Biodiesel Dry Purification Using Unconventional Bioadsorbents

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Keywords: bioadsorbents, biodiesel, waste cooking oil, purification

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Biodiesel Dry Purification Using Unconventional Bioadsorbents

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Abstract: The dry washing method is an alternative to replace water washing, thereby reducing the negative impacts of contamination. However, commercial adsorbents come from industrial processes that, due to their composition, may not be such a sustainable resource in the global biodiesel production process. In this study, the use of organic residues, such as sawdust, coconut fiber, nutshell, rice husk, and water hyacinth fiber, were proposed as bioadsorbents for the purification of biodiesel from waste cooking oil. Quality parameters such as the acid number, water content, and free and total glycerin content were evaluated and compared with those after purification with commercial adsorbents (Magnesol and Amberlite BD10DRY). Promising results were obtained using sawdust in the purification process, achieving a reduction in the acid number value of 31.3% respect to the unpurified biodiesel. Indeed, the reduction with sawdust was more efficient than with Amberlite BD10DRY (that increased the acid number). In addition, sawdust reduced free glycerin by 54.8%, again more efficient than Amberlite BD10DRY. The total glycerin values were similar between commercial adsorbents and sawdust. Water content after purification with sawdust was similar to the obtained with Amberlite BD10DRY and better than with Magnesol (399, 417, and 663 mg/kg respectively). These results show that sawdust can be used as an alternative bioadsorbent in a dry purification method for biodiesel, generating less environmental impact.

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1. Introduction

Currently, approximately 80% of the world's energy consumption comes from fossil fuels [1]. The environmental problems associated with its use include air pollution and global warming [2]. The high dependence on fossil fuels for industrial, transportation and domestic purposes has led to research on alternative energy sources [3]. Biodiesel is an alternative to petrodiesel with the aim to mitigate the problem of fossil fuel depletion and environmental impact [4]. The main raw materials are vegetable oils or animal fats, which are transformed into fatty acid methyl ester (FAME) through the transesterification process [3,4]. This method involves the conversion of triacylglycerides into methyl esters (methanol) or ethyl esters (ethanol) in the presence of a catalyst [4,5]. The use of biodiesel reduces greenhouse gas emissions in the production process, which is one of the most important advantages. Moreover, the biodegradability, low cost, and high availability of biodiesel if it is produced from waste cooking oil (WCO) are additional benefits [4,6].

To produce biodiesel, some important parameters have to be considered, such as the acid number and the moisture content in oils and fats. The presence of water hydrolyzes the triacylglycerides (TG), which causes the formation of free fatty acids (FFA). The high content of FFA facilitates the formation of soaps in a basic homogeneous transesterification process [7]; this reduces the efficiency of conversion of triacylglycerides to ester. To solve this problem, the esterification method is used as a pretreatment for the reduction of FFA (1.0% by weight) present in low-cost oils and fats [8]. There are different transesterification methods, such as homogeneous (acidic and basic), heterogeneous (acidic and basic), and enzymatic transesterification [9–11].

Currently, conventional catalysts such as KOH and NaOH are still used for the production of biodiesel; however, these generate undesirable compounds in production, which implies higher energy consumption due to purification. Heterogeneous catalysts and biocatalysts are an alternative to this problem, but due to higher costs and reaction time these are not yet extensively used at large scales [10,12–14]. Purification remains one of the most important stages in the production of biodiesel. The most used methods for biodiesel purification are water washing, ion exchange adsorbents (Amberlite BD10DRY), and adsorbents such as silica and Magnesol [15,16]. Water washing is distinguished by the removal of a large portion of biodiesel impurities, such as glycerin, methanol, soaps, and other hydrophilic compounds [17].

However, water washing has certain disadvantages such as the consumption of a large amount of water, the production of highly polluted wastewater, and, consequently, a higher cost for the treatment of produced wastewater [15,16,18]. The production of highly contaminated wastewater is the main shortage of this purification method. At this stage, the content of methanol, free glycerin, and soaps, among other impurities, may be decreased and, thus comply with ASTM D6751 [18] and EN 14214 [19] specifications and with the official Mexican guidelines [20].

