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Modification of The Integrated Agro-Waste-Based Palm Oil with PET for Wastewater Treatment

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Abstract

The most common reusable resources in Malaysia are waste-based palm oil plants: empty fruit bunches, fiber and palm kernel shells, all by-products from palm oil mills. This resource is classified as agro-waste and exhibits great potential to be used as a filter media for wastewater treatment applications. In this study, the selected polyethylene terephthalate (PET) flat sheet was treated with sodium hydroxide (NaOH) and coated with calcinated waste-based palm oil with the immersion of polyvinyl fluoride (PVDF) and dimethylformamide (DMF) by using the dip-coating method. This integrated composite is applied to analyze the performance of the color of palm oil final treated effluent based on the calcination temperature of 500 °C. Characterization of samples was conducted by Scanning Electron Microscopy (SEM) and Fourier Transformed Infrared Spectroscopy (FTIR) mainly to identify the morphology of the waste-based palm oil after calcination as well as determine the functional groups and chemical bonds that were involved. It can be seen morphologies and chemical structures between EFB, fiber, and PKS are different patterns. The reduction of the color value of effluent showed the hydrophobicity of the integrated palm oil waste coated with PET which enables the trap of the particles in the effluent, thus, this composite has potential use in the filtration of water treatment. This preliminary study also showed that it requires further research, as the ability of the sample to use the dip-coating method to reduce the effluent color showed potential for further use.

1. Introduction

One of Malaysia's most significant commercial crops, oil palm plantations, has grown in size yearly. One of the biomass materials, which is a by-product of the palm oil industry, is biomass-based oil palm trees [1], including the shell of the palm kernel, empty fruit bunch and the fibre from the palm oil fruit. The agro-waste-based palm oil is extracted from different parts of palm oil, which can be divided into three different types of agro-waste: empty fruit bunch, fiber and palm kernel shell. A previous study shows that palm kernel is used as activated carbon [1], empty fruit bunches as a fiber filter media [2], fiber as activated carbon [3]. These agro-wastes contain cellulose, hemicellulose, and lignin content for various purposes. Target in reducing pollution on the environment, many researchers have also applied these kinds of agro-waste in the development or improvement of properties of materials such as in construction building composite materials such as bricks [4], cement [5], aggregates, and act reinforcer [6] or filter materials [7]. They have focused on these agro-wastes-based palm oil fruits as reinforced materials for separation due to their sustainable availability, biodegradability, ease of collection, cheapness, and light [8-11]. Hence, it is crucial to generate alternatives in synthesizing agro-wastes-based composite that could significantly remove contaminants in wastewater or improve water quality.

So far, many porous materials-based polymer substrates have been widely used for the purification of water such as polyurethane (PU), polycaprolactone (PCL), polyethylene glycol and polyvinylidene fluoride (PVDF) and polyethylene terephthalate (PET). PET textile is widely used, consisting of porous structures, intrinsically hydrophobicity, rough surface and high flexibility. However typical substrates still have some drawbacks, such as a foul tendency, easily rupture after processes and some material not being produced due to their complicated process preparation. Thus, various effort has been explored to improve the surface intrinsic properties of substrates. For instances, superhydrophobic filtration fabric integrated fly ash or hydrogel composite has effectively separated oil/water mixture [12,13] These studies have paved the way for developing new functionalized wastewater treatment textiles.

Carbonaceous materials-based agro-wastes have recently been used to modify substrates such as absorbent and membrane composites to enhance their separation efficiency. For instance, the biochar-based wood coated with PVDF membrane showed excellent separation and good antifouling effect [14,15]. Hydroxyl groups of hydrophilic polymers could increase the hydrophilicity of PVDF membrane, could decrease the fouling effect. Depending on the applications, one way to utilize these agro-wastes is by modifying the substrate to enhance its properties, such as surface hydrophobicity [16]. A simple technique for changing the surface of the substrate is dip coating, commonly used on polymer, ceramic, and fiber. One example substrate is a polypropylene (PP) membrane, which consists of surface hydrophobicity that successfully produces a rougher surface using the dip-coating process [10].

