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APPLICATION OF NATURAL CLAYS AS ADSORBENTS FOR BIODIESEL PURIFICATION

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Abstract

Biodiesel has advantages such as the ability to totally or partially replace fossil diesel, as well as being a renewable source of energy. However, in the purification stage, the conventional aqueous washing method has a major environmental impact due to the high consumption of water to carry out the purification. With this in mind, this study sought to evaluate an alternative adsorption method in the biodiesel purification stage, in terms of the contaminant free glycerol. Three commercial clays were used, called green, pink and white clays, which were characterized using XRF. From the adsorption kinetics, using 50 mg of each clay at 30°C for 5, 10, 20, 30, 60, 90 and 1440 minutes, it was possible to assess the percentage removal and adsorption capacity of each clay. All the clays were able to adsorb free glycerol, and among the three adsorbents, green clay achieved the highest percentage of glycerol removal (59%) and the highest adsorption capacity (524 mg/g). Thus, the application of natural clays in the biodiesel purification process has great potential.

Keywords: Adsorption; green clay; free glycerol.

1. Introduction

The main justification for the production of biodiesel is based on global concern about climate change, which includes replacing oil-based sources with renewable ones [1]. The conventional biodiesel production route is transesterification, and the method used to purify it is aqueous washing. However, washing with water is not only costly, but also has an environmental impact due to the large consumption of water and consequent generation of effluents [2].

In recent decades, alternative purification methods have been explored, such as adsorption, and free glycerol, as one of the main contaminants in biodiesel, is used as a parameter to assess the quality of purified biodiesel [3].

Low-cost adsorbents such as passion fruit seed meal [4] and sugarcane bagasse [5] have already been evaluated in the removal of free glycerol from biodiesel and have shown efficiency in this process.

The aim of this study was to evaluate the adsorption capacity of natural clays in removing free glycerol from biodiesel.

2. Experimental

2.1 Biodiesel production

The biodiesel used in the adsorption tests was produced using soybean oil refined by alkaline ethyl transesterification. 1% catalyst (NaOH) was used in relation to the mass of oil and an oil: ethanol ratio of 1:7.5. The reaction was kept stirring at 45°C for one hour at 170 rpm.

After transesterification, the excess alcohol was removed by evaporation and the mixture was left to stand for 48 hours to separate the heavy phase containing the glycerol from the light phase containing the biodiesel. The heavy phase was discarded and the light phase was used for the tests.

2.2 Characterization of clays

Three commercial clays were used, identified in this work according to their color: green, pink and white. The clays were characterized by X-ray fluorescence spectroscopy (XRF), X-ray diffractometry (XRD) and textural parameters.

2.3 Adsorption kinetics

The adsorption capacity of the clays in terms of removing free glycerol from the biodiesel-rich phase was investigated using adsorption kinetics. For this test, 25 mL of biodiesel and 50 mg of clay were used in each flask. The adsorption times were 5, 10, 20, 30, 60, 90 and 1440 minutes. The samples were kept stirring at 170 rpm in a shaker (Marconi - Model MA42) at 30°C. At the end of the experiment, the adsorbent was separated from the solution by vacuum filtration using 80 g m^{-2} quality filter paper.

The adsorption capacity of free glycerol and the percentage of removal were calculated using Equations 1 and 2, respectively, with the C_0 and C_e concentrations being measured by titrimetric analysis, based on the work of Gomes et al. [6].

$$q_t = \frac{(C_0 - C_e)\,V}{m} \quad (1)$$

$$Removal\ (\%) = 100 - \left(\frac{100 \times C_e}{C_0}\right) \quad (2)$$

3. Results and discussion

Figure 1 shows the diffractogram with the crystalline phases present in the pink, green and white clays. Based on Figure 1, the pink clay is formed mainly by dolomite, whose characteristic peaks corroborate those presented in the work by Downs et al. [7]. In smaller quantities, the clay contains minerals such as kaolinite, calcite and quartz. Green clay is mostly composed of the mineral mica (muscovite), as well as montmorillonite, kaolinite, calcite and quartz, and these minerals were also found by Amari et al. [8]. White clay, on the other hand, is made up mainly of kaolinite, indicated by refractions at degrees two theta equal to 12.4°, 24.9°, 35°, 36°, 37°, 38° and 39°.