Among the quality parameters that interfere in the transesterification process is the acid number, on which the transformation of fatty acids depends [21], and this value is related to the degradation of the biofuel within the combustion chamber [22]. Another quality parameter is free glycerin, and at high concentrations it can form deposits in storage tanks, filters, and even injectors, reducing the useful life of engines [23]. Likewise, the water content is within biodiesel quality standards, as water is corrosive to the engine, and it is important to comply with the established limits [24]. These limits guarantee that the product obtained does not have negative effects on the engine and the environment; therefore, the biofuel must meet quality standards.

Another adsorbent currently used for dry cleaning of biodiesel is Amberlite BD10DRY, which is an ion exchange polymer for the removal of soaps and glycerin [16]. Among its disadvantages is the formation of FFA, which increases the acid number [25].

The use of commercial adsorbents causes a great economic impact, increasing the cost of biodiesel production, as well as an environmental impact due to their final disposition when become saturated. An alternative to this problem could be the use of bioadsorbents from industrial waste (wood and food) and water hyacinth (*Eichornia crassipes*), which is considered an invasive species that causes negative effects on aquatic ecosystems. *Eichornia crassipes* is now present on all continents except Antarctica and has invaded all tropical and subtropical countries, as well as some parts of the Mediterranean basin. It is considered one of the world's most invasive aquatic plants, and considerable effort is expended worldwide to manage *E. crassipes* and its impacts on agriculture, the environment, and human activities [26]. The species has reached up to two million plants per hectare [27]. Another alternative source of bioadsorbents is industrial waste. In 2018, the worldwide forestry waste production was 0.234 km^3, consisting of sawdust, chips, and bark [28].

In Mexico, large quantities of waste are produced, coming from the agricultural and forestry sector; the annual timber production generates approximately 2.8 million m^3 of waste, which is made of sawdust, chips, and bark [29].

One crop that generates large amounts of waste is rice. This cereal is a staple food that forms the basis of the traditional diet of a large proportion of the human population. According to Zou et al. (2019), global rice production in 2014 was 741.48 million tons [30].

The national production of rice in Mexico was 0.25 MMt in 2017 [31]. Rice husk is used to produce feed for cattle, among other applications, but could be an adsorbent to purify biodiesel [32].

Pecan husk is another alternative. The world pecan 2019/2020 crop was estimated at 139,739 metric tons. Production was led by Mexico and the USA with very similar shares, 47% and 43%, respectively. In Mexico, the pecan nut industry production is 65,750 MT and considering the pecan shells represent 49% of the pecan, the production of pecan shells is 32,217 MT [33,34].

Adsorbents from these wastes are used in different sectors, and sawdust is used to produce pellets, a substrate for plants and balanced food [29]. Currently, sawdust has taken a meaningful place in biodiesel purification methods. It is used as a technique for removing impurities of biodiesel. Ortiz et al. (2020) obtained a final yield of 89% postwashing using sawdust [35].

Coconut coir is applied in gardening, in production of ropes, mattress padding, and in industrial processes [36,37]. Regarding the coconut industry, 90% is in India and Sri Lanka, where the coconut fiber production is approximately 350,000 tons [38].

The absence of optimal management of these wastes represents an environmental problem; therefore, it is necessary to develop alternatives for their use. One solution could be the use of these resources as bioadsorbents for biodiesel purification. In this context, bioadsorbents are biodegradable and come from agroindustrial waste, this reduces the ecological impact and the costs relate to water consumption and treatment [39]. This article aims to (a) evaluate the efficiency of sawdust, coconut coir, nutshell, rice husk, and water hyacinth fiber in the removal of free and total glycerin, water, and acid number from biodiesel derived from WCO, and (b) to compare them with conventional purification methods, such as using Magnesol, Amberlite BD10DRY, and water washing.