In this context, integrating palm oil fruit-based materials ashes with substrate might enhance the efficiency of wastewater separation. Therefore, this preliminary research study mainly focused on preparing and characterizing the controlled and integrated agro-wastes-based palm oil fruits with PVDF/PET flat sheets by evaluating the chemical structure, morphology, and effect of the unmodified and modified PET sheet separation.

2. Materials and Methods

2.1 Materials

The materials and equipment used were PVDF, ethanol, palm kernel shell (PKS), fiber, empty fruit bunch (EFB), dimethylformamide (DMF), sodium hydroxide (NaOH), distilled water, beakers, fume hood, 10 ml pipette, furnace, crucible, hot plate, aluminum foil, thermometer, weighing boat, spatula, pestle and mortar, tweezer, magnetic stirrer, parafilm, analytical balance, oven, plastic petri dishes and glass petri dishes. All of these are available at Lab of Biology and Function (MBF1) and Lab of Engineering (MTK) in Universiti Tun Hussein Onn Malaysia (UTHM), Campus Pagoh.

2.2 Methods

2.2.1 Pre-Treatment of Agro-Wastes and PET

PKS, Fiber and EFB were calcined via furnace at 500 °C for each agro-wastes, respectively. These were calcined and cooled down entirely for about 24 hours before being crushed into fine powder. Then, samples of PET were immersed in the NaOH (1M) solution and was stirred under 60 °C for 2 hours. After that, sample of PET was rinsed with distilled twice and immersed in ethanol for 10 minutes. Finally, samples of PET were placed in the petri dish and dried for 24 hours.

2.2.2 PET Dip Coating

About 0.3 g and 0.5 ml of PVDF and DMF were measured, respectively. Then, the agro-waste ashes-based palm oil fruit (PKS, fibre and EFB) were added to the solution and stirred for 30 minutes each. Pour the mixed solution into a glass petri dish and insert the treated PET. Lastly, the samples were dried in an oven for 7 hours.

2.2.3 Characterization

The samples were examined regarding their surface chemistry and morphology using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS) at a magnification of 2000 times, respectively. Meanwhile, the performance of efficiency of wastewater separation was determined based on the effect of decolorization using DR6000 with a standard color unit in ADMI (10 mm).

3. Results and Discussion

3.1 Physical Appearance of Modified Samples

Fig. 1 shows the physical appearance of the sample before and after modification. Fig.1 (a) shows a white sample with hydrophobic characteristics. This sample controls PET and is still not treated yet. Meanwhile, it can be seen the different appearance of PET sample after the pre-treatment Fig. 1 (b). The water droplet remained on the surface in a particular time with a black appearance. This might be because the integration of palm oil ashes led to increased surface roughness.

(a) **(b)**

Fig.1 *Physical appearance of the sample (a) before modification; (b) after modification*

3.2 Morphology of Agro-Waste-Based Palm Oil

Fig. 2 shows the structures of palm oil fruits ashes based agro-waste, PKS, EFB and fibre, respectively. The surface and cross-section morphologies were highlighted at magnificent 2000 times. As can be seen for PKS surfaces (Fig. 2 (a)), both morphologies displayed almost the similar pattern and structures. This is most likely due to these PKS particles being incompletely broken down after calcination and improper crushing. Thus, these PKS remained structured as the characteristics of PKS is rugged structure and difficult to break. These details need more attention to obtain a consistent particle size that ultimately affects the integration process.

Fig. 2 (b) shows the structures of EFB. The EFB surface showed a messy pattern that may be caused by high force during the crushing process. The cross-section of EFB also expresses a bee network pattern for the same reason as explained in fiber. As for the last agro-waste-based palm oil which is fiber, many dots represent the rough surface where it acts as a vital part of the filtration process. The dots can prevent any big particles from passing through the integrated palm oil ashes with PET, finally, it might cause a decrease in the color of the wastewater. The bee-like network of the fiber cross-section, known as hollow areas, is the path for the water to pass through. After being integrated with PVDF/PET, it can increase the filtration accuracy to produce cleaner and clearer water from the influent used.

