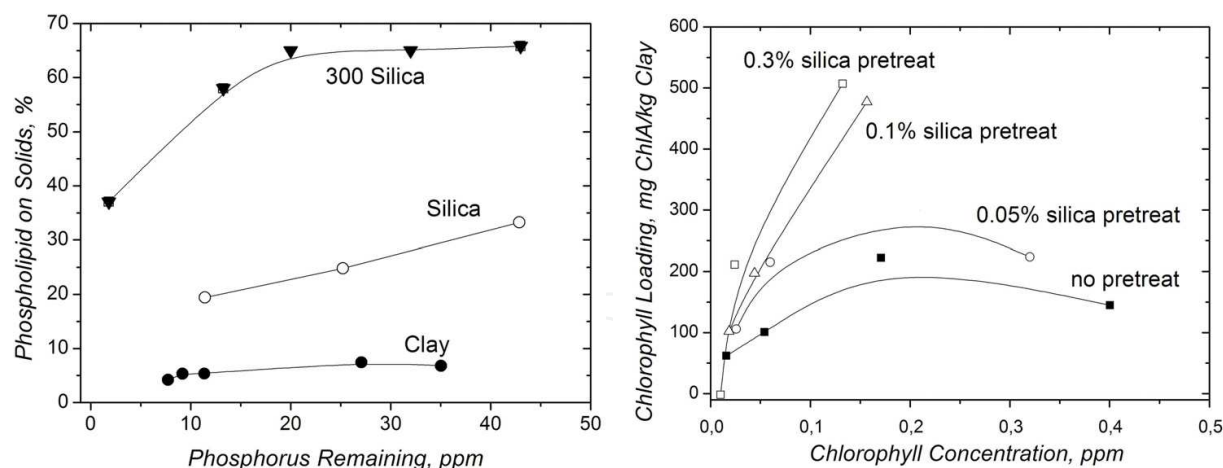


Fig. 1. Isotherms of adsorption of phosphatides on silica (left). Adsorption of chlorophyll on clay as a function of the silica adsorption pretreatment (right). Welsh et al. (1990).

Another adsorbent commonly used is silica, either alone or together with clays, though it is now accepted that best treatments should include some portions of both, since silicas adsorb preferably polar compounds and clays are more suitable for organic compounds. Treatment with silica has become increasingly widespread and silicas for edible oil refining have become highly tailored for this application, thus leading to the coining of the term “silica refining” (Welsh et al., 1990). The conditions for optimal silica refining can be

summarized as follows: (i) Oil temperature is raised to 70-90 °C. (ii) Silica is added at atmospheric pressure to the vessel containing the oil. (iii) The moisture content of the oil is reduced to 0.2-0.5% by evaporation, preferably in a vacuum. (iv) The contact time between the silica and the oil should be 10-15 min. (v) The moisture in the oil plays an important role in the mechanism responsible for transporting polar compounds from the oil to the silica, where they are trapped. (vi) After the removal of the polar contaminants the oil should be further dried if clays are to be used in the bleacher. During the vacuum drying process water is removed from the silica and the weight is reduced to even 40% of its original value; the solid reduces also in size and so does the load on the filters downstream the bleachers, which can then be operated at higher filtration flowrates and longer filtration cycles.

As silicas are far more efficient adsorbents for polar contaminants, if colour is not an issue (like in the case of biodiesel fuel) they can easily replace bleaching clays. If colour reduction is necessary then clays can be used in a second step after silicas have removed the polar contaminants. This reduces the amount of adsorbent used and enhances the quantity of oil produced because a lower quantity of filter cake is produced and oil losses are reduced. In this sense, a common industry perception is that 20-25% of oil is present in the filter cake but as oxidized and polymerized oil are not extracted in the extraction tests, the typical oil content in the cake can be as high as 40%.

The claimed advantages of silica (Grace, 2011) for refining biodiesel feedstocks are: (i) Lower costs of residue treatment by means of the reduction of effluents. (ii) Lower costs by elimination of washing steps. (iii) Lower product losses. (iv) Higher yield of the biodiesel fuel precursor. (v) Lower demand of catalyst in the transesterification reactor due to a lower FFA content. (vi) Lower consumption of acid for neutralization of the catalyst. (vii) Higher yield of biodiesel due to an enhanced separation of the glycerol and biodiesel phases (absence of soaps and glycerides). (viii) Purer glycerol due to a low content of impurities. (ix) Lower costs of production of biodiesel. (x) Quality improvement due to an enhanced stability (absence of metals and FFA).

One additional benefit of silica addition in the case of the caustic refining for oil treatment (e.g. for biodiesel alkaline processes of low FFA tolerance) is that water-wash centrifuges can be eliminated because silicas efficiently remove residual metals, phospholipids and soaps. These must be otherwise washed away to prevent them reaching the bleaching units.

4. Refining of crude biodiesel

After transesterification is completed, many contaminants can still be present in the biodiesel product depending on the technology of transesterification used (Table 2). Removal of these impurities will be treated separately in the next subsections.

4.1 Glycerides

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. The ASTM D6751 and EN 14214 standards establish a maximum amount of 0.24-0.25% 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.

<i>Impurity</i>	<i>Alkali-catalyzed</i>	<i>Acid-catalyzed</i>	<i>Supercritical</i>
<i>Soaps</i>	Yes. By neutralization of FFA with catalyst	After neutralization of the catalyst	If feedstock treatment was ineffective.
<i>Metals, P</i>	If feedstock treatment was ineffective.	If feedstock treatment was ineffective.	If feedstock treatment was ineffective.
<i>FFAs</i>	No	Yes. Due to incomplete esterification.	Yes. Due to hydrolysis of the feedstock.
<i>Monoglycerides</i>	Yes. Product of transesterification.	Yes. Product of transesterification.	Yes. Product of transesterification.
<i>Diglycerides</i>	Yes. Product of transesterification.	Yes. Product of transesterification.	Yes. Product of transesterification.
<i>Triglycerides</i>	Yes. Due to incomplete conversion.	Yes. Due to incomplete conversion.	Yes. Due to incomplete conversion.
<i>Glycerol</i>	Yes. Product of transesterification.	Yes. Product of transesterification.	Yes. Product of transesterification.

Table 2. Contaminants in biodiesel product depending on transesterification technology.

In the specific case of monoglycerides (MG), diglycerides (DG) and triglycerides (TG), they are the raw materials and the intermediates of the transesterification reaction. This is an equilibrium reaction with an equilibrium constant close to unity (D’Ippolito et al., 2007), that dictates that a methanol excess must be used to shift the equilibrium to the right and to decrease the concentration of triglycerides and intermediates in the final product mixture. Nouredдини & Zhu (1997) and Darnoko & Cheryan (2000) studied the kinetics of transesterification of oil and they reported that the conversion value for the 1-step reaction of transesterification of soy oil with methanol in a stirred tank reactor, using a methanol-to-oil ratio of 6 was 80-87% at 1 h of time of reaction. Busto et al. (2006) indicated that in supercritical tubular reactors a methanol-to-oil ratio of 6 yields an equilibrium value of 94-95% at high Péclet numbers. In the case of processes with two reaction steps, after the final step of glycerol removal, the amount of TG, MG and DG is sufficiently low to almost comply with the ASTM D6751 limits. It can be however deduced that this final content of bound glycerol is a function of the methanol-to-oil ratio used in the reaction and the number of reaction steps. For the alkali catalized process with two reaction steps this methanol-to-oil ratio is 6. In the case of the supercritical method with one reaction step (Goto et al., 2004) the adequate methanol-to-oil molar ratio is reported to be 42. The final adjustment of the glycerides content is made in the standard industrial practice by water washing. Some authors however propose separating the glyceride fraction (Goto et al., 2004; D’Ippolito et al., 2007) and recycling it to the reactor.

One interesting issue is that of the relative concentration of MG, DG and TG in the final product. According to data of Nouredдини and Zhu (1997) the equilibrium constants for the partial transesterification (producing 1 mol of FAME) of triglycerides, diglycerides and monoglycerides are $K_1=0.45$, $K_2=0.18$, $K_3=34.6$. TGs would therefore be thermodynamically more stable. It is however found in practice, probably because of kinetic limitations, that MGs and DGs are main impurities (He et al., 2007). This points to the adequacy of adsorption treatments since MGs are efficiently removed by adsorption over silica, even in the presence of water and soaps (Mazzieri et al., 2008).

Some points seem clear: (i) The final bound glycerol content is a function of the methanol-to-oil ratio. (ii) An adequate separation/recycling or removal/disposal of glycerides could

reduce the complexity of the process by reducing the methanol-to-oil ratio and the amount of recycled methanol. (iii) MG and DG should be the focus for reducing bound glycerol. Steps in the direction of (ii) have been hinted by D'Ippolito et al. (2007) and Manuale et al. (2011) for the supercritical method. The first proposed using 2 reaction steps with a low methanol-to-oil ratio (6-10), retaining glycerol and glycerides in packed bed adsorbers and recycling them to the reactor. The second indicated that the combination of 1-step reaction, a methanol-to-oil ratio of 15-20 and silica refining could produce EN14214 grade biodiesel.

4.2 Glycerol

Liquid-liquid equilibrium studies of biodiesel-methanol-glycerol mixtures have been undertaken in the past by Kimmel (2004), Negi et al. (2006) and Zhou & Boocook (2006). They determined that the equilibrium glycerol content in biodiesel depends strongly on the residual content of methanol acting as a cosolvent. When methanol is completely removed the free glycerol content depends only on the temperature, being approximately 0.2% at 25 °C and increasing linearly with temperature (Kimmel, 2004). Even if methanol is not present hydrophilic glycerol can be solubilized in the oil phase by amphiphilic MG and DG. These glycerides can separate from the oil during storage and precipitate as a result of temperature changes or long residence times. Glycerol then precipitates as a consequence of the reduced solubility, leading to the formation of deposits. Soluble glycerol is also a problem because glycerol polymerizes on hot surfaces (cylinders, injectors) with formation of deposits or "tarnishes". For all these reason glycerol should be thoroughly removed.