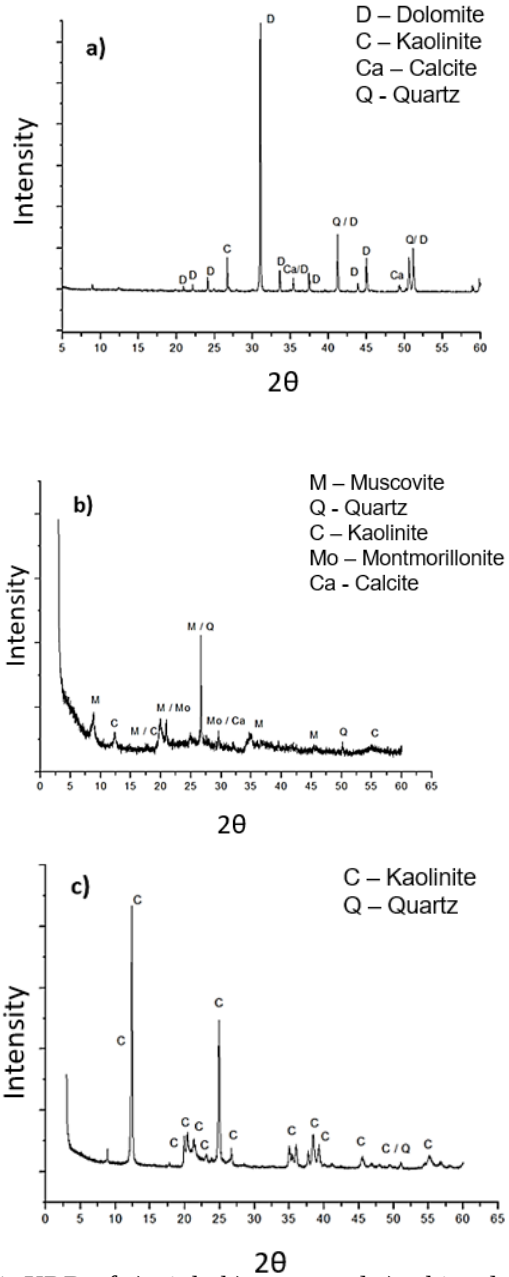

Fig. 1. XRD of a) pink, b) green and c) white clays.

The clay-forming minerals were identified in conjunction with XRF analysis, as shown in Table 1. The main oxide detected in the green clay was SiO_2, which accounted for more than half of the sample (54.2%) by mass, followed by Al_2O_3 which accounted for 27.9% of the clay composition. These results are consistent with the phases indicated by XRD, since the chemical formulas of quartz and muscovite show the oxides detected. This clay has

an iron content of 8.61%, and the presence of this oxide was also reported by Velasco et al [9].

Table 1. Chemical composition of green, white and pink clays using XRF analysis.

Chemical Composition	Clay		
	Green (%m)	White (%m)	Pink (%m)
SiO_2	54.2	46.1	21.6
Al_2O_3	27.9	52.8	10.7
CaO	2.75	0.064	50.1
Fe_2O_3	8.61	0.345	2.13
MgO	1.28	0.0633	13.6
K_2O	3.63	0.384	1.41
Na_2O	0.118	0.0358	0.0959
P_2O_5	0.463	0.0548	0.0209
TiO_2	0.893	0.0645	0.31
MnO	0.154	-	0.0421

In contrast, white clay is mostly made up of Al_2O_3 (52.8%) and SiO_2 (46.1%). Based on the chemical formula of kaolinite, the XRD and XRF analyses corroborate each other. For pink clay, 50.1% of the sample is made up of CaO. This result was expected, given that dolomite and calcite have calcium in their composition. In addition, iron oxide, which accounts for 2.13% of the clay, is possibly responsible for the color of this clay.

With regard to textural parameters, the pink, white and green clays had specific surfaces of 1, 12 e 111 m^2g^{-1}, and pore volumes of 0.0045, 0.06 and 0.184 $cm^3\ g^{-1}$, respectively.

Regarding the removal of free glycerol using the clays, the results obtained are summarized in Figure 2. The three clays were able to remove free glycerol, with maximum values of 59.4, 53.7 and 49% for the green, white and pink clays, respectively. In the first five minutes of adsorption, only the pink and white clays removed the contaminant. However, in this time interval, removals of less than 7% were achieved.

