

## Adsorption of Free Fatty Acid in Biodiesel from Palm Fatty Acid Distillate using KOH-Activated Starch

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The elimination of free fatty acids (FFA) from biodiesel is usually performed in industrial practice using different units for neutralization with caustic, washing and drying of the fuel. However, adjustment of the free fatty acids can be performed in only one operation using bleaching tanks and commercial adsorbents. In this work, purification of crude biodiesel fuel from palm fatty acid distillate (PFAD) has been done by employing dry washing method for the removal of FFA using modified potato and cassava starch and compared with commercial magnesium silicate. The molar ratios of KOH/starch in modified potato and cassava, i.e. 0.10:1, 0.15:1 and 0.25:1 were obtained by varying concentrations of KOH: starch samples. The morphology, crystal structures, surface area and pore size of the adsorbents were characterized by scanning electron microscopy (SEM), X-ray diffraction method (XRD) and Brunauer-Emmett-Teller technique (BET). The adsorption efficiency of the synthesized adsorbents in biodiesel was studied by varying dosage of adsorbents for 50 g of biodiesel at 30 °C for 30 min. The results showed that the modified potato and cassava at 0.25:1 KOH/starch molar ratio at room temperature presented the highest efficiency in adsorption of residual FFA at 69.46 % and the highest adsorption capacity of modified cassava and potato starch was 233 mg and 228 mg of FFA per gram of adsorbent. The comparison of dry washing with commercial magnesium silicate, presented good efficiency in the removal of FFA and depicted similar behaviour independent of the kind of adsorbent employed.

### 1. Introduction

The quest to come-up with sustainable energy supply and climate change mitigation has motivated the development of alternative fuels from waste of edible vegetable oils refining based on local and renewable use of agricultural resources. Among the edible oils, extensive attention has been devoted to palm oil during the past few years but recent efforts for diversification of the feedstocks to secure biodiversity and low cost materials has directed scientific research towards by-products of the palm oil refining (Nair et al., 2012). The vegetable oils, animal fats, waste frying oils (WFO) and PFAD have vast industrial applications and are commonly used in biodiesel production. The last one is an undesirable residue of palm oil industries with severe environmental impact, its use in production of biofuels not only aid in the environmental protection but also allows the generation of an alternative source of energy contributing to a global economy (Manique et al., 2012). PFAD had been classified as a cheaper low quality grade feedstock due to its high FFA content (>85 wt.%), thus, PFAD have received high recommendation as the potential's starting material for biodiesel production (Lokman et al., 2015). The utilization of biodiesel as a renewable and environmentally friendly diesel fuel presents important characteristics as biodegradability, non-toxicity and low emission profiles that make it more carbon neutral and contributable to the reduction of CO<sub>2</sub> emission (Alves et al., 2016).

One essential issue in the refining of biodiesel produced in acid-catalyzed process is the adjustment of the acidity of the biodiesel product. It has been reported that biodiesel produced by reacting supercritical methanol had a residual FFA content of 1-3 % (Manuale et al., Anitescu et al., 2008). The standard solution for adjusting the acidity of biodiesel could be neutralizing the FFAs and washing away the formed soap stock. This option generates a sizable amount of process wastewater (Manuale et al., 2011). The conventional biodiesel purification process with water is normally utilized because of its ability to solubilize these contaminants such as glycerin, methanol and catalyst, allied to its abundance and low cost. It is possible to obtain a biodiesel with