Glycerol removal by adsorption was early performed by Griffin and Dranoff (1963) using sulfonic resin beads. Glycerol adsorption over polar surfaces is favored if dissolved in organic media that have little affinity for the adsorbent. Nijhuis et al. (2002) reported that adsorption of organic esters (e.g. biodiesel) over polar surfaces such as those of silica and Nafion resins, is negligible. Yori et al. (2007) studied the reversible adsorption of glycerol from biodiesel and reported that silica has a great capacity for glycerol removal, its saturation capacity being 0.13 g of glycerol per gram of adsorbent. When operated in packed beds, for a glycerol concentration of 0.11–0.25% typical of biodiesel streams issuing from gravity settling tanks, an effluent limit of $C/C^0=0.01$ and an entrance velocity of 11 cm min⁻¹, a 2 m high silica bed with 1/8" beads would have a net processing capacity of 0.01–0.02 m³_{biodiesel} kg_{silica}⁻¹. Much of the good performance of silica is related to the favorable thermodynamics of adsorption, since glycerol-silica displays an almost irreversible, square isotherm (Yori, 2008).

4.3 Soaps, salts and metals

Soaps are produced by the reaction of FFAs during the first steps of caustic refining of the fatty feedstock or by the reaction of the remaining FFAs with alkaline homogeneous catalysts in the transesterification reactor. These reactions lead to the formation of estearates, oleates, palmitates, etc. of sodium and potassium, that are amphiphilic substances that bring phase separation and plugging problems downstream the reactor. Other salts of sodium or potassium come from the neutralization of acid homogeneous catalysts in the acid-catalized process. These inorganic salts lead to corrosion in lines and vessels and they must also be completely eliminated in the final biodiesel product because of quality issues.

Metals are minor components in all oils as they are present as oligoelements in highly specialized molecules such as chlorophylls (magnesium) and porphyrins (magnesium, iron, manganese). Other sources of metals are the contamination from iron and copper surfaces

during the process of oil extraction or biodiesel production. Certain metals, such as cobalt, manganese and chromium, but particularly iron and copper, exhibit a prooxidant effect in oil. The manifestations of oxidation are flavor, color and odor deterioration. Copper is perhaps the most active catalyst, exhibiting noticeable oxidation properties at levels as low as 0.005 ppm (Flider & Orthoefer, 1981). Though flavor, color and odor deterioration are probably not an issue for biodiesel, oxidation stability is indeed required.

For soaps, salts and metals, adsorption on silica adsorbents seems the most suitable means of removal (Welsh et al., 1990). Clays offer only a small adsorption capacity for soaps and an almost null capacity for metals.

4.4 Free fatty acids

FFAs have negligible values in biodiesel produced by the alkaline method. Depending on the efficiency of esterification they can be present in non-negligible amounts in biodiesel produced by the acid-catalyzed method or the supercritical method. Manuale et al. (2011) reacted different feedstocks with acidities ranging from 0.08 to 23.6% and found that the esterification with supercritical methanol (280 °C, 20=methanol-to-oil ratio) reduced the FFA content to 1-2.5% after 1 h and 0.4-0.6% after 1.5 h of reaction time. Reduction of the FFA content to values lower than those of the international norms can be done by washing. Adsorption however can prove simple, robust and efficient. For these application silicas are found to be superior than other adsorbents in both bleaching capacity and bleaching rate.

Adsorbent	Adsorbent conc., mass %	Bleaching time, min	Adsorption capacity, $g_{FFA} g_{ads}^{-1}$
Virgin activated carbon	5	720	6.0
Mg doped activated carbon	5	720	5.0
Diatomaceous earth	1	30	10.1
Silica gel	0.36	90	140.0

Table 3. Adsorbents capacity for FFA removal from biodiesel (Manuale et al., 2011).

5. Adsorption

In the last years there has been a great progress in adsorbent design and cyclic adsorption process developments, thus making adsorption an important separation tool (King, 1980). Adsorption is usually performed in columns packed with adsorbent but it can also be performed in stirred tanks with the adsorbent in suspension. The latter are usually known as bleachers since their most common application is the bleaching of edible oils with clays.

The high separating power of the chromatographic effect, achieved in adsorbent-packed columns, is a unique advantage of adsorption as compared to other separation processes. The high separating power is caused by the continuous contact and equilibration between the fluid and sorbent phases. If no diffusion limitations are considered, each contact is equivalent to an equilibrium stage (theoretical plate) and several hundreds or more of such equilibrium stages can be achieved within a short column. Adsorption is thus ideally suited for purification applications and difficult separations.

The adsorptive separation is achieved by one of three mechanisms: adsorption equilibrium, steric effect and kinetic effect. Most processes, especially those in solid-liquid phase, operate with the principle of adsorption equilibrium and hence they are called equilibrium

separation processes. In this processes the amount of adsorbate retained is primarily determined by the thermodynamic adsorbate-adsorbent activity with little regard to mass transfer phenomena. The steric effect derives from the molecular sieving properties of zeolites and other molecular sieves and can be taken as an extreme case of adsorption controlled by mass transfer phenomena. In this case either small or properly shaped molecules can diffuse into the adsorbent while other molecules are partially or totally excluded. Typical examples are the separation of linear and branched alkanes (Silva et al., 2000) or the dehydration of aqueous ethanol (Teo & Ruthven, 1986), both performed using molecular sieves. Kinetic separation is achieved by virtue of the differences in diffusion rates of different molecules. This kind of separation is mostly found in gas-gas separation as in the separation of the component gases of air (Ruthven & Farooq, 1990).

In the case of the biodiesel feedstock and product, the low elution rates in the packed columns makes the dynamic separation (kinetic effect) of no use for a practical separation. In the case of the steric effect this is expected to work fine for molecules differing widely in size and this could be the case for molecules of the organic and polar phases normally found at the outlet of the transesterification reactors. Triglycerides, diglycerides, monoglycerides, free fatty acids and fatty acid methyl esters have high molecular weights and long acyl chains and they are the main components of the organic phase. On the other side glycerol, water and methanol have small molecular sizes and could be retained in packed beds containing suitable adsorbents. Because of their relative high vapor pressure, water and methanol need a relatively few number of theoretical plates to be separated from the organic phase by distillation/evaporation (Zhang et al., 2003) and this is indeed the preferred method of water and methanol removal. However some reports on the use of hygroscopic adsorbents for biodiesel drying can be found (Lastella, 2005). Removal of glycerol from biodiesel using adsorbents has already been proved but only equilibrium adsorption on open pore adsorbents has been tried (Yori et al., 2007; Mazzieri et al., 2008). The use of the steric effect in the adsorption of water on zeolites has however been proposed for the drying of the methanol to be recycled to the biodiesel process (McDonald, 2001).

This leaves equilibrium adsorption as the main principle behind the adsorption refining of biodiesel and makes the adsorption isotherm as the main piece of information for the accurate design and scale-up of adsorption units. In this sense, though a lot of information is available for adsorption of impurities from plant oils (biodiesel feedstock) in relation to bleaching with clays (Hussin et al., 2011) or silicas (Rossi et al., 2003) only scarce information for purification of biodiesel by adsorption has been published (Manuale et al., 2011; Schmitt Faccini et al., 2011; Vasques, 2009; Mazzieri et al., 2008).

6. Adsorption isotherms

The function that describes the relation between the amount of adsorbate on the solid and its liquid-phase concentration is called adsorption equilibrium isotherm. Different functions can be used to describe this equilibrium. The Langmuir-type isotherm remains to be the most widely used for practical applications (Eq. 1).

$$\theta = \frac{q^*}{q_m} = \frac{K_L C^*}{1 + K_L C^*} \quad (1)$$

Only liquid phase applications will be discussed in this review and therefore also only liquid phase isotherms. The constant K_L is called Langmuir constant. C^* and q^* are the

equilibrium values of the bulk concentration of the adsorbate in the liquid phase and the concentration in the solid phase. θ is the fractional coverage of the surface and q_m the maximum or saturation load. At low pressures or in dilute solutions, the Langmuir isotherm reduces to a linear form, or Henry's law form (Eqs. 2-3).

$$\theta = K_L C^* \quad (2)$$

$$q = K_L C^* q_m = H C^* \quad (3)$$

All isotherms should reduce to the Henry's law form at extreme dilution. Since high dilution is the condition for many systems that need to be purified to extremely small amounts of certain impurities, the Henry's constant becomes the most important factor for purification. Both K_L and H are proportional to the exponential of the heat of adsorption ($-\Delta H$). For physical adsorption, ΔH is proportional to the bond energy between the adsorbate molecule and the adsorbent surface. Thus bond energy becomes critical for purification. Strong bonds are typical of adsorbate-adsorbent systems in ultrapurification.