Over time, the green clay showed better free glycerol removal compared to the others, reaching its maximum value in 60 minutes. Pink clay, on the other hand, showed low removal values throughout the test. For the three clays, it can also be seen that after 60 minutes (green clay) and 90 minutes (pink and white clays) there was a desorption process which reduced the free glycerol removal achieved.

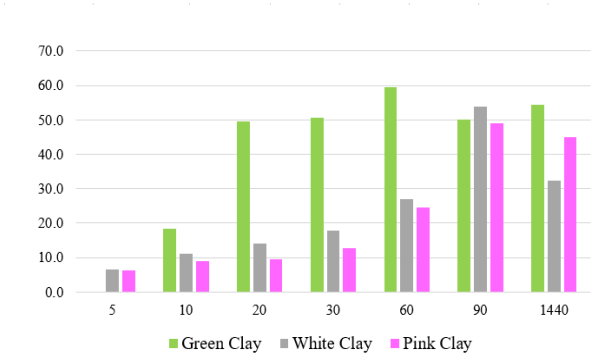

Fig. 2. Removal of free glycerol using natural clays.

With regard to adsorption capacity (Table 2), expressed in mg of adsorbate per g of adsorbent, it can be seen that white clay showed the lowest results as a function of time, followed by pink clay. Green clay, on the other hand, not only showed the highest percentage removal of glycerol, but also the highest adsorption capacity, reaching a value of 524 mg/g.

Santos et al. [10], when studying the adsorption of free glycerol from biodiesel with a clay from ceramic waste, composed of 56.5% silica and 35.7% alumina, concluded that adsorption was promoted by the affinity of glycerol with silica and alumina. Based on the XRF analysis, the green clay has the highest amount of silica because it is mostly composed of quartz and muscovite, which may have helped to increase its adsorption capacity. In addition, this clay has a much higher specific surface area than the others.

Table 2. Adsorption capacity of free glycerol using natural clays.

Time (min)	q_t (mg/g)		
	Green clay	White clay	Pink clay
5	0	30.59	43.69
10	161.67	52.43	61.17
20	436.95	65.54	65.54
30	445.69	83.02	87.39

60	524.34	126.72	170.41
90	441.32	251.25	338.64
1440	480.65	150.75	310.23

In addition, the free glycerol removals achieved by Santos et al. [10] ranged from 57.9 to 81.2%, the latter result being obtained with 5% (w/v) clay at 50°C. Thus, there is potential for obtaining greater contaminant removals with green, pink and white clays when carrying out an adsorption isotherm study.

Considering the better performance of the green clay, the kinetic data was plotted and the pseudo-first order model fitted to the experimental data, as shown in Figure 3.

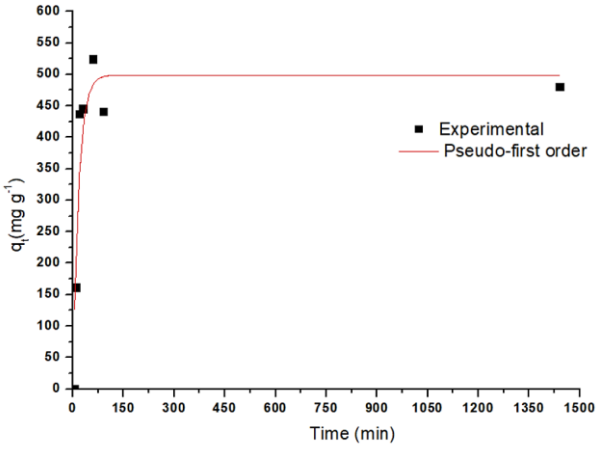

Fig. 3. Pseudo-first order kinetic model fitted to experimental data with green clay.

Using the pseudo-first order kinetic fit, a q_e of 498.9 mg g^{-1} was obtained with an R^2 of 0.8216. The pseudo-first order model was the best fit for the experimental data and proposes that adsorption is proportional to the number of free sites.

4. Conclusion

This study investigated the use of natural clays (green, pink and white) as adsorbents in the purification of biodiesel. Of the results found, green clay was the most outstanding, consisting of 54.2% silica and 27.9% alumina. Using 50 mg of clay at 30°C, it was possible to achieve 59.4% removal of free glycerol and an adsorption capacity of 524 mg/g, after 60 minutes of adsorption. Thus, the use of natural clays has potential in the biodiesel purification process.

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