good quality but with the disadvantage of generating high volumes of liquid effluent (Berrios and Skelton, 2008). In this last fact, it can be overcome by applying dry purification methods which avoid use of water to wash the biodiesel. Dry washing processes are those that use adsorbents for biodiesel purification. The process is based on the physical adsorption thus, is promising for removing the contaminants present in the biodiesel because of its low cost, simplicity of design and operation and because of the sustainability of some adsorbents. However, different materials are proposed in the literature for removing different compounds from biodiesel (Stojković et al., 2014). Faccini et al. (2011) compared different commercial adsorbents (Magnesol<sup>®</sup>, silica, Amberlite BD10 DRY<sup>®</sup> and Purelite<sup>®</sup>) for biodiesel purification and observed that Magnesol<sup>®</sup> and silica had better performance. Fadhil and Dheyab (2014) has reported that the dry washing method using activated carbon was able to purify the produced methyl ester in the same way as wet washing process. However, the main drawbacks considered in using dry washing processes are related to the cost of the adsorbent and its reusability purposes, some low cost materials are proposed in the literature for biodiesel purification. Manique et al. (2012) has carried out the purification process using rice husk ash and commercial adsorbent (Magnesol<sup>®</sup>) and verified that both adsorbents presented removal results similar to the wet washing process with phosphoric acid solution. Alves et al. (2016) evaluated the biodiesel purification processes for dry cleaning, adsorption process with sugarcane bagasse presented results for biodiesel purification similar to those for the wet washing process and Magnesol<sup>®</sup>. The use of cellulose and starch from different sources (corn, potato, cassava and rice) for biodiesel purification showed that the application of these natural adsorbents is efficient in removal of impurities such as free fatty acids, free glycerine, sodium metal and water for biodiesel obtained by base catalyzed transesterification of commercial sunflower oil. Substantially, the best results were reported for potato starch (5 % and 10 %), cassava starch (1 % and 2 %) and Select 450<sup>®</sup> (1 %, 5 % and 10 %) in removal of turbidity of biodiesel. Additionally, the amount and kind of adsorbents did not significantly influence the resulting acidity index, showing no specific selectivity of the kind of adsorbent employed (Gomes et al., 2015). Although there is a certain progress in dry purification of biodiesel using pretreated starch materials, its chemical treatment for biodiesel refining is as yet insufficiently studied. This concerns the properties related to the efficiency of its practical application. Hence, the main purpose of this study is to investigate the adsorption of residual free fatty acids after the production process of biodiesel from PFAD, using modified potato and cassava starch adsorbents, along with a commercial adsorbent, Magnesol<sup>®</sup>, in the purification of biodiesel.

## **2. Experimental**

### **2.1 Biodiesel production from PFAD**

The biodiesel employed in this study was obtained from PFAD by acid esterification via methyl route. In the method employed for obtaining biodiesel from PFAD, methanol (v/v) and a catalysts concentration 1.8 wt. % sulphuric acid (v/v) were employed with respect to the PFAD oil. Initially, sulfuric acid was mixed with methanol under constant stirring until complete homogenization. Then, the PFAD oil was heated to the desired temperature (70 °C) before starting the reaction. At this point, the solution of methanol and sulphuric acid was slowly added into the preheated PFAD oil and the mixture was kept under constant stirring for 60 min. At the end of the reaction, the mixture was transferred to a separatory funnel in order to separate the phases. After resting, two distinct phases were observed: the top phase contained excess methanol and water formed during the reaction, while the FAME phase was taken off at the bottom and passed into evaporator to removed traces of methanol.

### **2.2 Synthesis of modified adsorbent**

The adsorbent materials examined included two commercial potato and cassava starch, KOH was used for their chemical treatment. In this modification, pre-treated potato and cassava starch powder was first oven-dried at 80 °C for 24 h and then sieved to obtain the mean particle sizes (Lokman et al., 2016). Three different concentration ratios of KOH were chosen for adsorbent synthesis. The concentration (Molar) ratios of KOH to starch was 0.10:1, 0.15:1 and 0.25:1. The potato and cassava starch samples were stirred in a beaker with different KOH solutions at room temperature for 12 h. The solid phase was recovered by vacuum filtration and ambient air-dried overnight. Finally, the resultant dried samples were crushed and sieved to a consistent powder size, then stored in some tightly capped bottles for further use.