2. Materials and Methods

2.1. Biodiesel Production

An institutional restaurant donated the WCO and it was characterized to obtain the acid number and thus know the amount of catalyst to use. Biodiesel production was carried out in a pilot plant with an effective volume of 150 L, and the water was removed from the oil by heating at 100 °C for 60 min. Forty liters of WCO were mixed with a methoxide solution (12.7 L of methanol and 360 g of KOH) in an 8:1 molar ratio. The transesterification process lasted four hours by recirculating the oil in the equipment pump. The separation phase lasted 24 h. A rotary evaporator system removed methanol (Sagaon V3) for 15 min at a pressure of 0.07 MPa and 80 rpm. The same batch of biodiesel was used to perform purification studies (each purification treatment by duplicate).

2.2. Purification

2.2.1. Conventional Methods

Purification with Magnesol and Amberlite BD10DRY

A total of 100 mL of unpurified biodiesel was measured and added to a 250 mL beaker. The purification was carried out in duplicate batches at room temperature (15 °C) and stirred at 700 rpm. The Magnesol concentration used in the sample was 1% (w/w), and the purification time was 20 min. In the case of Amberlite BD10DRY, the amount was 10 g. Subsequently, the sample was filtered on a 50 mL column and a 1 µm filter using a vacuum system. The samples were stored for later analysis. Purification was carried out in duplicate. Magnesol and Amberlite BD10DRY were provided by The Dallas Group, Inc. and Dow Mexico, respectively. Samples were freezer-stored for subsequent analysis.

Water Purification

A total of 100 mL of unwashed biodiesel was measured by duplicate, and a 1:1 (v/v) ratio of distilled water was added at a temperature of 40 °C and stirred gently for 10 min. Three washes were performed until the washings were clear. The biodiesel was washed at

15 °C and separated by gravity in a separatory funnel. Subsequently, the sample was dried at 100 °C for 30 min and 700 rpm on a magnetic stirrer. Samples were freezer-stored for subsequent analysis.

2.2.2. Bioadsorbents

Local producers provided sawdust, coconut coir, nutshell, rice husk, and water hyacinth fiber that were used as bioadsorbents. All samples were dried in an electric oven at 100 °C for three hours. The water hyacinth from Lake Cuitzeo (Michoacán, Mexico) was donated by a local university (Universidad Michoacana de San Nicolás de Hidalgo). Each of these samples was added to unpurified biodiesel at a concentration of 5% (w/w) and 15 °C. In a previous study, we found that the amount needed to absorb a gram of biodiesel was 5% and was equivalent to 1% Magnesol. In the case of Amberlite BD10DRY, the application is different since the amount in grams is given by the manufacturer (1 g of Amberlite BD10DRY can treat around 0.9–1.6 kg of biodiesel). The samples were stirred for 20 min at 700 rpm, filtered on a 50 mL column and a 1 µm filter using a vacuum system and freezer-stored for subsequent analysis.

2.3. Characterization of Biodiesel

The biodiesel (purified and unpurified) was analyzed by duplicate following the ASTM D664 acid number standard by potentiometric titration [40] and the ASTM D4928 standard for moisture content by Karl Fischer coulometric titration [41]. Subsequently, gas chromatography–mass spectrometry (GC–MS) was performed to measure the content of free and total glycerin following ASTM D6584 [42].

The FTIR analysis was carried out in a Perkin Elmer FTIR system device equipped with a mercury–cadmium–tellurium detector. The spectrum was recorded in attenuated total reflectance (ATR) mode in Spectrum GX software with a spectral range from 4000 to 650 cm^{-1} at a resolution of 4 cm^{-1}. Approximately 5 mg of each biodiesel sample was placed in the sampling accessory. ASTM biodiesel standard sample was donated by LIBBA (CIATEJ, Guadalajara, Mexico).

