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Study of Banana Stem, Sugarcane Bagasse and Orange Peel as Adsorbent for Treatment of Palm Oil Mill Effluent (POME) Wastewater

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Abstract: Palm oil mills (POME) comprises a high concentration of organic compounds and residual oil, resulting in a high biological oxygen demand (BOD) and chemical oxygen demand (COD). It is dark brownish in color and has a high acidic value and total suspended solids (TSS). This happen because raw POME is a highly polluting effluent, it cannot be dumped freely and/or directly into any source of water or river without previous adequate treatment [1]. In this study, natural adsorbent is one of the alternative methods in minimizing the usage of chemical adsorbent in water treatment. Banana stem, sugarcane bagasse and orange peels as natural adsorbent help to form a low-cost adsorbent agent for adsorption process in water treatment plant and act as an important environmentally friendly product. The goals of this study are to investigate the effects of dosage of banana stem, sugarcane bagasse and orange peels as natural adsorbent and the maximum pH and the percentage removal of the turbidity and COD in the water sample. The potential of natural adsorbent in removing turbidity in wastewater are tested at a different dosage and pH by using JAR test apparatus [2]. The result shows that the adsorbent produced can remove the organic pollutants and color of POME at the dosage of 10g and 25g. Highest turbidity removal is 80% at pH 10.5 with same amount of three adsorbent and followed by highest COD removal at pH 11 with 72%. In conclusion, the integration system of conventional POME treatment with bio-adsorbents could be considered as a sustainable approach, thus solving environmental problems of waste disposal and pollution control for the oil palm industry [2].

Keywords: Palm Oil Mill Effluent (POME), Natural Adsorbent

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1. Introduction

The world population is on the approach of a water shortage, necessitating proper water resource management to meet the needs of the rapidly rising population. The primary concern now is to treat wastewater effluent discharge for safe disposal while also preserving the environment [1]. Waste generation from industrial operations is unavoidable. A considerable portion of the effluent will be treated as wastewater. For example, printed circuit board (PCB) wastewaters and electroplating wastewaters contain large amounts of heavy metals such as nickel and copper. In sewage, the organic carbon present in three quarters of the effluent contains amino acids, proteins, fats, carbohydrates, volatile acids, and more. On the other hand, the inorganic constituents, which include chlorine, magnesium, and calcium, are high. In addition to heavy metals, such as phosphate, and sulphur, the effluent of a palm oil mill also contains various soluble materials, which can be harmful to the environment due to their composition. Some of these include methane gas, sulphur dioxide, ammonia, and halogens. It has a high chemical oxygen demand and biological oxygen consumption. Without proper treatment, the contaminants in the wastewater can lead to water pollution [4].