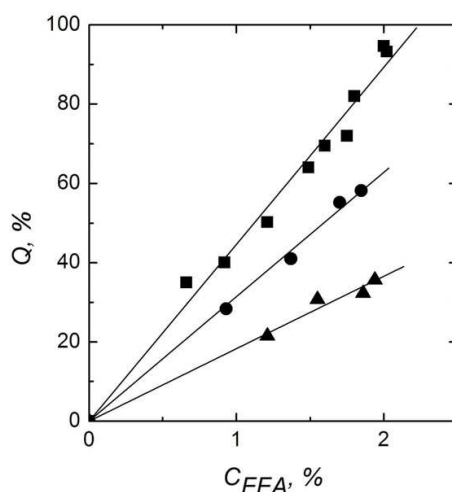


Fig. 2. Adsorption isotherm for silica TrySil 3000 at three different temperatures (Manuale, 2011). 70 °C (■), $H=44.6$. 90 °C (●), $H=31.4$. 110 °C (▲), $H=18.3$. $\Delta H=-5.7$ kCal mol⁻¹.

Zeldowitsch (1934) and previously Freundlich (1906) supplied an equation that is widely used to describe the data for heterogeneous adsorbents (Eq. 4).

$$q^* = K_F C^{*1/n} \quad (4)$$

In this formula q^* and C^* are the equilibrium adsorbate concentrations in the solid and fluid phase, respectively. Zeldowitsch obtained this formula assuming an exponentially decaying function of site density with respect to ΔH , while Freundlich proposed it on an empirical basis. Freundlich's isotherm is customarily used to express the equilibrium concentration of metals and colorant bodies (chlorophylls, carotenes, etc.) in oils (Liu et al., 2008; Toro-Vázquez & Proctor, 1996) and is expected that it should also be convenient for the same adsorbates in biodiesel precursor oils and fats. In the case of the biodiesel product probably the fit of the data of adsorption of some impurities could also be good, but in this case the oil has already been refined before entering the transesterification reactor and in so diluted condition the Henry's linear isotherm could better apply.

To avoid indefinite increase in adsorption with concentration, the so-called Langmuir-Freundlich isotherm is sometimes proposed (Sips, 1948) (Eq. 5). This isotherm can be derived from the Langmuir isotherm by assuming each adsorbate molecule occupies n sites. It can also be considered as the Langmuir isotherm on nonuniform surfaces.

$$(q^*/q_m) = \frac{K_{LF} C^{*1/n}}{1 + K_{LF} C^{*1/n}} \tag{5}$$

Langmuir’s formula has been successfully used to express the adsorption of glycerides from biodiesel over silica gel (Mazzieri et al., 2008). In the case of free fatty acids (FFAs) Nawar and Han (1985) also concluded that the Langmuir isotherm was followed by octanoic acid adsorption on silica. The better adjustment of free fatty acid (oleic, linoleic, etc.) adsorption over several solids by the Langmuir model (in comparison to Freundlich’s) has also been reported by Proctor and Palaniappan (1990) and Cren et al. (2005, 2010). The Langmuir and Langmuir-Freundlich isotherms for adsorption of single components are readily extended to an n -component mixture to yield the extended multicomponent Langmuir isotherm (Yang, 1997) (Eq. 6) and the so-called loading ratio correlation (LRC) (Yon & Turnock, 1971) (Eq. 7). In these equations it is assumed that the area occupied by one molecule is not affected by the presence of other species on the surface. This is not thermodynamically consistent but the equations remain nonetheless useful for design.

$$(q_i^*/q_{m,i}) = \frac{K_{L,i} C_i^*}{1 + \sum K_{L,i} C_i^*} \tag{6}$$

$$(q_i^*/q_{m,i}) = \frac{K_{LF,i} C_i^{*1/n}}{1 + \sum K_{LF,i} C_i^{*1/n}} \tag{7}$$

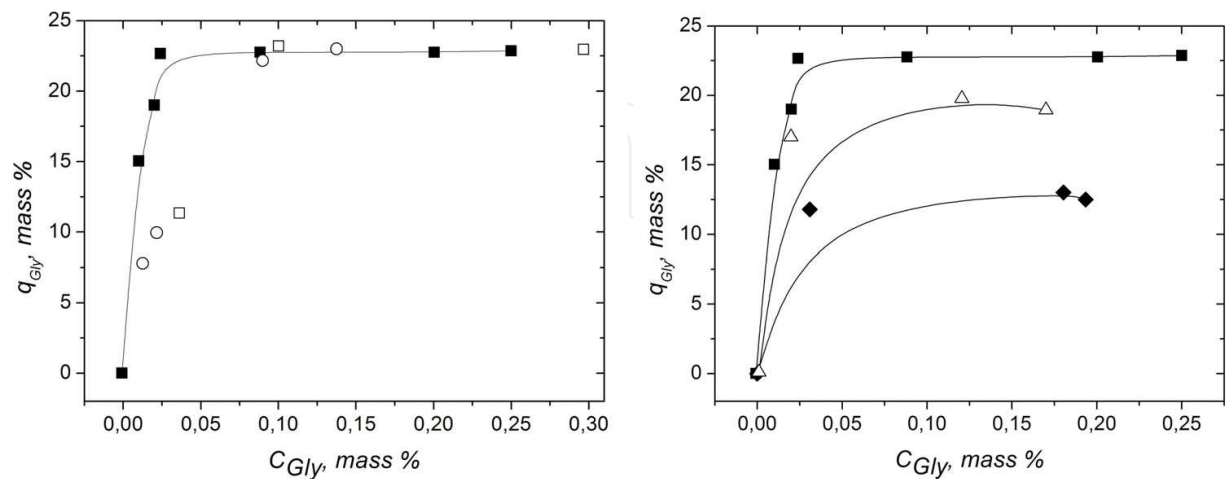


Fig. 3. Adsorption of glycerol over silica (Mazzieri et al., 2008). (■) Pure biodiesel. (□) Biodiesel spiked with water (944 ppm). (○) Biodiesel spiked with soap (270 ppm). (Δ) Biodiesel spiked with MG (7500 ppm). (◆) Biodiesel spiked with methanol (12000 ppm).

Mazzieri et al. (2008) used the multicomponent Langmuir isotherm to express the simultaneous adsorption of glycerol and monoglycerides. They found that adsorption of glycerol is not influenced by the presence of small amounts of water and soaps. Conversely the presence of MGs and/or methanol lowers the adsorption capacity of glycerol because of the competition of MGs for the same adsorption sites.

7. Mass transfer kinetics and models for adsorption in the liquid phase

It is generally recognized that transfer of adsorbates from the bulk of a liquid occurs in two stages. First molecules diffuse through the laminar film of fluid surrounding the particles and then they diffuse inside the pore structure of the particle. Most authors assume that the concentration gradient of any species along the film is linear and that the mass transfer to the adsorbent surface is proportional to the so-called film coefficient, k_f (Eq. 8). In this equation, q is the adsorbent concentration on the solid particle, r_p is the particle radius and ρ_p is the average density of the particle. C is the concentration of the adsorbate in the bulk of the fluid and C_s the value of adsorbate concentration on the surface. k_f is often predicted with the help of generalized, dimensionless correlations of the Sherwood (Sh) number that correlate with the Reynolds (Re) and Schmidt (Sc) numbers and the geometry of the systems. The most popular is that due to Wakao and Funazkri (1978) (Eq. 9).

$$\frac{\partial q}{\partial t} = \left(\frac{3k_f}{r_p \rho_p} \right) (C - C_s) \quad (8)$$

$$Sh = \frac{2r_p k_f}{D_m} = \left(2.0 + 1.1 Sc^{\frac{1}{3}} Re^{0.6} \right) \quad (9)$$

$$Sc = \frac{\mu}{D_M \rho} \quad (10)$$

In the case of the homogeneous surface diffusion model (HSDM) the equation of mass transport inside the pellet is that of uniform Fickian diffusion in spherical coordinates (Eq. 11). Sometimes this model is modified for system in which the diffusivity is seemingly not constant. The most common modification is to write the surface diffusivity, D_s , as a linear function of the radius, thus yielding the so-called proportional diffusivity model (PDM). A detailed inspection of the available surface diffusivity data indicates that surface diffusivity is similar but expectedly smaller than molecular diffusivity, D_M . Some values of D_M are presented in Table 4.

$$\frac{\partial q}{\partial t} = D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (11)$$

In the case of fatty substances there is not much reported data on the values of surface diffusivity. Yang et al. (1974) found that stearic acid had a surface diffusivity on alumina of about 10^{-9} - 10^{-11} m²s⁻¹ depending on the hydration degree of the alumina. Allara and Nuzzo (1985) reported values of D_s of 10^{-10} - 10^{-11} for different alkanolic acids on alumina.