2.4. Characterization of the Adsorbents

Scanning electron microscopy was used to analyze the samples of sawdust, coconut coir, nutshell, rice husk and water hyacinth fiber, as well as Magnesol and Amberlite BD10DRY. SEM analyses were performed on a JEOL JSM-IT300 LV electron microscope. To avoid charge effects, the samples were observed in low vacuum mode between 20 and 50 Pa at an acceleration voltage of 20 keV. The elemental chemical composition of each sample was determined using energy-dispersive spectroscopy (EDS) by means of two Oxford-X-ManN silicon drift detectors (SDDs) with an active area of 20 mm^2 and energy resolution of 127 eV, developed by Oxford instruments; these detectors were coupled to the microscope. The EDS spectra were acquired with the parameters of 20 keV and 300 s live time. Aztec software was used to analyze the spectral data. It is important to note that by using two SDDs, the noise-signal relation is diminished, and studies with high precision can be performed.

3. Results

3.1. Biodiesel Characterization

Table 1 shows the different purification methods used in this study, as well as the results for the most relevant reference parameters concerning biodiesel quality. Among the bioadsorbents that reduced the acid number to levels below those established in the ASTM standard are water hyacinth fiber, rice husk, sawdust, and coconut coir. The use of some of the bioadsorbents even proved to be more efficient than conventional methods, demonstrating their ability to remove free fatty acids associated with a high acid number. The acid number is a reference used to relate the amount of impurities and free fatty acids (FFA) within the fuel, as well as the relationship that exists in terms of oxidative stability [7,43].

Table 1. Biodiesel quality analysis under different purification methods. The variation coefficient was less than 5 % except for Amberlite BD10DRY in the case of total glycerin.

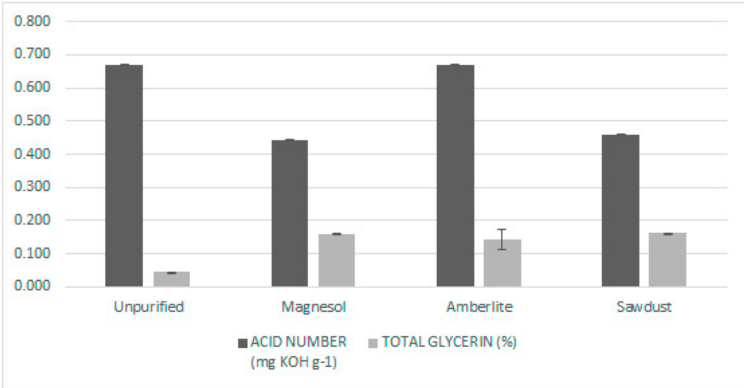
	Acid Number (mg KOH g^{-1})	Free Glycerin (% m)	Total Glycerin (% m)	Water Content (mg/kg)
ASTM	0.50	0.020	0.240	500
Unpurified	0.67	0.031	0.044	465
Magnesol	0.44	0.007	0.159	663
Amberlite BD10DRY	0.67	0.022	0.142	417
Water washing	0.46	0.001	0.009	313
Sawdust	0.46	0.014	0.161	399
Coconut coir	0.48	0.021	0.181	551
Nutshell	0.53	0.014	0.172	718
Rice husk	0.38	0.021	0.177	694
Water hyacinth fiber	0.35	0.064	0.217	927

The free and total glycerin content is a very important parameter since it is related to both the efficiency of the reaction in terms of conversion and the efficiency of the purification process. Table 1 shows the most efficient bioadsorbents for free glycerin removal, which is related to the glycerin remaining in the biodiesel after transesterification. The bioadsorbents that reduced free glycerin are sawdust and nutshell, which can lower the free glycerin values below the ASTM standard, even better than Amberlite BD10DRY. It is also observed that in the case of the commercial methods, the amount of glycerin increases with respect to that in the unpurified biodiesel, which could be due to the existence of residual methanol, as well as mono-, di-, or triglycerides that continue reacting in the presence of the catalyst.