Biological processes like an anaerobic and aerobic ponding systems are the most commonly used POME treatment methods [3]. However, inch all around because the processes rely on microorganisms to break down contaminants, these systems require proper monitoring [11]. Furthermore, using a biological strategy simply to manage POME is problematic, making compliance with the Department of Environment's regulatory discharge limit impossible (DOE) [2]. Among these, adsorption is a promising approach because it may be used to treat highly diluted effluents with high removal efficiency, allowing public health authorities to set high water quality criteria. Furthermore, the adsorption method is simple to use, and there are a variety of adsorbents accessible, including some renewable materials such as banana stem, sugarcane bagasse and orange peel [1]. These agriculture wastes are low-cost, non-hazardous, and biodegradable biomaterials that can be employed in water treatment as an adsorbent [5]. Researchers found that five orange peel coagulant doses in range of 0.2 to 1g/l were applied to wastewater and the turbidity was found to be reduced from 260NTU to 8NTU with the dosage of 0.2g, 0.4g, 0.6g, 0.8g, 1g [4] Other than that, the use of sugarcane bagasse as a bio sorbent is deemed economically viable because it is a common agricultural by-product. Sugarcane bagasse is the fibrous waste left after sugarcane stalks are crushed to obtain their juice. It contains roughly 50% cellulose, 27% polyoses, and 23% lignin. These diverse compounds, which have a lot of carboxyl functionalities, may bind organic matter cations quite strongly in aqueous solution, giving sugarcane bagasse a lot of promise as a bio sorbent [5] In addition, the use of banana stem has been studied and showed it has high removal adsorption for heavy metal (Daud et al., 2015). Natural adsorbents are generally thought to be safe for human health. The adsorption process is the most extensively utilized method and has been used to pre-treat raw water and industrial wastewater since ancient times [10]. This is owing to its adaptability and great efficacy in removing COD, turbidity, color, and metals depending on the type of absorbent used [6]. The study will be using three agriculture waste which is banana stem, sugarcane bagasse and orange peel as natural adsorbent. These three-agriculture waste will be collected at fruit factory SMI Senggarang located at Batu Pahat Johor. Every agriculture waste will be collected 5 kilogram each. The characteristic of natural adsorbent (banana stem, sugarcane bagasse, orange peel) will be investigate on Fourier-Transform Infrared Spectroscopy (FTIR) for determine the functional group of each adsorbent and Scanning Electron Microscope (SEM) to determine the porosity and surface structure of natural adsorbent. The performance of natural adsorbent will be compared depends on pH of wastewater and its dosage use in adsorption method. The process will be conducted in jar test and contact time will be recorded [5].

2. Methodology

In this study, banana stem, sugarcane bagasse, and orange peel are prepared as natural adsorbents. The sample undergo pre-treatment and preparation of activated carbon. Natural adsorbents also have been analyzed by using the mechanical testing to determine the surface morphology by using SEM and FTIR to analyze functional group of each adsorbent. The optimization study was conducted with different dosage of adsorbent and different pH of wastewater.

2.1 Pre-treatment Preparation

The banana stem (BS) sugarcane bagasse (SB) and orange peel (OP) was collected at the nearby Parit Raja Small Medium Industry (SMI premises with a weight approximately ten kilogram as waste product. Then, the adsorbent was brought back to laboratory and thoroughly washed with tap water to remove attach dust and dirt. After that, the banana stem, sugarcane bagasse and orange peel were washed with distilled water and leaved for sun dry for a week [11]. Next, the adsorbent was oven dry for 5 hours with temperature of 60°C and the weight was taken after the oven dry [12]. The banana stem, sugarcane bagasse and orange peel were kept in a thigh container. The BP, SB and OP are ready to use in the activated carbon production as starting material.

2.2 Preparation of Activated Carbon

The activation agent used in this study is phosphoric acid (H_3PO_4). About 60 gram of banana peel, sugarcane bagasse and orange peel are soaked in IL of activating chemical agent for 6 hours. This step is to ensure that the reagents are completely soaked and adsorbed into the adsorbent. The beaker contain adsorbent with phosphoric acid was covered with parafilm in order to avoid any contamination or evaporation of the chemical agent. Then, the adsorbents were dried in the oven with temperature 110°C for 24 hours [10]

After that, the adsorbent undergo carbonization in tubular furnace with temperature of 450°C 30 minutes durations. After carbonization process, Adib et al., 2018 mentions that the adsorbents are washed with warm distilled water (90°C) until the pH achieved 5.5-6.5 pH. This measure is to ensure there are no traces amounts of impurities which may trap in pores of activated carbon and eventually, will interrupt the adsorption capacity later on. The adsorbents are weighted after each steps. This is the last step where the adsorbents will turn into activated carbon [9].

During the carbonization, the small ramp level has been used to reduce the temperature gradient inside the carbonized mixture. This is because the sample need to maintain sufficient time at 450ºC temperatures to achieve optimal carbonation and to evaluate the good carbonation temperature [15]

The activated carbon will be characterized based on the pores and surface morphology by using SEM and FTIR. Lastly, the adsorbents were labelled and stored in an impenetrable container to prevent humidity contaminating the samples.