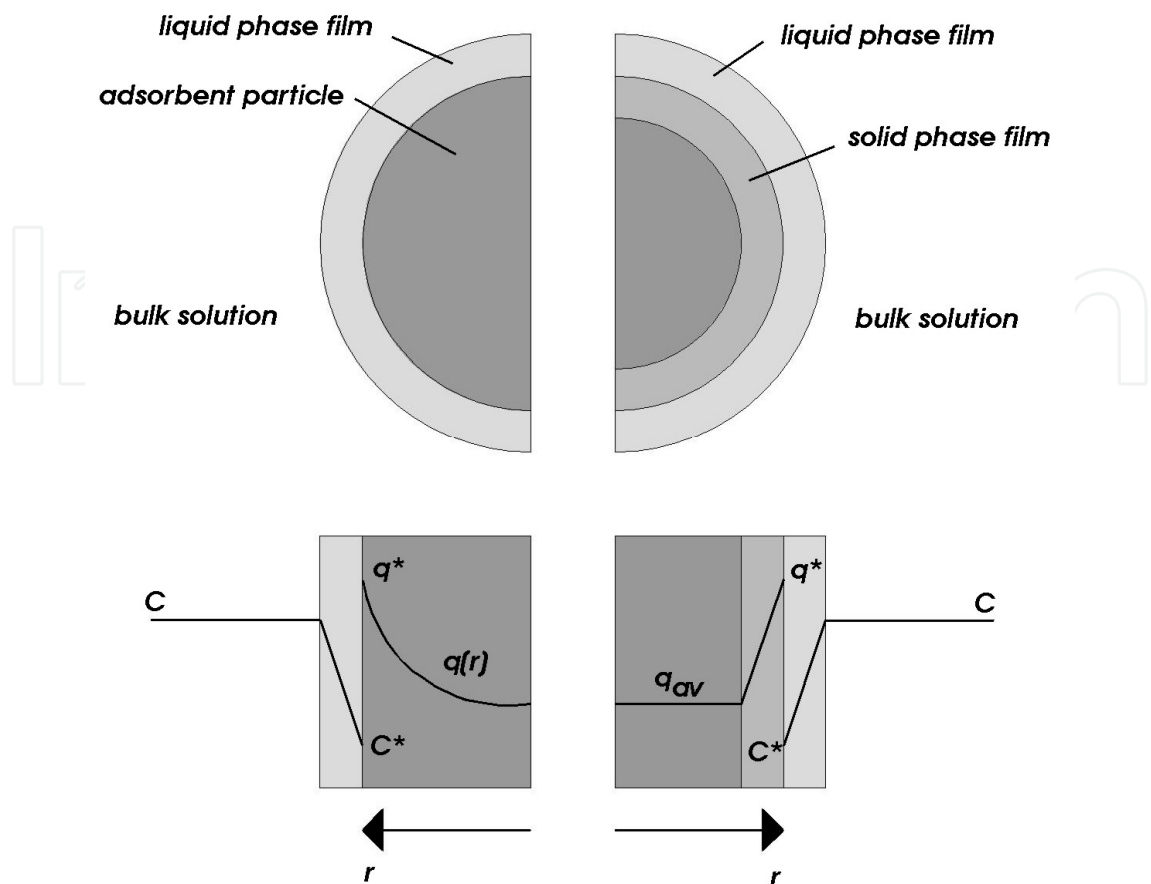


Fig. 4. Homogeneous surface diffusion (left) and linear driving force (right) models.

Molecule	T, °C	Solvent	D _M , m ² s ⁻¹	Reference
Stearic acid	130	Nut oil	4.2x10 ⁻¹⁰	Smits (1976)
Oleic acid	130	Nut oil	3.7x10 ⁻¹⁰	Smits (1976)
Monoolein	25	Water	1.3x10 ⁻¹⁰	Geil et al. (2000)
Triolein, Tristearin	70	Triolein, tristearin	1-2x10 ⁻¹⁰	Callaghan & Jolley (1980)
Sodium oleate	25	Sodium oleate	3.3x10 ⁻¹⁰	Gajanan et al. (1973)
Sodium palmitate		Sodium palmitate	4.8x10 ⁻¹⁰	Gajanan et al. (1973)
Glycerol	130	Biodiesel	6.18x10 ⁻⁹	Kimmel (2004)

Table 4. Values of molecular diffusivity of several biodiesel impurities.

$$\frac{\partial q}{\partial t} = K_{LDF}(q^* - q_{av}) \tag{12}$$

In the case of the linear driving force model (LDFM) all mass transfer resistances are grouped together to give a simple relation (Eq. 12). q_{av} is the average adsorbate load on the pellet and is obtained by the time-integration of the adsorbate flux. q^* is related to C^* , through the equilibrium isotherm. It must be noted that in this formulation $q_s=q^*$ and $C_s=C^*$, indicating that the surface is considered to be in equilibrium. In the case of adsorption for refining of biodiesel, the LDF approximation has been used to model the adsorption of free

fatty acids over silicas (Manuale, 2011). FFA adsorption was found to be rather slow despite the small diameter of the particles used (74 microns). This was addressed to the dominance of the intraparticle mass transfer resistance. This resistance was attributed to a working mechanism of surface diffusion with a diffusivity value of about $10^{-15} \text{ m}^2 \text{ s}^{-1}$. The system could be modeled by a LDFM with an overall coefficient of mass transfer, $K_{LDF}=0.013\text{-}0.035 \text{ min}^{-1}$ (see Table 5). These values compare well with those obtained for the adsorption of sodium oleate over magnetite, $0.002\text{-}0.03 \text{ min}^{-1}$ (Roonasi et al., 2010).

Adsorbent	T, °C	K_{LDF}, min^{-1}	Adsorbent	T, °C	K_{LDF}, min^{-1}
Silica TrySil 3000	70	0.035	Silica TrySil 300B	70	0.032
	90	0.019		90	0.022
	110	0.013		110	0.018

Table 5. Values of the LDF overall mass transfer coefficient for the silica adsorption of free fatty acids from biodiesel at different temperatures (Manuale, 2011).

The authors provided a further insight into the internal structure of the LDF kinetic parameter by making use of the estimation originally proposed by Ruthven et al. (1994) for gas phase adsorption (Eq. 13). D_s is the intrapellet surface diffusivity and ε is the porosity of the pellet. The additivity of the intrapellet diffusion time (τ_D) and the film transfer time (τ_f) to give the total characteristic time ($1/K_{LDF}=\tau_{total}$) is sometimes questioned because of the large difference between them. In the case of the adsorption of oleic acid from biodiesel it was shown that $\tau_f\approx 0.07$ seconds (estimated) and $\tau_{total}\approx 1700$ seconds (experimental) indicating that the silica-FFA system is strongly dominated by intrapellet diffusion (Manuale, 2011).

$$\frac{1}{K_{LDF}} = \frac{r_p}{3k_f} + \frac{r_p^2}{15\varepsilon D_s} = \tau_f + \tau_D$$

(13)

The LDF model was first proposed by Glueckauf and Coates (1947) as an “approximation” to mass transfer phenomena in adsorption processes in gas phase but has been found to be highly useful to model adsorption in packed beds because it is simple, analytical, and physically consistent. For example, it has been used to accurately describe highly dynamic PSA cycles in gas separation processes (Mendes et al., 2001). Yet, a difference is sometimes found in the isothermal batch uptake curves on adsorbent particles obtained by the LDFM and the more rigorous HSDM. The LDF approximation has also been reported to introduce some error when the fractional uptake approaches unity (Hills, 1986). In practice however saturation values might never be approached because adsorption capacity is severely decreased due to unfavourable thermodynamics in the saturation range. The precision of LDFM can be also improved by using higher order LDF models (Álvarez-Ramírez et al., 2005).

8. Experimental breakthrough curves

Breakthrough curve. It is the “S” shaped curve that results when the effluent adsorbate concentration is plotted against time or volume. It can be constructed for full scale or pilot testing. The breakthrough point is the point on the breakthrough curve where the effluent adsorbate concentration reaches its maximum allowable concentration, which often corresponds to the treatment goal, usually based on regulatory or risk based numbers.

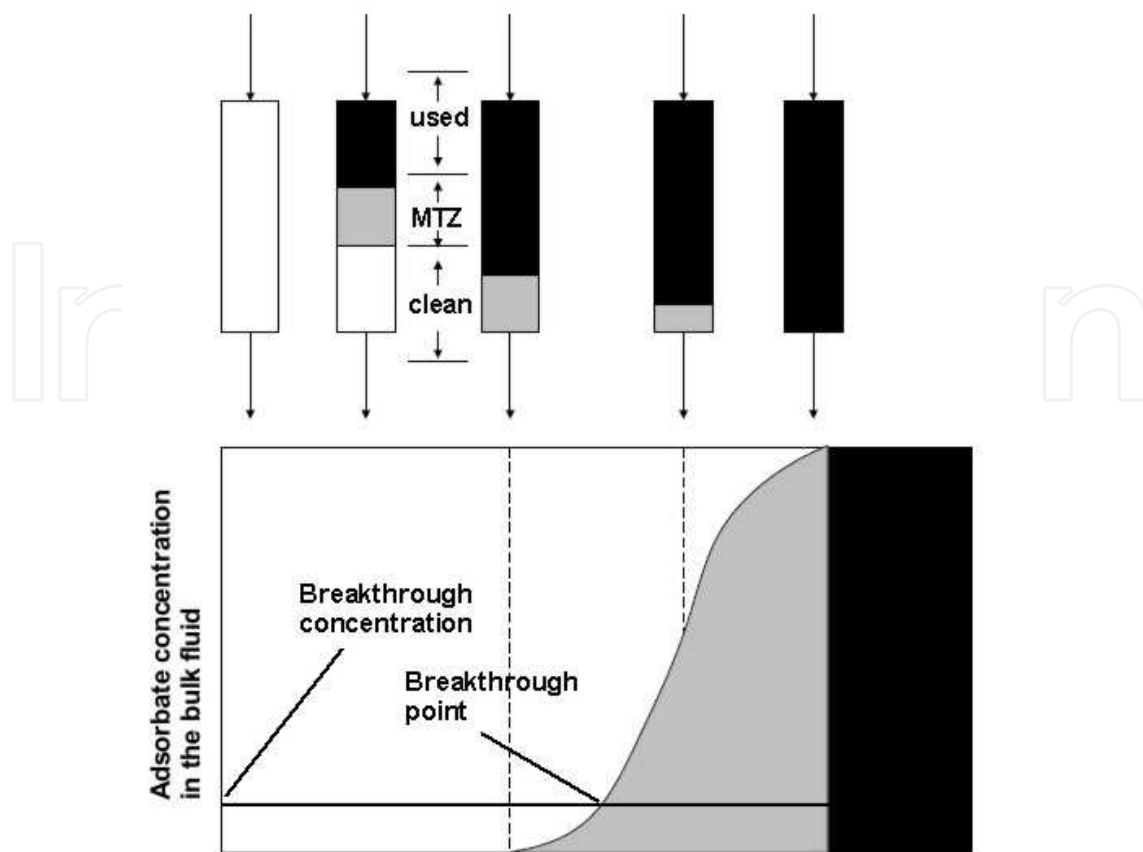


Fig. 5. Adsorption column zones. Relation to breakthrough curve.