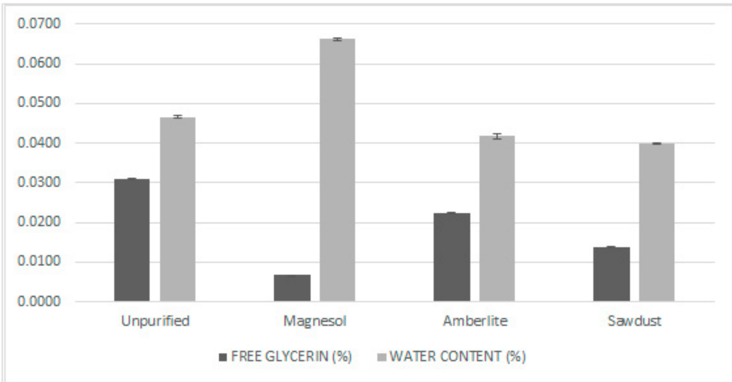
In the case of total glycerin, which reflects the amount of oil that is unconverted or partially converted to biodiesel [44], the best bioadsorbents were coconut coir and sawdust, although for most of the treatments, except water washing, the total glycerin increased compared to the unpurified biodiesel. With the use of bioadsorbents, the limits of the ASTM standard were not exceeded. The increase in total glycerin for the commercial adsorbents and some bioadsorbents may be due to the reversibility of the reaction process between esters (fatty and methyl).

Table 1 shows that among the bioadsorbents used, sawdust was the one that accomplished the removal of byproducts and conforming to ASTM parameters, which was in contrast to other adsorbents that increased the final water content. This result may be due to the humidity of the environment [45], as well as the inefficiency of the drying process of the bioadsorbents. As a result of this analysis, it can be verified that sawdust can remove impurities at low concentrations, such as glycerin, free fatty acids, and water, in the same way as or even more efficiently than commercial adsorbents. Amberlite BD10DRY decreases water content and total glycerin, but increases free glycerin and acid number, which was noted before as a disadvantage of this adsorbent [25].

Figure 1a shows the comparison between sawdust and the dry purification methods of biodiesel. There is a significant difference in the acid number reduction with respect to unpurified biodiesel for sawdust. The reduction was similar with sawdust and Magnesol, but more efficient than that with Amberlite BD10DRY. The total glycerin reduction is slightly significant between the commercial adsorbents and sawdust. In Figure 1b, it is shown that sawdust was able to remove water from the unpurified biodiesel, being more efficient than Magnesol but with a behavior similar to that of Amberlite BD10DRY. For free glycerin removal, sawdust achieved a low reduction compared to that with unpurified biodiesel and Amberlite BD10DRY, but was not as efficient as Magnesol.



(**a**)



(**b**)

Figure 1. Comparison between sawdust and conventional purification methods of biodiesel from waste cooking oil (WCO): (**a**) acid number (mg KOH g^{-1}) and total glycerin (%), (**b**) free glycerin (%) and water content (%). Error bars are based on standard deviation of duplicate analysis.

Table 2 lists different organic adsorbents or bioadsorbents that were used by other authors as biodiesel purification methods. In this table, removal percentages have also been added for each of the quality parameters, such as acid number, water content, total glycerin, and free glycerin. Compared to other studies where the acid number increased after purification, in this study the value decreased below 0.5 mg KOH g^{-1}, the ASTM standard value.

The removal percentages obtained by the biosorbents were between 22% and 48% lower, compared to the unpurified biodiesel. These values are remarkable in comparison with commercial adsorbents such as Purolite PD 206, Amberlite BD10DRY, and TULISON T-45 BD, used by Banga et al. [46]. Comparing the coconut coir with the experiments realized by Ott et al. [47], there was not an increment of the acid number, but there was a reduction of 27%, with values under those established in the ASTM norm. In contrast with the use of the rice husk experiments of Manique et al. [32], the remotion values were inferior; this can be due to the absence of the use of rice husk as an ash. In consequence, there is a different composition and morphology of the material, notwithstanding the difference, it was possible to reduce it by 43%, with the advantage of not using an extra material treatment for combustion, decreasing the total energy cost.