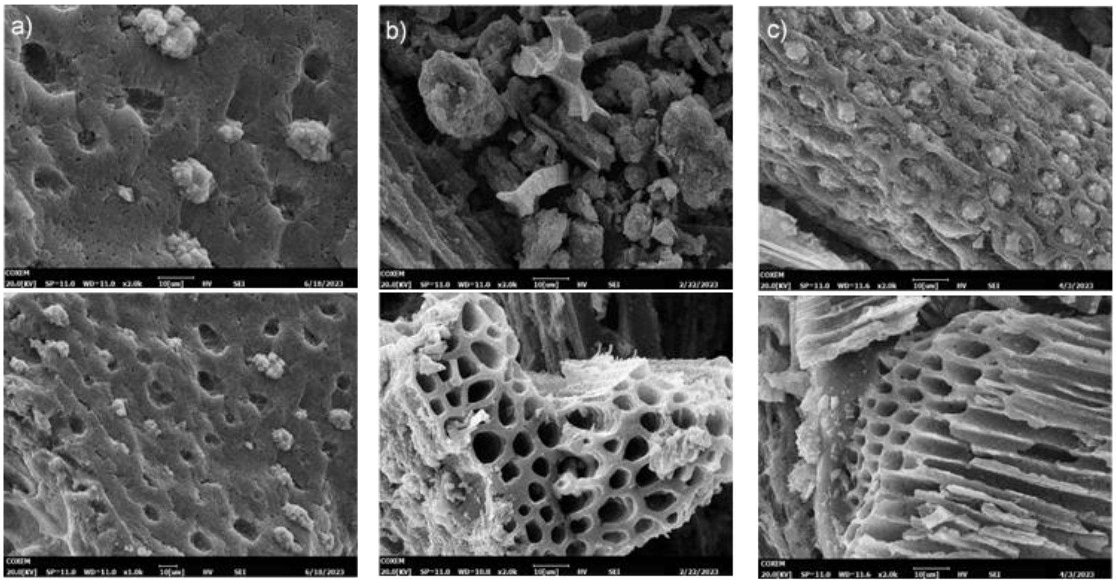

Fig. 2 *Surface particles of agro-wastes ashes (a) palm kernel shell (PKS); (b) empty fruit bunch (EFB); (c) firer*

3.3 Fourier-Transform Infrared (FTIR) Analysis

Fig. 3 shows three zones with peaks presenting each type of agro-waste ashes-based palm oil fruit (PKS, EFB, fibre). Firstly, the weak peak around 2100 cm^{-1} can be seen, proving that the alkyne group. Plants have an abundance of carbon element which justifies the presence of triple bond carbon shown by the graph. Next, the peak at around 1350 cm^{-1} shows the presence of S=O, which represents Sulfur's strong and sharp peak at EFB graph. This indicates that EFB ashes contained higher Sulfur than other agro-waste types. The third zone at 1100 cm^{-1} shows a medium peak for all the agro-wastes ashes-based palm oil fruits. A medium peak around the 1250-1020 cm^{-1} range is called amine, which is C-N. Nitrogen is commonly seen in plants' chemical structure as a nutrient for them to grow. Thus, this is a reasonable fact to support that amine are the most suitable compound to exist at that peak. Among all the samples, EFB has the most apparent difference in peaks, specifically at the peak of 1350 cm^{-1}, and is more robust and sharper than PKS and fragile fiber.