2.3 Adsorption Process Using JAR Test

A Jar Test (Figure 2.1) was carried out to perform and understand the process of adsorption. The beakers are prepared and filled with 1000 mL of wastewater. 2 mL of water samples was collected at a depth of 2 cm from the top of the beakers for turbidity analysis and 20 ml wastewater sample and dilute with factor of 50 for COD sample. pH was measured before the adsorption process. The wastewater pH was adjusted using 1M HCl or 1M NaOH until reach 6.5, 7,5, 8.5, 9.5, 10.5 and 11. The wastewater was stirred at 100 rpm for 2 min. Then, adsorbent was added and stirred again at 100 rpm for 15 min. After 15 min of mixing, the beakers are moved to a flat surface to allow the floc to settle at the bottom of the beakers. The beakers were left for 15 min.

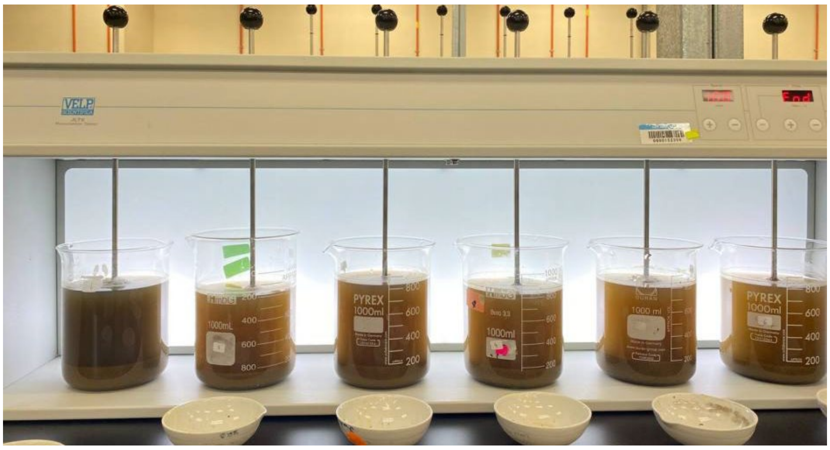

Figure 2.1: JAR Test

Other than that, after got maximum percentage removal in pH the POME wastewater is taken into six beakers with 1000 mL wastewater sample and adds varying dosages (5 to 30g) of banana stem powder, sugarcane bagasse powder and orange peel powder. Different dosage uses in this study because want to determine the efficiency of each adsorbent that has high adsorbent rate in reducing COD and turbidity for POME wastewater. Then the beaker was set into the jar test. Again, 2mL of water samples was collected at a depth of 2 cm from the top of the beakers for turbidity analysis and 20 mL wastewater sample was diluted with a factor of 50. COD before and after the adsorption process were analyzed.

3. Result and Discussion

This chapter discussed the result and analysis based on the experiment of this project that conducted at UTHM laboratory. Data analysis of this experiment included the characteristics of palm oil mill effluent wastewater which are chemical oxygen demand (COD) and Turbidity. The current studies were also carried out to evaluate the characteristics from banana stem, sugarcane bagasse and orange peel using SEM and FTIR. Finally, the result of optimization using natural adsorbent in adsorption process will be calculated based on percentage of removal.

4.1 Fourier Transform Infrared Spectrometer (FTIR)

FTIR spectroscopy was performed to analyse the surface functional groups of the samples. Figure 4.1, Figure 4.2, and Figure 4.3 show the FTIR based on the different type of adsorbent which is banana stem, sugarcane bagasse and orange peel.

Figure 4.1 indicates that the frequency for banana stem powder is 954.2 cm^{-1} which consists of bending C=C and broad peak of intermolecular H bonds. Intermolecular H bond (broad) means there are presence of hydrogen bond between two different alkene molecules and free NH bond means no NH bond found inside the sample [12]. It is certainly no NH bond inside the banana stem activated carbon because the chemical that used during the acidification phase for carbonization is using phosphoric acid

($HyPO_4$) [15] in their research said that activated carbon which consists of double bond and halogen will increase the rate adsorption of the sample or media. Besides, the frequency at peak of 2117.1 cm^{-1} at the graph show the presence of C≡C stretching vibrations conjugated and alkyne compound class [14].