The content of free glycerin observed, after purification, ranged between 32% and 56%. Although some percentages obtained with bioadsorbents were lower compared to the commercial adsorbents used by other authors, sawdust and nutshell powder managed to lower the values below the ASTM standard. In the case of free glycerin high removal rates were obtained compared to other studies, like the one developed by Ahmad et al. [48], where bentonite and silica gel were used for the elimination of free glycerin.

For total glycerin, the values increased slightly with respect with the unpurified biodiesel. This may be due to the moisture control treatment in the bioadsorbents. However, for purposes of compliance with the ASTM standard, all the bioadsorbents used in this study were not allowed to exceed the quality limits of total glycerin.

The water content results were similar to those reported by Alves et al. [45] and Berrios et al. [17], who also observed an increase in the water content after purification due to the hydrophilic nature of biodiesel, which may have adsorbed water from the environment during the process [45].

The bioadsorbents used in this study were able to eliminate impurities by using dry washing methods, which makes them a low-cost alternative that can achieve a sustainable process for biodiesel purification.

Biodiesel FTIR Analysis

In Figure 2, the FTIR spectra from 650 to 4000 cm^{-1} are shown, corresponding to the samples of unpurified and purified sawdust biodiesel, as well as the ASTM biodiesel standard sample. This figure shows the region from 1750 cm^{-1} to 1730 cm^{-1}, which indicates the existence of functional groups assigned to the carbonyl groups (C=O) typical of methyl esters. In the region of 700–800 cm^{-1}, bands corresponding to the methylene groups =CH and $–CH_2$ are observed [49]. In the fingerprint region, a band between 1200 and 1300 cm^{-1} appears; this band is attributed to $O\text{-}CH_2$ groups related to glycerin, which means there are triacylglycerides, diacylglycerides, and monoacylglycerides present in the final biodiesel [50,51]. For each spectrum, the absorption band from 2950 to 3000 cm^{-1} corresponds to the stretching vibrations of CH_3, CH_2, and CH bonds. The bands between 3200 and 3600 cm^{-1} correspond to OH groups, indicating the presence of glycerin and water [51,52].

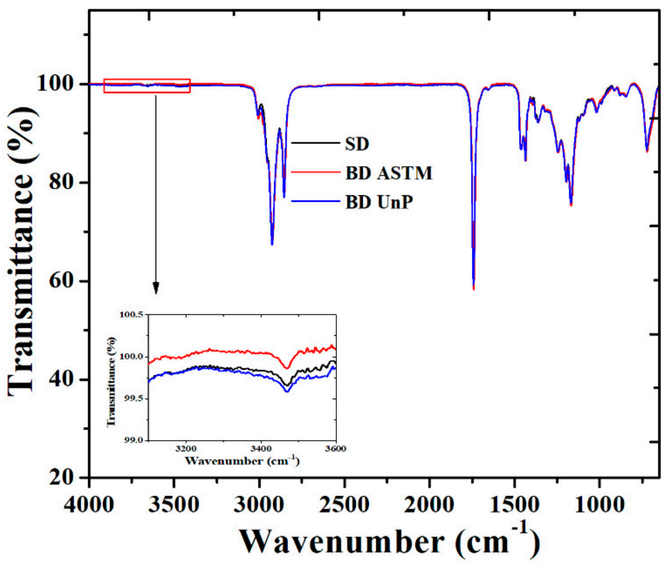


Figure 2. FTIR spectra of sawdust (SD), unpurified biodiesel (BD UnP), and ASTM purified biodiesel (BD ASTM) samples.

Table 2. Comparison of various studies that used adsorbents and bioadsorbents in biodiesel purification.