### **2.3 Characterization of the adsorbents**

The morphology of each adsorbent (potato starch, cassava starch, modified potato and cassava starch, and Magnesol<sup>®</sup>) were analyzed by scanning electron microscopy (SEM) in a Jeol JSM 6390 equipment with 5 kV and magnification of up to 5,000x. The equipment used for XRD analyses was (High Resolution X-ray diffractometer model Rigaku Smartlab) with an X-Ray tube containing a copper anode (Cu-K $\alpha$  wavelength), at

a scan rate of  $8^\circ \text{ min}^{-1}$ ,  $2\theta$  ranging from 20 to 100 with step of  $0.02^\circ$ , voltage at 40 kV and current at 30 mA. The total surface area and pore size distribution was measured using the multipoint BET- $\text{N}_2$  at 77 K on a surface and pore size analyzer (Micromeritics, model 3Flex). The specific surface area and the pore size distribution was evaluated by the BET (Brunauer, Emmett and Teller) and the BJH (Barrett-Joyner-Halenda) methods.

## 2.4 Adsorption capacity of adsorbents

Five different amounts of adsorbents were added into 50 g of crude biodiesel to study the contaminates adsorption. The crude biodiesel was treated using potato and cassava starch, commercial solid adsorbent (Magnesol<sup>®</sup>) and alternative forms of potato and cassava starch (modified potato and cassava starch). Initially, methanol was removed by drying and the resulting ester phase was purified using 1 %, 3 %, 5 %, 7 % and 10 % (w/v) of adsorbents with respect to the biodiesel. The samples were kept under constant stirring in a round bottom flask at a rate of 150 rpm and room temperature for 30 min. After agitation, the adsorbent was removed and purified biodiesel was analysed for the contaminations. In order to determine the effectiveness of purification, free fatty acid was measured before and after processing. The amount of remaining free fatty acid was determined by acid value titration according to EN14104 standard (Tubino and Aricetti, 2011). Adsorption efficiency was defined as percentage of fraction between adsorbed and initial contaminate.

## 3. Results and discussion

### 3.1 Adsorption synthesis and characterization

The average surface area and pore size distribution of synthetic magnesium silicate, pure and modified potato and cassava starch were determined and presented in Table 1. According to IUPAC classification, the isotherms of all the adsorbents presents typical type IV curve of hysteresis loops, characteristics of mesoporous materials and associated with capillary condensation. However, the modified starches were found to adsorbed nitrogen in low  $P/P_0$ , indicating the presence of mesoporous, with diameter range between 20 to 500 Å. Meanwhile, the pore diameter of all the adsorbents tested were expressed between 30 to 150 Å which indicated that the diameters of the pores are in mesoporous region. The commercial magnesium silicate (Magnesol<sup>®</sup>) exhibited higher surface area of 137.8073  $\text{m}^2/\text{g}$  and a larger pore volume of 0.389863  $\text{cm}^3/\text{g}$ , followed by modified cassava and potato starch with a surface area (1.3492 and 1.341  $\text{m}^2/\text{g}$ ) and pore volume of (0.001163 and 0.001507  $\text{cm}^3/\text{g}$ ) respectively. It is important to point out that although the (Magnesol<sup>®</sup>) presents high specific area, this surface is predominantly larger in mesoporous region allowing an easy diffusion of the species to be adsorbed while the other adsorbents are present in smaller mesoporous region (Manique et al., 2012).