Mass Transfer Zone. The mass transfer zone (MTZ) is the area within the adsorbate bed where adsorbate is actually being adsorbed on the adsorbent. The MTZ typically moves from the influent end toward the effluent end of the adsorbent bed during operation. That is, as the adsorbent near the influent becomes saturated (spent) with adsorbate, the zone of active adsorption moves toward the effluent end of the bed where the adsorbate is not yet saturated. The MTZ is generally a band, between the spent adsorbent and the fresh adsorbent, where adsorbate is removed and the dissolved adsorbate concentration ranges from C^0 (influent) to C^e (effluent). The length of the MTZ can be defined as L_{MTZ} . When $L_{MTZ}=L$ (bed length), it becomes the theoretical minimum bed depth necessary to obtain the desired removal. As adsorption capacity is used up in the initial MTZ, the MTZ advances down the bed until the adsorbate begins to appear in the effluent. The concentration gradually increases until it equals the influent concentration. In cases where there are some very strongly adsorbed components, in addition to a mixture of less strongly adsorbed components, the effluent concentration rarely reaches the influent concentration because only the components with the faster rate of movement are in the breakthrough curve. Adsorption capacity is influenced by many factors, such as flow rate, temperature, and pH (liquid phase). The adsorption column can be considered exhausted when C^e equals 95 to 100% of C^0 .

9. Model equations for flow in packed beds

We should start by writing the general equation for flow inside a packed bed, isothermal, and with no radial gradients (Eqs. 14-17). In these equations, u is the interstitial velocity

($u=U/\varepsilon_B$), where U is the empty bed space velocity and ε_B is the bed porosity. The last three equations are the “clean bed” initial condition and the Danckwerts boundary conditions for a closed system.

$$\frac{\partial C}{\partial t} - D_L \frac{\partial^2 C}{\partial z^2} + \frac{\partial(uC)}{\partial z} + \frac{1-\varepsilon_B}{\varepsilon_B} \rho_p \frac{\partial q}{\partial t} = 0 \quad (14)$$

$$C(0, t) = C^0 \quad (15)$$

$$\frac{\partial C}{\partial z} = 0, \quad z = L \quad (16)$$

$$C(z, 0) = 0 \quad (17)$$

In order to solve a specific problem of adsorption, mass transfer kinetics equations must be added, such as those of the HSDM or LDFM. The film equation is customarily replaced in the general equation of flow along the bed (Eq. 14) and thus the total system is reduced. The system still remains rather complex and in most instances can only be solved numerically. For faster convergence and accuracy special methods can be used, such as orthogonal collocation, the Galerkin method, or finite element methods. The general solution of the system is a set of points of C as a function of z , t and r . Often much of this information is not necessary and only the fluid bulk concentration at the bed outlet as a function of time, i.e. the “breakthrough” curve, is reported.

In order to obtain analytical breakthrough curves some simplifications can be made. For example the first implication of a high intrapellet diffusion resistance in liquid-solid systems (as in biodiesel refining) is that the Biot number that represents the ratio of the liquid-to-solid phase mass transfer rate, takes very high values. In Biot’s equation (Eq. 18), q^0 is the equilibrium solid-phase concentration corresponding to the influent concentration C^0 and r_p is the particle radius. The film resistance in high Bi systems can be disregarded; their breakthrough curves being highly symmetrical. Experimental symmetrical curves have indeed been found for the adsorption of glycerol over packed beds of silica (Fig. 6).

$$Bi = \frac{k_f r_p C^0}{D_s \rho_p q^0} \quad (18)$$

Another simplification is related to the longitudinal dispersion term in Eq. 14. D_L is usually calculated together with the film coefficient k_f by using the Wakao & Funazkri (1978) correlations for the mass transfer in packed beds of spherical particles (Eqs. 9 and 19). Due to the dependence of Sc on the molecular diffusivity, the value of D_L is dominated by D_M . The importance of D_L in systems of biodiesel flowing in packed bed adsorbers could be disregarded in attention to the value of the axial Péclet number (Eq. 22), since $Pe > 100$ in these systems. For very big Pe numbers the regime is that of plug flow (no backmixing) and when Pe is very small the backmixing is maximum and the flow equations are reduced to the equation of the perfectly mixed reactor (Busto et al., 2006).

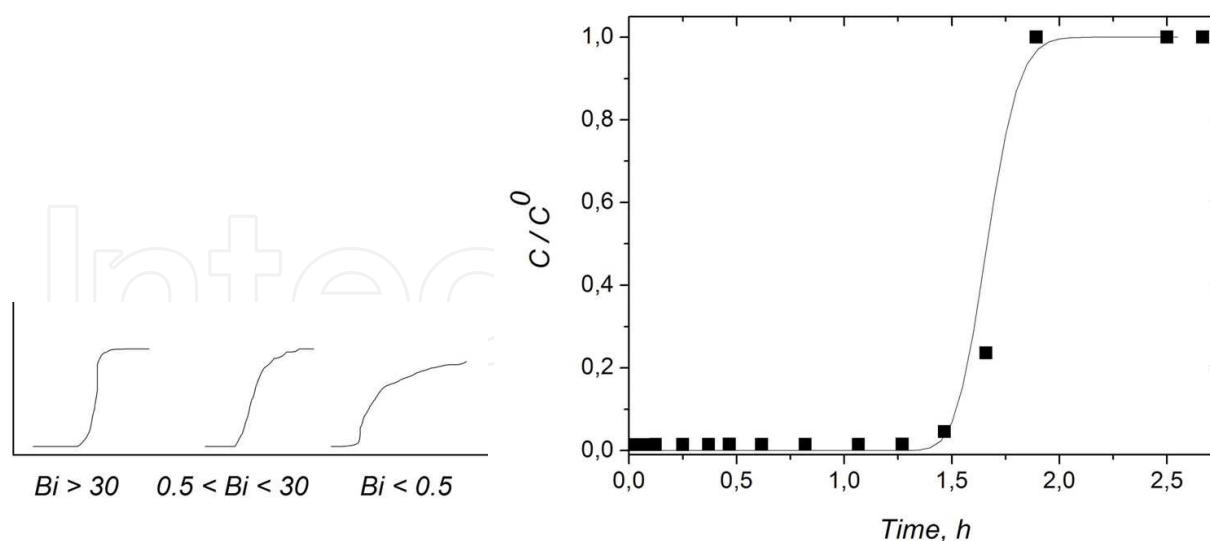


Fig. 6. Left: appearance of breakthrough curves as a function of the Biot number. Right: breakthrough curve for glycerol adsorption over silica (Yori et al., 2007).

$$\frac{D_L}{2\mu r_p} = \frac{20}{\text{Re } Sc} + 0.5 \quad (19)$$

$$Pe = \frac{uL}{D_M} \quad (20)$$

Another degree of complexity is posed by the nature of the isotherm equilibrium equation. Langmuir and Langmuir-Freundlich formulae are highly linear and propagate this non-linearity to the whole system. However some simplifications can be done depending on the strength of the affinity of the adsorbate for the surface and the range of concentration of the adsorbate of practical interest.

Sigrist et al. (2011) have indicated that Langmuir type isotherms for systems with high adsorbate/solid affinity can be approximated by an irreversible “square” isotherm ($q=q_m$), while systems in the high dilution regime can be represented by the linear Henry’s adsorption isotherm. Combining the linear isotherm or the square isotherm with the equations for flow and mass transfer along the bed, inside the pellet and through the film, analytical expressions for the breakthrough curve of biodiesel impurities over silica beds can be found (Table 6) (Yori et al., 2007).

For the square isotherm, the Weber and Chakravorti (1974) model is depicted in equations 21-25. A square, flat isotherm curve yields a narrow *MTZ*, meaning that impurities are adsorbed at a constant capacity over a relatively wide range of equilibrium concentrations. Given an adequate capacity, adsorbents exhibiting this type of isotherm will be very cost effective, and the adsorber design will be simplified owing to a shorter *MTZ*. Weber and Chakravorti took a further advantage of this kind of isotherm and simplified the intrapellet mass transfer resolution by supposing that the classical “unreacted core” model applied, i.e., that the surface layers could be considered as completely saturated and that a mass front diffused towards the “unreacted core”.