Adsorbent	Acid Number Reduction (%)	Free Glycerin Removal (%)	Total Glycerin Removal (%)	Water Removal (%)	Ref.
Magnesol	48.4	92.3	60.5	61.5	[15]
Silica	54.5		ND	46.0	
Rice husk ash	60.6	47.0	33.3	43.0	[32]
Sugarcane bagasse	14.3	82.3	ND	*	[45]
Potato starch	38.3	100	ND	ND	[53]
Corn starch	39.5	95.3	ND	ND	
Rice starch	41.9	100	ND	ND	
Cassava starch	43.0	100	ND	ND	
Eggshell	30.5	83.6	ND	ND	[54]
Oil palm empty fruit bunch	36.6	13.0	ND	66.7	[48]
Bentonite	66.6	34.7	ND	72.4	
Silica gel	66.6	34.7	ND	78.9	
Banana peel	*	99	93	54.0	[46]
Mushroom powder	*	ND	ND	27.0	
Purolite PD 206	*	91	93	63.0	
Amberlite BD10DRY and TULSION T-45 BD	*	ND	ND	72.0	
Bentonite	24.1	20.0	ND	*	[17]
Coconut coir	*	ND	ND	ND	[47]
Sawdust	31.3	54.8	*	14.3	This study
Coconut coir	27.0	33.3	*	18.4	This study
Nutshell powder	22.1	56.3	*	*	This study
Rice husk	43.3	32.1	*	*	This study
Water hyacinth fiber	47.5	*	*	*	This study

* = Increased the value. ND = Not disclosed.

3.2. *Adsorbent Characterization*

Morphology of Adsorbents

Figure 3 shows the surface morphology of sawdust, Magnesol, and Amberlite BD10DRY, as revealed by SEM images. Analyzing Figure 3A,B, an irregular surface and rough shape are observed, as well as small cavities in the woody structure [55–57] that can influence the adsorption of compounds such as glycerin, soaps, and water from the transesterification process. The spherical shape of Magnesol [15] is shown in Figure 3C,D, revealing spaces between each adsorbent particle, which could diminish the surface contact with the biodiesel impurities. Figure 3E,F present the surface morphology of Amberlite BD10DRY, which only shows a spherical and refined surface. In contrast to sawdust, the free spaces are more visible due to the size of the spheres, which affect the retention time between the adsorbent and biodiesel.