Table 1: Physicochemical properties of pure and modified starches with Magnesol<sup>®</sup> as adsorbents

Adsorbent	Surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size diameter (Å)	Crystal size (nm)
Potato starch	0.6545	0.0008	42.3	5.00
Cassava starch	0.8595	0.0015	51.5	5.33
Modified potato starch	1.3410	0.0012	36.1	4.62
Modified cassava starch	1.3492	0.0012	48.8	4.23
Magnesol <sup>®</sup>	137.81	0.3899	145.3	1.64

XRD patterns of modified potato and cassava starch shows sharp crystalline phases when compared with the peaks from the patterns of unmodified starches with a minimal intensity corresponding to the crystalline fraction of the starches (at  $15^\circ \leq 2\theta \leq 40^\circ$ ) respectively (Alvani et al., 2011). These similar peaks were identified in the diffraction patterns of modified potato and cassava starch without additional peak nor broadening peak been detected. The XRD pattern and structure of the sample of synthetic magnesium silicate was found to be amorphous phase and it was in agreement with commercial magnesium silicate (Clowutimon et al., 2011). The crystallite size for each adsorbent shown in Table 1 was calculated using Scherrer formula based on the highest starch crystal XRD diffractogram peak. Among the adsorbents, the smaller crystallite sizes of modified cassava and potato suggested that strong interaction between the alkaline solutions and starch species enhanced the dispersion of alkaline solutions on the surfaces of the starch materials.

The morphology of pure and modified adsorbents is shown in Figure 2. The parent and modified potato and cassava starch possess semi spherical, and oval granular shapes. The surface of the particles was observed to be well crystalline for unmodified potato and cassava starch than modified starches. The image of

magnesol materials it is possible to observed spherical shape conforming a similar trend of magnesol images (Faccini et al., 2011) .

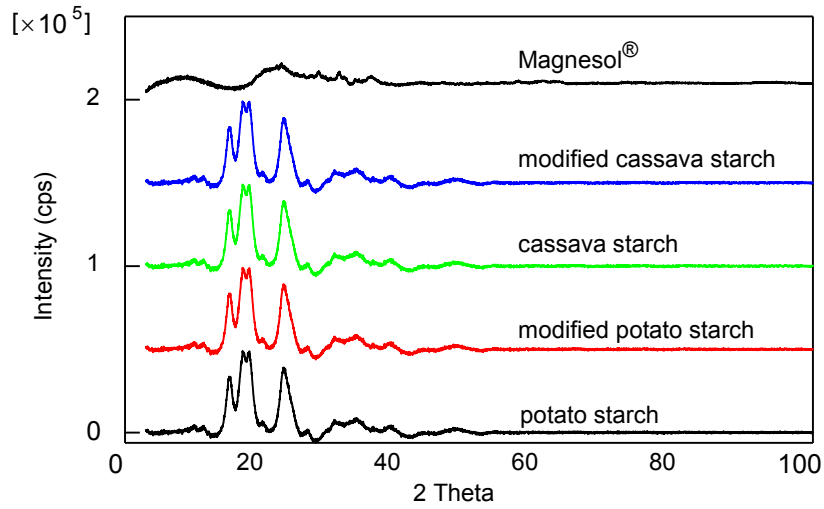


Figure 1: The XRD pattern of the different adsorbents: (a) potato starch (b) modified potato starch (c) cassava starch (d) modified cassava starch (e) Magnesol®