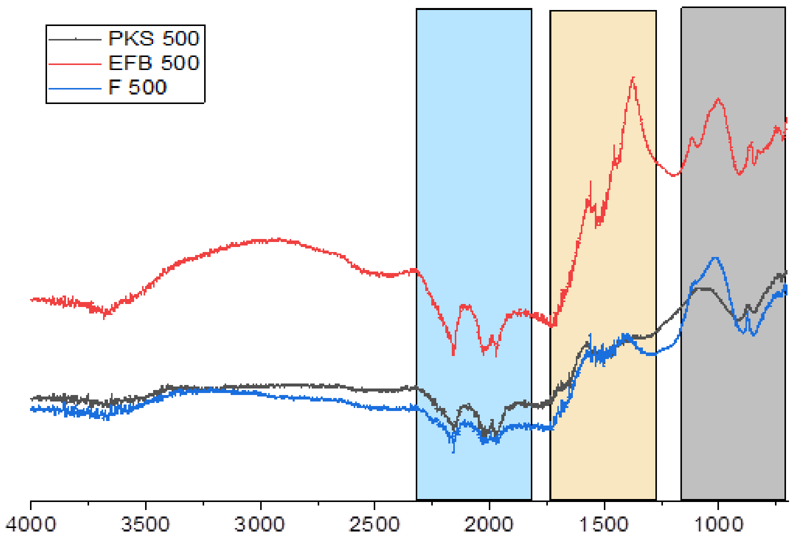

Fig. 3 *The agro-wastes ashes-based palm oil fruit biomass*

3.4 Decolorization of Palm Oil Effluent

Fig. 4 depicts the benchmark of the PET sheet filter without modification; there is no change of color value at all. Then, the average data obtained was around 1100 ADMI. The difference between each bar indicates that the difference in the effluent's efficiency of absorbing dissolved solids differs based on the agro-waste-based palm oil, where EFB shows a significant differential value rather than PKS and fibre. Each bar represents the average value of the data obtained from 3 data recorded for each temperature of the agro-wastes, respectively. Then, the standard deviation was calculated based on the average values, summarized in the graph above, and compared to the initial value of the wastewater before filtration. As a result, these data showed that all three agro-waste-based palm oil is relatively possible for treating wastewater that acts as an adsorbent to decrease color value.

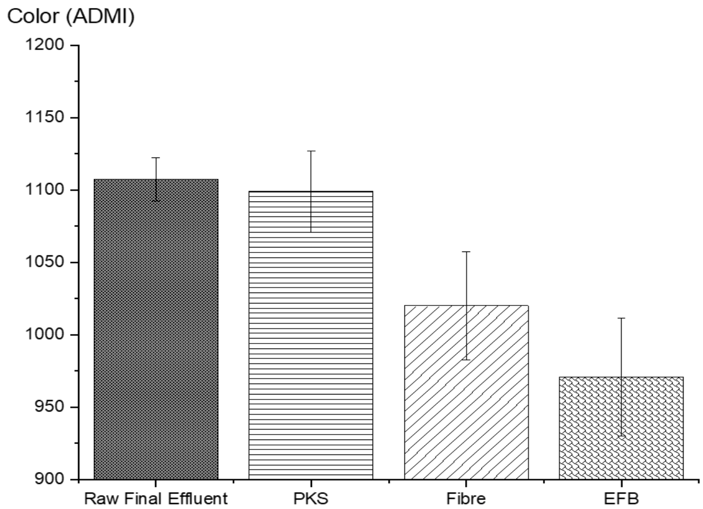

Fig. 4 *Decolorization of wastewater by using unmodified and modified coated PET with agro-wastes based palm oil fruit biomass*

4. Conclusion

In this study, it is shown that the agro-wastes based palm oil biomass exhibits various pattern of surface chemistry and morphologies. After the calcination process, agro-wastes ashes-based palm oil fruits material ashes were turned black, which caused the change in appearance, and fragments of agro waste modified the surface to become rougher. As for the morphology of EFB, it showed distorted fragments on the surface, which may have been caused by high force during the crushing process and a bee-like network for the cross-section. There are different peaks at specific regions and similar functional groups, such as the alkyne group, which is C≡C bond, C=O bond, N-H bond, Si-O bond, and C-H bond. It also shows that EFB gave a high amount of Sulphur (S=O) element. In conclusion, EFB ashes-based palm oil fruit are the most promising in reducing effluent color, with a value of 983 ADMI. This study shows the potential of using palm oil fruit biomass to reduce the color in effluent but requires further research before becoming a viable alternative.

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Conflict of Interest

Authors declare that there is no conflict of interests regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design:*** *Afiq Zikri Zool Pakar, Rahman Hamimi Abd Hamid, Siti Samahani Suradi;* ***data collection:*** *Afiq Zikri Zool Pakar, Rahman Hamimi Abd Hamid, Siti Samahani Suradi;* ***analysis and interpretation of results:*** *Afiq Zikri Zool Pakar, Rahman Hamimi Abd Hamid, Siti Samahani Suradi;* ***draft manuscript preparation:*** *Afiq Zikri Zool Pakar, Rahman Hamimi Abd Hamid, Siti Samahani Suradi. All authors reviewed the results and approved the final version of the manuscript.*

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