Isotherm	Film resistance	Intrapellet resistance	Adsorption	Biodiesel system	References
Linear	Yes	Fick, CD	Reversible	FFA-silica	Rasmusson & Neretnieks (1980)
Square	Yes	Fick, CD	Irreversible	Glycerol-silica	Weber & Chakravorti (1974)

Table 6. Breakthrough models for square and linear isotherms. CD: constant diffusivity.

$$\tau - N_p = \frac{15}{\sqrt{3}} \tan^{-1} \left[\frac{2(1-Q)^{1/3}}{\sqrt{3}} + 1 \right] - \frac{15}{2} \ln \left[1 + (1-Q)^{1/3} + (1-Q)^{2/3} \right] + 2.5 - \frac{5\pi}{2\sqrt{3}} + \left(\frac{N_p}{N_f} \right) \ln(Q+1) \tag{21}$$

$$\tau = \left[\frac{15 \varepsilon D_s}{r_p^2} \right] \left[\frac{C^0}{q_m} \right] (t - z / u). \tag{22}$$

$$N_p = \left[\frac{15 \varepsilon D_s}{r_p^2} \right] \left[\frac{1 - \varepsilon_B}{\varepsilon_B} \right] \left(\frac{z}{u} \right) \tag{23}$$

$$N_f = k_f \left[\frac{1 - \varepsilon}{\varepsilon} \right] \left(\frac{3z}{u r_p} \right) \tag{24}$$

$$Q = \frac{q}{q_s} = \frac{C}{C^0} \tag{25}$$

τ is the dimensionless time variable, Q is the fractional uptake, N_p is the pore diffusion dimensionless parameter and N_f is the film dimensionless parameter. The constant pattern condition is fulfilled in most of the span of the breakthrough experiments ($\tau > 5/2 + N_p/N_f$) except in the initial region when the pattern is developing. The simplified expression for dominant pore diffusion (high Bi) can be obtained by setting $(N_p/N_f)=0$. For glycerol adsorption over silica Yori et al. (2007) provided a sensitivity study based on Weber and Chakravorti’s model. These results are plotted in Figures 7 and 8. The influence of the pellet diameter (d_p) can be visualized in Figure 7 at two concentration scales. For small diameter (1 mm) the saturation and breakthrough points practically coincide and the traveling MTZ is almost a concentration step. For higher diameters the increase in the time of diffusion of glycerol inside the particles produces a stretching of the mass front and a more sigmoidal curve appears. The breakthrough point was defined as $C/C^0=0.01$ because for common C^0 values (0.1-0.25% glycerol in the feed) lowering the glycerol content to the quality standards for biodiesel (0.002%) demands that C/C^0 at the outlet is equal or lower than 1% the value of the feed. The results indicate that for a 3 mm pellet diameter the breakthrough time is reduced from 13 h to 8 h and that for a 4 mm pellet diameter this value is further reduced to 4.5, i.e. almost one third the saturation time. It can be inferred that the

pellet diameter has a strong influence on the processing capacity of the silica bed. Small diameters though convenient from this point of view are not practical. d_p is usually 3-6 mm in industrial adsorbers in order to reduce the pressure drop and the attrition in the bed.

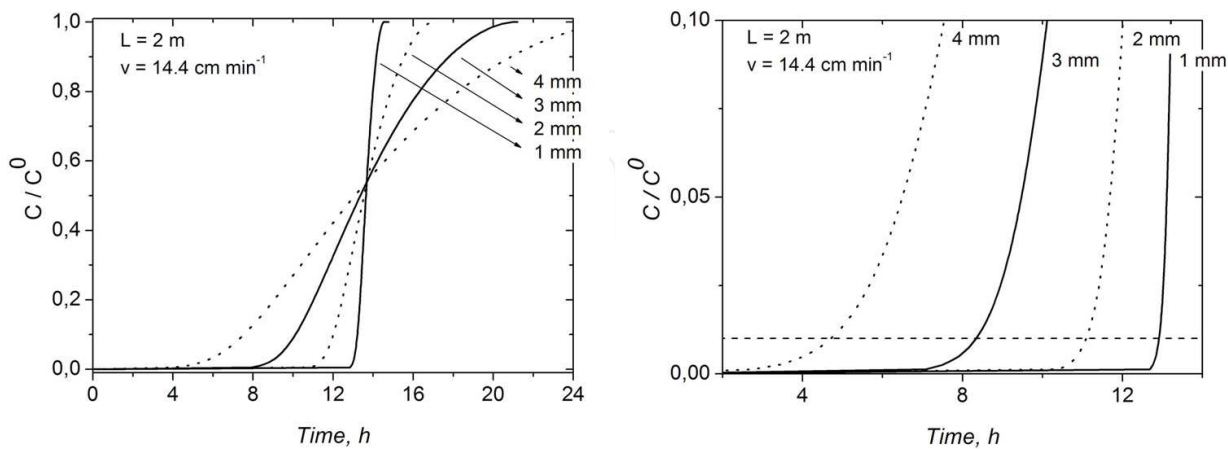


Fig. 7. Adsorption of glycerol from biodiesel. Breakthrough curves as a function of pellet diameter (d_p). Breakthrough condition $C/C^0=0.01$, $L=2\text{ m}$, $U=14.4\text{ cm min}^{-1}$.

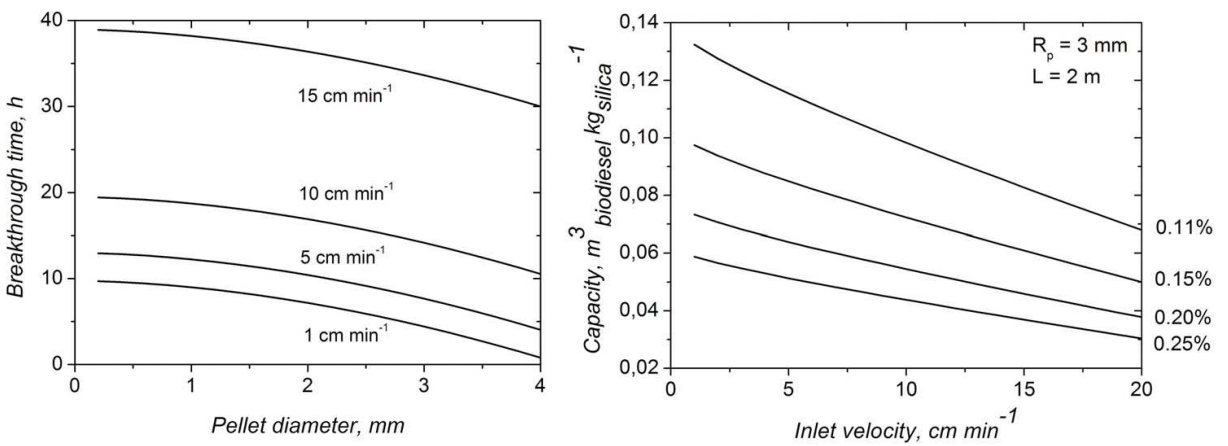


Fig. 8. Adsorption of glycerol from biodiesel. Left: breakthrough time as a function of U and d_p ($L=2\text{ m}$, $U=14.4\text{ cm min}^{-1}$). Right: influence of U and C^0 on the processing capacity ($d_p=3\text{ mm}$, $L=2\text{ m}$).

The combined influence of pellet diameter and inlet velocity on the breakthrough time is depicted in Figure 8 (left). The breakthrough time seems to depend on d_p^{-n} ($n>0$) and also on U^{-n} ($n>0$). This means that longer breakthrough times are got at smaller pellet diameters and smaller feed velocities. The processing capacity per unit kg of silica is displayed in Figure 8 (right) as a function of d_p and the inlet velocity, U^0 . When U^0 goes to zero the bed capacity equals q_m , and decreases almost linearly when increasing U^0 . For a typical solid-liquid velocity of 5 cm min^{-1} the capacity decreases at higher glycerol concentration, but the silica bed is used more efficiently because the relative MTZ size is reduced.

$$y(\tau)=\frac{1}{2}\mu^0\left(1+erf\left\{\frac{(\ln(\tau)-\mu)}{(\sigma\sqrt{2})}\right\}\right)\tag{26}$$

$$Bi^* = \frac{k_f r_p}{HD_s \rho_s} \quad (27)$$

$$\Theta = \frac{\varepsilon_B LD_s}{u r_p^2} \quad (28)$$

The breakthrough curve for the linear isotherm model is depicted in equations (26-28). This is the Q-LND (quasi log normal distribution) approximation of Xiu et al. (1997) and Li et al. (2004), of the general solution of Rasmusson and Neretnieks (1980). This approximation is known to be valid in systems of high Bi . y is the adimensional adsorbate concentration in the fluid phase, τ is the adimensional time, μ and σ parameters are functions of the Péclet number (Pe), the modified Biot number (Bi^*) and the time parameter (Θ).

10. Experimental scale-up of adsorption columns

The Rapid Small Scale Column Test (RSSCT) was developed to predict the adsorption of organic compounds in activated carbon adsorbents (Crittenden et al., 1991). The test is based upon dimensionless scaling of hydraulic conditions and mass transport processes. In the RSSCT, a small column (SC) loaded with an adsorbent ground to small particle sizes is used to simulate the performance of a large column (LC) in a pilot or full scale system. Because of the similarity of mass transfer processes and hydrodynamic characteristics between the two columns, the breakthrough curves are expected to be the same. Due to its small size, the RSSCT requires a fraction of the time and liquid volume compared to pilot columns and can thus be advantageously used to simulate the performance of the large column at a fraction of the cost (Cummings & Summers, 1994; Knappe et al., 1997). As such, RSSCTs have emerged as a common tool in the selection of adsorbent type and process parameters.

Parameters of the large column are selected in the range recommended by the adsorbent vendor. The RSSCT is then scaled down from the large column. Based on the results of the RSSCT, the designer develops detailed design and operational parameters. The selection and determination of the following parameters is required:

- Mean particle size: the designer must find an adequate mesh size, 100-140, 140-170, 170-200, etc., that can be used to successfully simulate the large column. Too small particles can however lead to high pressure losses and pumping problems.
- Internal diameter (ID) of column: 10-50 mm ID columns are preferred to keep all other column dimensions small and more important, to reduce the amount of time and eluate used. The $d_{SC}/d_{p,SC}$ should be higher than 50 to keep wall effects negligible.