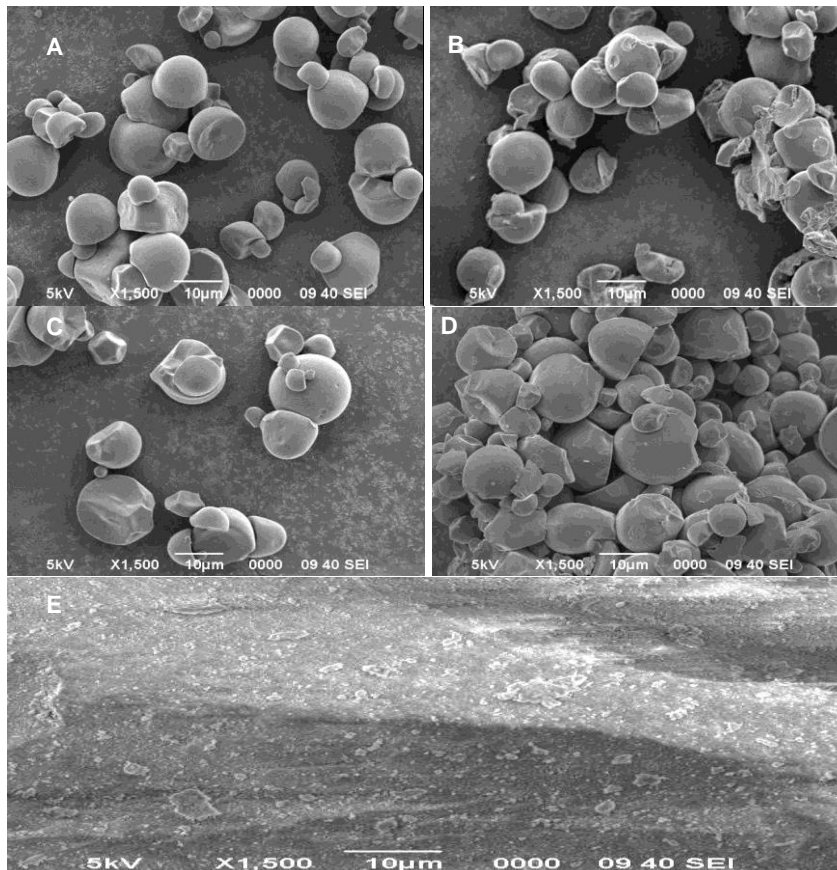


Figure 2: SEM images of the different adsorbent: (a) potato starch – magnification 1,500x (b) modified potato starch – magnification 1,500x (c) cassava starch – magnification 1,500x (d) modified cassava starch 1,500x (e) Magnesol® – magnification 1,500x.

### 3.2 Adsorbent Efficiency

Adsorption of FFA in biodiesel by synthetic magnesium silicate, pure and treated potato and cassava starch, at a different molar ratio of KOH/starch were investigated and shown in Figure 3. From the results obtained, dosage amount of adsorbent had direct variation with efficiency of FFA adsorption. Modified potato and cassava starch at 0.25:1 KOH/starch molar ratio and 0.5 g of adsorbent showed the highest efficiency in adsorption of FFA at 59.50 % and adsorption capacity of 223 - 233 mg FFA per g of adsorbent. For Magnesol, a commercial magnesium silicate, the adsorption capacity was 233 mg FFA per gram of adsorbent. Similarly, untreated potato and cassava starch could adsorb 124-152 mg FFA per gram of adsorbent. On the other hand, the trends of commercial magnesium silicate for biodiesel purification was reported to adsorb FFA 90 mg/g of adsorbent (Clowutimon et al., 2011, Assawasaengrat P., 2015).