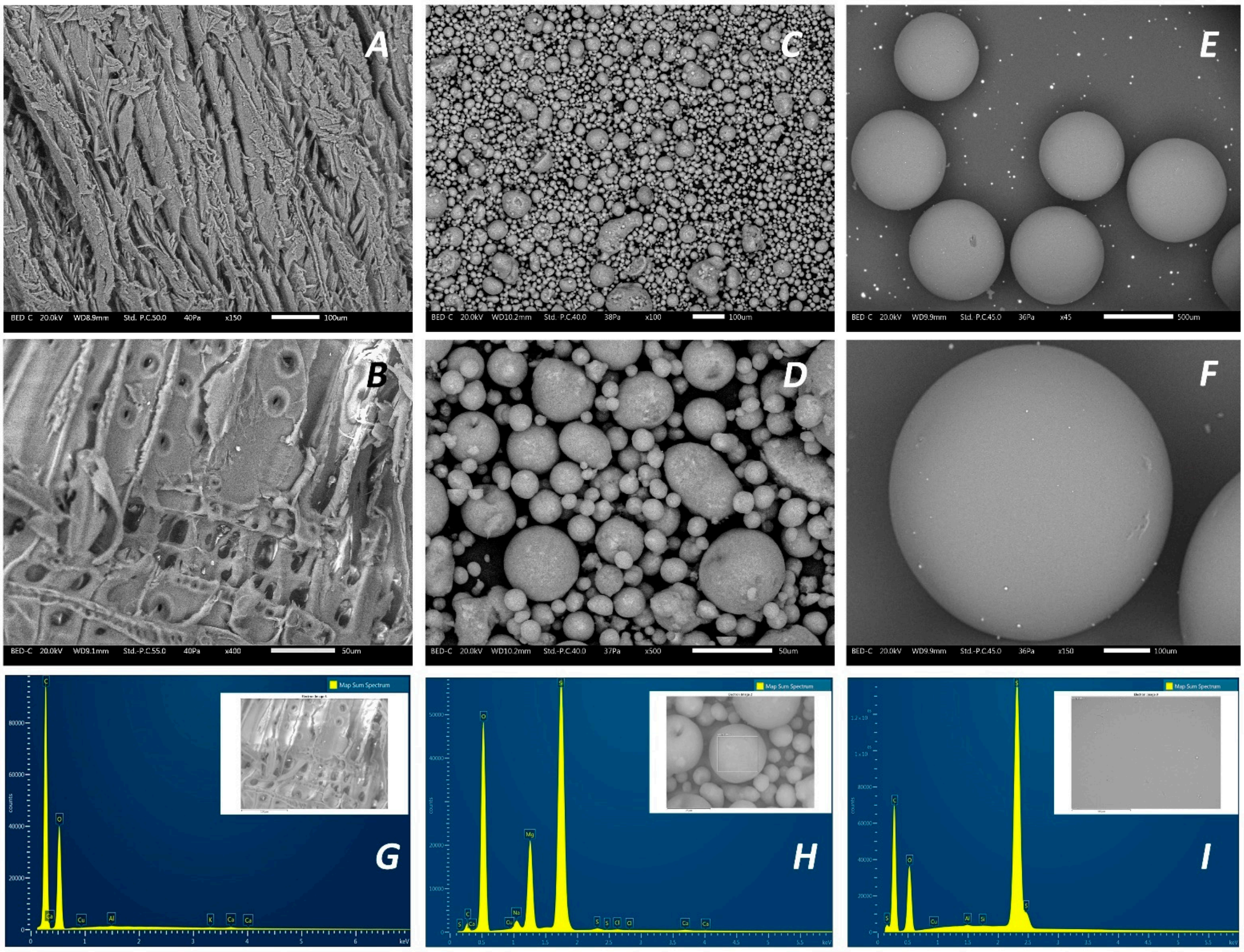


Figure 3. SEM images and EDS analysis for sawdust (**A** × 150, **B** × 400, **G**), Magnesol (**C** × 100, **D** × 500, **H**), and Amberlite BD10DRY (**E** × 45, **F** × 150, **I**).

The EDS results obtained during SEM analysis are shown in Figure 3G. The elements with the highest content are C (61%) and O (39%) by weight of sawdust [56–58], in addition to the presence in a smaller proportion of Ca, K, Cu, and Al. The appearance of Al might be because the samples were in contact with aluminum foil for storage, and Cu was part of the fixation support tape. Figure 3H,I shows the characteristic composition of Magnesol and Amberlite BD10DRY, containing elements such as Si (32%) and Mg (10.79%), as well as C (64.3%) and S (13.43%), respectively. It is worth mentioning that the reported particle size for sawdust is 400–600 µm, 60 µm for Magnesol, and 900 µm for Amberlite BD10 DRY [15,58].

4. Conclusions

Sawdust was the most effective adsorbent in purifying WCO biodiesel, statistically showing considerable adsorption of impurities. The efficiency of sawdust in removing impurities was similar to and, in some cases, better than conventional purification methods. The FTIR analysis shows that sawdust improves reductions in the proportions of the OH functional group corresponding to glycerin. The more porous morphology of sawdust can facilitate the diffusion of impurities in addition to improving liquid–solid surface contact. Sawdust can decrease the biodiesel acid number, water content, and free glycerin content, with values below the ASTM standard. In the case of total glycerin, the results were not significant compared with those using Magnesol and Amberlite BD10DRY. We should not discard the use of the other bioadsorbents analyzed in this study. One of the main advantages of using sawdust as an adsorbent is that it is biodegradable and organic waste, ensuring that the biodiesel production system has a lower environmental footprint. While the results were promising in some cases, more research is needed to assess their potential as bioadsorbents.

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