Next, for the sugarcane bagasse FTIR graph was focused on Figure 4.2. At the first peak of frequency was 2340.8 cm^{-1}, the of stretching vibrations is under the carbon dioxide group class O=C=O and free NH as it indicated under the range frequency of that group [12]. Then, at the second frequency which was 957.9 cm^{-1} it indicated the presence of C=C stretching vibrations with conjugate [12]

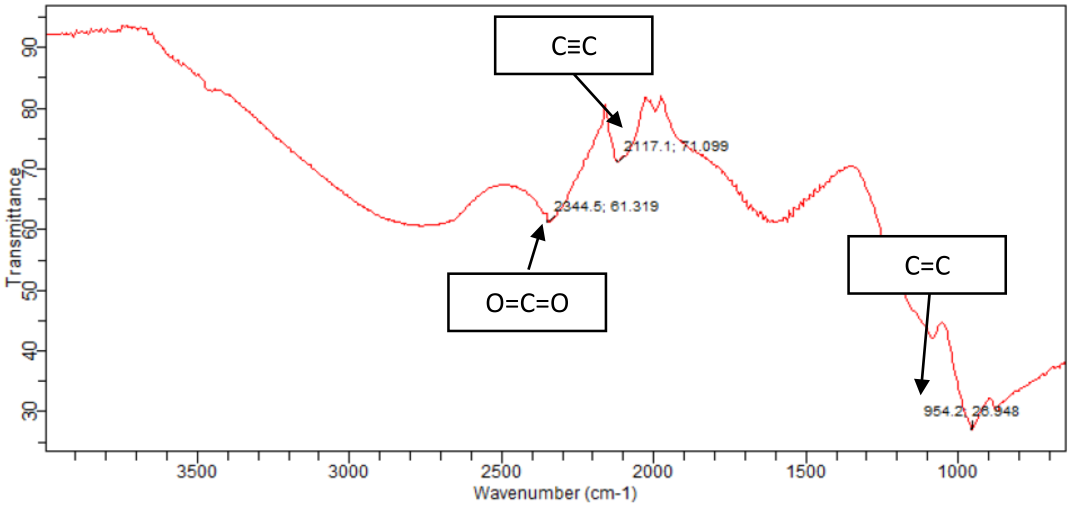

Figure 4.1 Banana stem powder

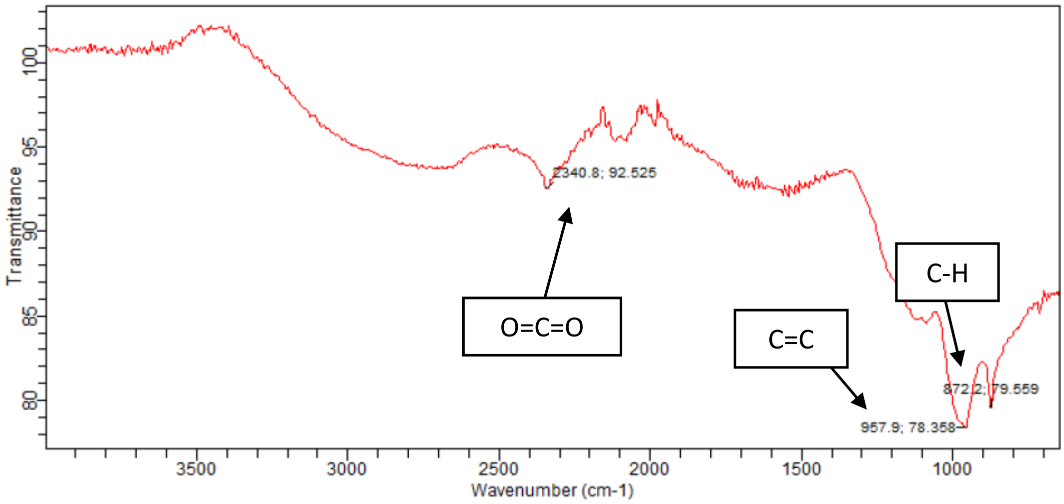

Figure 4.2 Sugarcane bagasse powder

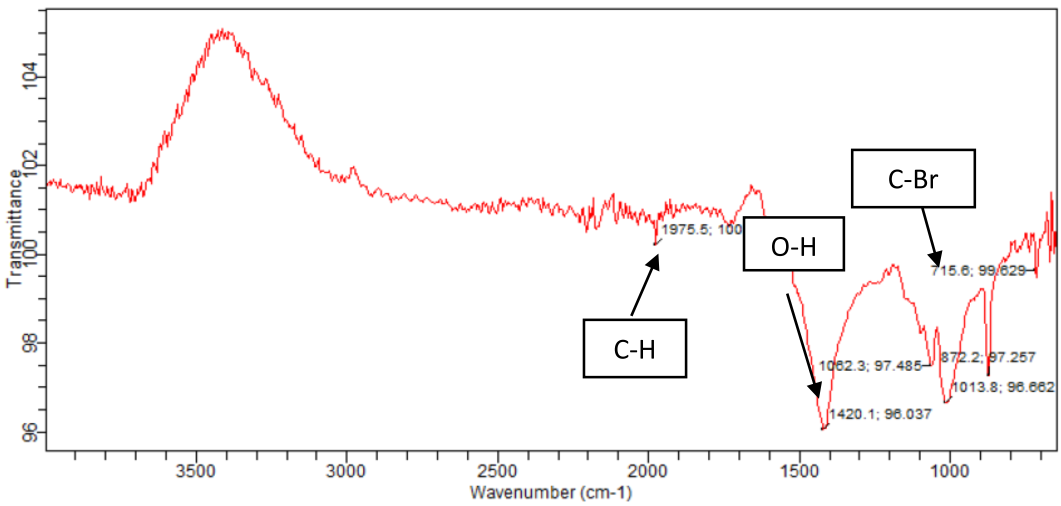

Figure 4.3 Orange peel powder

Based on Figure 4.3, it shows the FTIR graph for orange peel with two different frequencies. For the first frequency peak which was 1420.1 cm^{-1}. It indicates the frequency was under intermolecular H bonds for the O-H stretching vibrations group and free NH [12]. From the literature, O-H stretching functional group has been detected in most of activated carbons [10] and activated carbon prepared from banana peel [13]. For the second frequency, 1975.5 cm^{-1}, it can be seen that the presence of aromatic compound bending vibrations with conjugated [12]. Orange peel that typically contains more than 90% of an aromatic compound called limonene. Limonene ($C_{10}H_{16}$) comprises a 6-membered ring and two C=C double bonds which give different smells for orange peel [14]

Furthermore, Figure 4.3 shows that the first peak of the graph is in functional group of OH stretching with intermolecular H bonds (broad) with range frequency was 1420.1 cm^{-1} [12]. These range of frequency also indicated that there is free NH in the orange peel under the NH stretch functional group [12]. For the next peak of frequency, it indicated that 715.6 cm^{-1} was under functional group of C-Br. Next, represented the third peak frequency which was 872.2 cm^{-1}. This range of frequency was under the C-H, bending vibrations of functional group [12].