RSSCT scaling equations have been developed with both constant (CD) and proportional (PD) diffusivity assumptions. The two approaches differ if D_s values are independent (for CD) or a linear function (for PD) of the particle diameter, d_p . Equations 29-30 can be used to select the small column (SC) RSSCT parameters based upon a larger column (LC) that is being simulated. t is the time span of the experiment for a common outlet concentration. For CD and PD scenarios the values for X are zero and one, respectively. Additional X values have been suggested based upon non-linear relationships between d_p and D_s .

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left(\frac{d_{p,SC}}{d_{p,LC}} \right)^{2-X} = \frac{t_{SC}}{t_{LC}} \quad (29)$$

$$X = \log \left(\frac{d_{p,SC}}{d_{p,LC}} \right) / \log \left(\frac{D_{s,SC}}{D_{s,LC}} \right) \tag{30}$$

- The spatial or interstitial velocities (U, u) are scaled based on the relation written in Eq. 31. However, this equation will result in a high interstitial velocity of water in the small column, and hence, high head loss. Crittenden (1991) recommended that a lower velocity in the small column be chosen, as long as the effect of dispersion in the small column does not become dominant over other mass transport processes. This limitation requires the Re_{SCSc} value remain in the range of 200-200,000, which is the mechanical dispersion range.

$$\frac{u_{SC}}{u_{LC}} = \left(\frac{d_{p,LC}}{d_{p,SC}} \right) \tag{31}$$

Variable	Small column	Large column
d_p	0.3 mm	3 mm
EBCT	105 s	2.9 h
U	2.4 mm s ⁻¹	0.24 mm s ⁻¹
L	25 cm	2.5 m
t_{run}	3 days	300 days

Table 7. Variables for a scaled-down constant diffusivity RSSCT packed with silica gel for adsorption of glycerol. Values for the small column taken from Yori et al. (2007).

In the case of biodiesel, no results of RSSCTs designed for scale-up purposes have been published so far, though some tests in small columns have been published (Yori et al., 2007). The validity of RSSCTs holds anyway. In this sense one first step for their use for scale-up purposes would be to determine the kind of D_s - d_p relation that holds, since it is unknown whether CD or PD approaches must be used. In order to show the usefulness of the technique, a procedure of comparison between a biodiesel large column adsorber and a scaled down laboratory column is made in Table 7.

11. Advantages of adsorption in biodiesel refining

As pointed out by McDonald (2001), Nakayama & Tsuto (2004), D’Ippolito et al. (2007), Özgül-Yücel & Turkay (2001) and others, the principal advantage of the use of adsorbers in biodiesel refining is that of reducing the amount of wastewater and sparing the cost of other more expensive operations such as water washing and centrifugation. For big refiners that can afford the cost of setting up a water treatment plant the problem of the amount of wastewater might not be an issue but this can be extremely important for small refiners. In the common industrial practice water-washing is used to remove the remaining amounts of glycerol and dissolved catalyst, and also the amphiphilic soaps, MGs and DGs. Theoretically speaking if water-washing is used to remove glycerol and dissolved catalyst only, large amounts of water should not be required. However in the presence of MGs and DGs the addition of a small amount of water to the oil phase results in the formation of an emulsion upon stirring. Particularly when this operation is performed at a low temperature

separation of the aqueous phase from the emulsion becomes difficult. In order to prevent the formation of such an emulsion in the conventional water-washing practice a large amount of water must be used. Karaosmanoglu et al. (1996) concluded that a minimum of 3-5 grams of water per gram of biodiesel at 50 °C were needed to efficiently remove the impurities of the fuel (3000-5000 litres of water per Ton of biodiesel). These numbers should be considered typical of once-through water-washing operations but are not representative of closed-loop water washing schemes. Accurate numbers are included in Table 8.

It has been suggested that the methanol removal step needed for succesful adsorption be performed before glycerol separation and under vacuum conditions (D'Ippolito et al., 2007; Bournay et al., 2005). The data in Table 8 suggests that the best operation of dry refining is that with cyclic reversible adsorption of glycerol/glycerides in twin packed beds, as early suggested (D'Ippolito et al., 2007).

	<i>Lurgi</i>	<i>Crown Iron</i>	<i>Dry</i>
Glycerol removal from biodiesel	Water wash column	Water mixer/settler	Packed bed, bleacher
Methanol removal from biodiesel	Water wash column	Steam Stripper	Vacuum flash drum
Methanol removal from wash water	Rectifier column	Rectifier column	Not needed
Final polishing by bleaching	n.a.	Yes	Not needed
Wash water consumption	200 kg Ton _{bio} ⁻¹	200 kg Ton _{bio} ⁻¹	None
Adsorbent consumption	n.a.	n.a.	11 kg Ton _{bio} ⁻¹ (bleacher) < 1 kg Ton _{bio} ⁻¹ (cyclic bed)

Table 8. Comparison of unit operations for two alkali-catalyzed processes (Lurgi, 2011; Crown Iron Works, 2011; Anderson et al., 2003) and a process with a “dry” step of adsorption of glycerol and glycerides (Manuale et al., 2011). Adsorbent consumption calculated for glycerol removal only (0.15% in raw biodiesel) (Yori et al., 2007).

Other advantages of adsorption are the low capital investment (provided common adsorbents are used), the absence of moving parts, the simplicity and robustness of operation. Possible drawbacks are the need for disposal and replacement of the spent adsorbent in the case of the use of bleaching tanks.

12. Adsorbers operation

12.1 Bleaching tanks

Manuale et al. (2011) used bleaching silicas for the removal of FFA in biodiesel in a series of tests in a stirred tank reactor under varying temperature and pressure conditions (70 and 110 °C, 760 and 160 mm_{Hg}). Their results confirm the pattern already seen in the case of the silica refining of edible oils. For the same adsorbent and in the presence of vacuum the influence of temperature is low. For example for TriSyl 3000 in vacuo, after 90 min, and from a similar initial acidity level (1.5%), the adsorbate load at two different temperatures is: $q_{70\text{ }^{\circ}\text{C}}=99.3\%$, $q_{110\text{ }^{\circ}\text{C}}=75.0\%$. Similarly, for TriSyl 300B, 90 min bleaching time, 1.7-1.9% initial acidity: $q_{70\text{ }^{\circ}\text{C}}=82.0$, $q_{110\text{ }^{\circ}\text{C}}= 69.0\%$. The trend is clear. Higher temperatures lead to lower

adsorption capacities. This is related to the fact that adsorption is exothermal and thus adsorption equilibrium is favored at low temperatures. In the absence of vacuum, adsorption is very low, one order of magnitude the value at 160 mmHg. Water adsorption reportedly inhibits the diffusion and adsorption inside the pore network of the silicas. At 90 °C or higher temperatures water desorption from an adsorbent dipped in oil can only proceed to a non-negligible extent in the presence of vacuum. Therefore if the adsorbent is not previously dehydrated, dehydration occurs simultaneously with adsorption during the bleaching experiment. In some cases the release of water from the silica goes directly into the biodiesel phase and the water content of the oil phase is increased.

These results indicate that surface diffusion of FFA over several adsorbents is very slow and the limiting step of the whole adsorption process. This leads to two negative consequences: (i) if a high level of FFA removal and a short bleaching time is required then big amounts of adsorbent must be used and these adsorbents are only partially used; (ii) if a total utilization of the adsorbent is desired, unconveniently high bleaching times must be used.

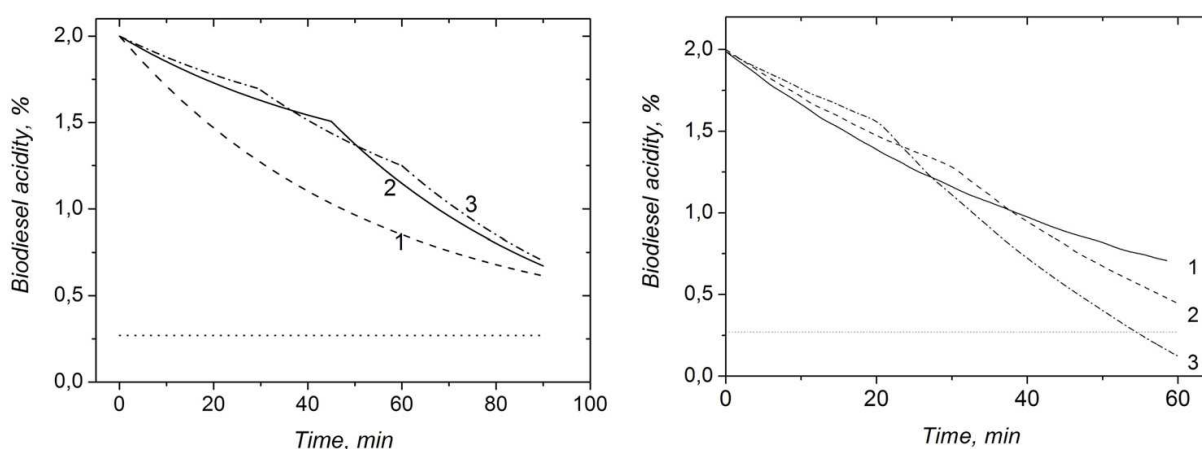


Fig. 9. Biodiesel acidity as a function of time and the number of countercurrent tank bleaching steps (1, 2 and 3) (Manuale, 2011). Adsorbent load=2%, initial biodiesel acidity=2%, $K_{LDF}=0.0188 \text{ min}^{-1}$. Left: Linear adsorption (Henry's law, $H=37.6$). Right: Irreversible adsorption (square isotherm). Dotted line: FFA European standard EN 14214, FFA limit.