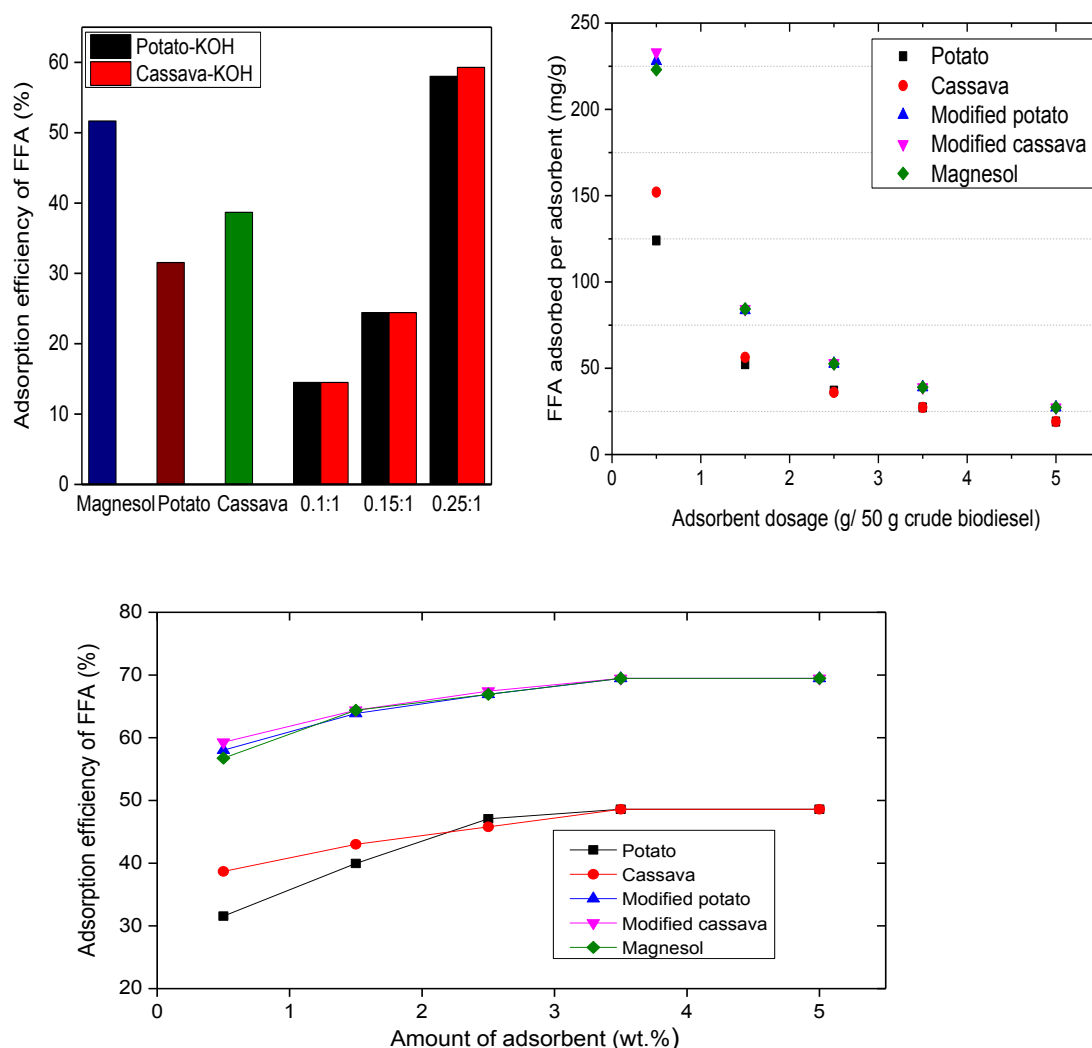


Figure 3: Comparison of adsorption efficiency of FFA from different adsorbents; potato starch; modified potato starch; cassava starch; modified cassava starch; Magnesol®

### 4. Conclusions

In this study, the use of alternative form of potato and cassava starch to adsorb residual FFA and purify crude biodiesel from PFAD was successfully developed. The adsorbents were prepared and characterized using XRD, SEM, BET. The samples were crystalline with average surface area and pore diameter size. The adsorbents had some mesoporous volume for FFA molecules from crude biodiesel. In comparison with Magnesol®, the adsorption efficiency of the adsorbents tested in biodiesel containing residual FFA was studied

by varying dosage number of adsorbents for 50 g of biodiesel at room temperature for 30 minutes. It was found that modified potato and cassava starch at 0.25:1 KOH/starch molar ratio had the highest efficiency in adsorption of FFA at 69.46 %. The adsorption capacity was 223 and 233 mg FFA per gram of adsorbent respectively. The adsorption performance of the adsorbents increased with increased in the amount of adsorbent dosage. However, the adsorption capacity of FFA increases with the decrease in adsorbent dosage. BET results characterized the mesoporous structure region with pore diameter between 30 to 150 Å, pure and modified samples indicated the presence of mesoporous structures.

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