Manuale et al. (2011) discussed the conditions for total total adsorbent utilization and for quasi complete FFA removal. They used the LDF model with both linear and square isotherms. They tested by simulation the use of serial cocurrent and countercurrent bleachers in order to assess their bleaching performance. The results are presented in Figure 9. In the case of the linear adsorption isotherm the use of countercurrent bleachers does not lead to a reduction of the adsorbent consumption. An effective reduction only occurs when the isotherm is square. These conclusions hold independently of the number of serial bleachers. Therefore when adsorption is strong and irreversible, spent adsorbents can be used advantageously to bleach streams highly contaminated while fresh adsorbents can be used to polish bleach the most lean streams. In the case of the linear isotherm the modulation of the adsorption capacity results in an operation that depends only on the bleaching time (all traces in Figure 9-left coincide at the end of the bleaching cycle).

Figure 10 is a plot of $q(t)$ for a train of countercurrent beds packed with adsorbents having a linear isotherm. The results show that all traces for the multistep operation are practically parallel to the 1-bleacher trace. Hence the adsorption capacity q is only a function of the

“total” bleaching time. No benefits can then be got from the multi-tank countercurrent bleaching operation. The only possibility of multiple units is that of parallel bleaching tanks working long times (e.g. 2 h) in order to increase the adsorbent usage.

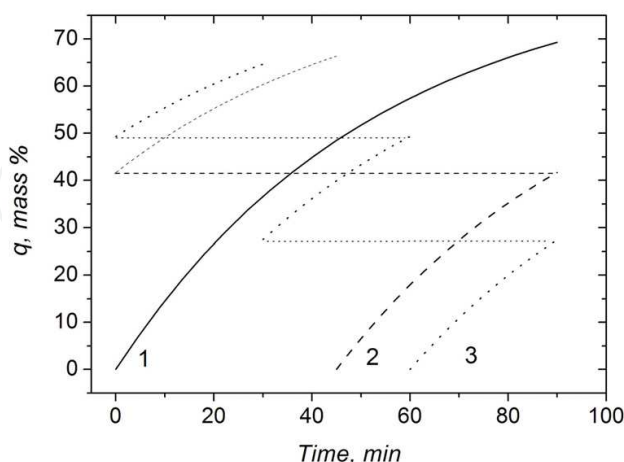


Fig. 10. Adsorbent load as a function of time and the number of countercurrent bleaching steps (1, 2 and 3) (Manuale, 2011). Process conditions as in Figure 9.

12.2 Packed beds

Lead-lag operation. Most liquid phase packed beds are operated in series. This means passing all of the flow through one column bed, a lead column, and then passing flow through another similar sized column bed, the lag vessel. This method offers several advantages over a single column. The series configuration allows the maximum use of the adsorbent throughout the entire bed. This assumes that the MTZ is contained within a single properly sized packed bed. By placing two or more columns in series, the MTZ is allowed to pass completely through the first (lead) bed as the leading edge of the MTZ migrates into the second (lag) bed. By allowing this to happen, the maximum contaminant concentration is allowed to come into contact with adsorption sites in the lead vessel that require a greater concentration gradient to hold additional contamination. When the MTZ exits the lead vessel, that vessel is then exhausted, and requires change out with virgin or regenerated adsorbent. Even though the adsorption capacity of the lead vessel is exhausted, treatment continues in the lag vessel. Then, during change out, the lead vessel is taken off-line and the lag vessel is placed in the lead position. The former lead vessel is then replenished with adsorbent and then becomes the lag vessel and brought on-line. Further insights on the operation of serial and parallel adsorbers can be found elsewhere (Sigrist et al., 2011).

Regeneration. For the removal of glycerol and to a lower extent of MGs and DGs, the methanol concentration in the fluid is important. Methanol adversely affects the adsorption capacity because it increases the activity of glycerol and glycerides in the liquid phase. This was studied by Yori et al. (2007) with the method disclosed by Condoret (1997) and Bellot (2001). The method is based on the knowledge of the curves describing the variation in the glycerol activity with respect to its concentration, established separately for each phase (solid and liquid). Henry's constants were obtained from the slope of the isotherms in the diluted range using the UNIFAC method for calculating the liquid phase activity coefficients. The results are shown in Fig. 11 and indicate that for all practical purposes the adsorption of glycerol over silica is null at high methanol concentrations.

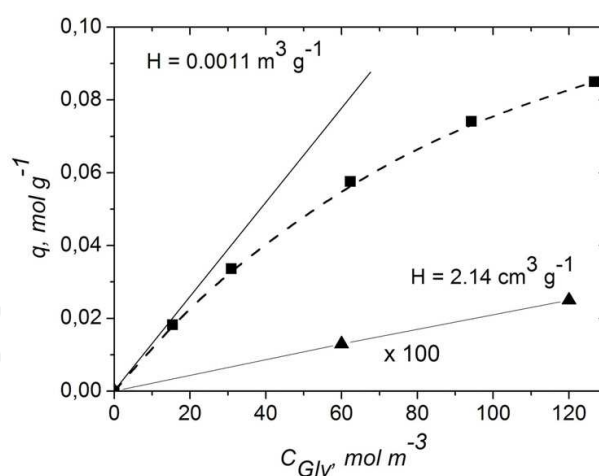


Fig. 11. Silica adsorption isotherms for the Gly-FAME (squares) and Gly-MeOH (triangles) systems. H values calculated from the slope of the traces. Yori et al. (2007).

The elution of 4 bed volumes of methanol through the exhausted packed bed is reported to restore the adsorbent capacity. Elimination of the adsorbed methanol from the silica was done by blowing nitrogen through the bed but could be performed using any other gas. Elimination of the solvent produced a decrease of the bed temperature because methanol evaporation needs 1104 J g^{-1} . This translates to $200 \text{ kJ kg}_{\text{silica}}^{-1}$ for the fully saturated silica and hence provisions should be made in order to maintain the bed temperature and prevent biodiesel flow problems at inconvenient low temperatures. In this sense flushing the bed with a hot gas seems the most suitable means for desorbing methanol.

$$(H / H^0) = e^{-\frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]} \quad (32)$$

The thus recommended way of regenerating the silica bed seems superior to other means used for regeneration of adsorbent packed beds, notably the thermal swing. A thermal swing with purified hot biodiesel could be used to regenerate the bed. Manuale et al. (2011) found that the silica adsorption of oleic acid from biodiesel has a heat of adsorption of $-5.7 \text{ KCal mol}^{-1}$. This is similar to reported values for similar systems (Sari & Ipýldak, 2006). In order to decrease the adsorption capacity 100 times ($H/H^0=0.01$, Eq. 32) the thermal swing should be $\Delta T=480 \text{ }^\circ\text{C}$. For mild regenerations with $H/H^0=0.1$ and $H/H^0=0.25$, the required thermal swings are still high, $\Delta T=200 \text{ }^\circ\text{C}$ and $\Delta T=140 \text{ }^\circ\text{C}$. The results indicate that though for the silica-FFA system adsorption is weak enough to yield a linear isotherm, the heat of adsorption is too high and discourages the use of a thermal swing for regeneration.

13. Conclusions

Adsorption is a robust and reliable operation for the refining of biodiesel and its feedstocks. Hydrophilic adsorbents seem the best choice, because most of the undesired impurities are polar. In this sense silicas offer a high saturation capacity (10-15%) for glycerol and glycerides, and enough affinity for soaps, FFA, metals and salts.

One advantage of adsorption units for the removal of glycerol, glycerides, soaps, phosphatides and metals from biodiesel and its feedstocks, is the reduction in wastewater

effluents and the sparing of washing, oil-water separation and wastewater treatment units. Other advantages are small capital expenditure, robustness and easiness of operation. Cost-effective means for the scale-up of packed bed adsorbers for biodiesel refining seem to be accurate models for flow and adsorption and scaled-down RSCCTs. Accurate models for flow and adsorption can be solved in their full complexity only with the aid of numerical calculations but analytical solutions for rapid design and sensitivity analysis can be got using approximations, such as the use of square and linear isotherms and LDF models. Further approximations can be obtained for low Biot and high axial Péclet numbers. The operation of adsorbers should minimize the consumption of adsorbent. From this point of view countercurrent bleaching tank arrays should be used but this mode of operation cannot be exploited in the case of adsorbents with linear isotherms. In the case of packed bed adsorbers common lead-lag setups of 2 or more serial columns are recommended.

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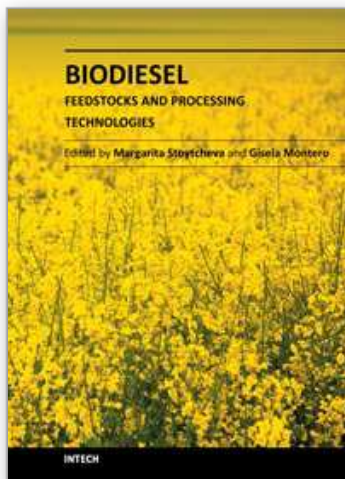
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The book "Biodiesel: Feedstocks and Processing Technologies" is intended to provide a professional look on the recent achievements and emerging trends in biodiesel production. It includes 22 chapters, organized in two sections. The first book section: "Feedstocks for Biodiesel Production" covers issues associated with the utilization of cost effective non-edible raw materials and wastes, and the development of biomass feedstock with physical and chemical properties that facilitate its processing to biodiesel. These include Brassicaceae spp., cooking oils, animal fat wastes, oleaginous fungi, and algae. The second book section: "Biodiesel Production Methods" is devoted to the advanced techniques for biodiesel synthesis: supercritical transesterification, microwaves, radio frequency and ultrasound techniques, reactive distillation, and optimized transesterification processes making use of solid catalysts and immobilized enzymes. The adequate and up-to-date information provided in this book should be of interest for research scientist, students, and technologists, involved in biodiesel production.

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