4.2 Scanning Electron Microscope (SEM)

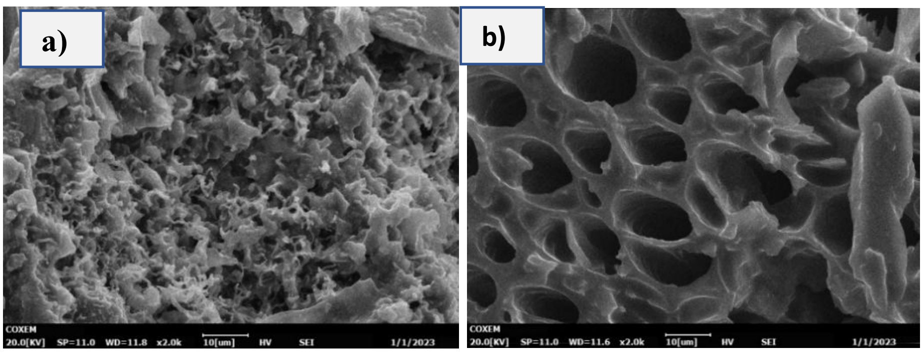

Figure 4.4: SEM Imaging of Banana Stem with x2.0k Magnification Fixed

Figures 4.5a and 4.5c demonstrated the macroporous network structure of surface of sugarcane bagasse powder [16]. Intertwined and coalescing fibers were observed obviously on the adsorbent surface [16]. Yenisoy-Karakaş et al said the fibers indicated the presence of calcium carbonate which enhanced the adsorption of organic material. There were depicted fibrous pattern of fractures on adsorbent surface owing to the crystalline structure of sugarcane bagasse particles [13]. The surface was observed to be not smooth and irregular. In addition, the blisters on the surface showed the presence of vesicular holes within the palisade layer of sugarcane bagasse for Figures 4.5b [21]. However, the fibrous structure in Figure 4.4a was not as obvious as in Figures 4.2b. In short, sugarcane bagasse proved its efficiency in organic material removal as it was made of a porous structure with numerous fibres, which undoubtedly helped in adsorption of organic material.

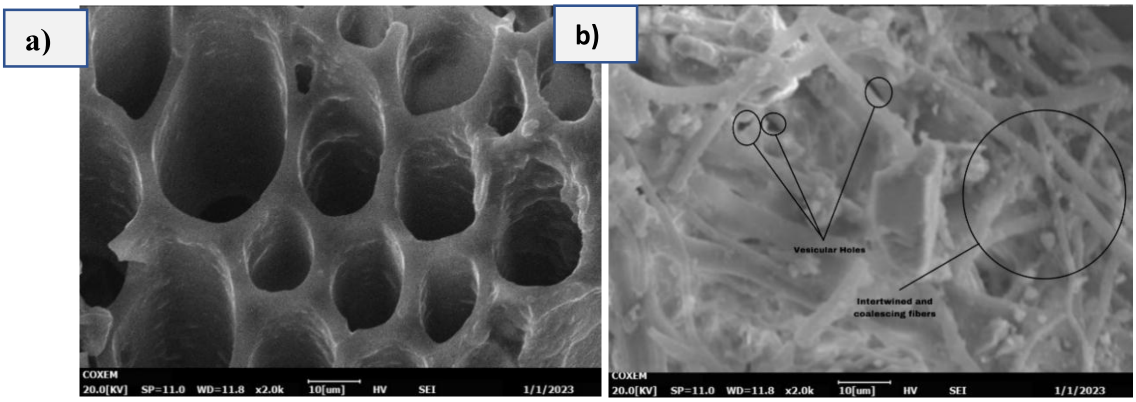

Figure 4.5 SEM Imaging of Sugarcane Bagasse with x2.0k Magnification Fixed

Figure 4.6 exhibited heterogeneous, irregular and rough surfaces similar to the banana stem. Meanwhile, Figure 4.6 illustrated the diffrent network structure of pores of the orange peel powder surface. The pore evolution occurred due to the compounds trapped inside the particles were forced to diffuse out [17]. The compound were formed by non-carbonic elements, namely oxygen and hydrogen during decomposition [18]. The porous structure presented in Figure 4.6 evidently showed that orange peel had the potential to be reused for adsorption process.

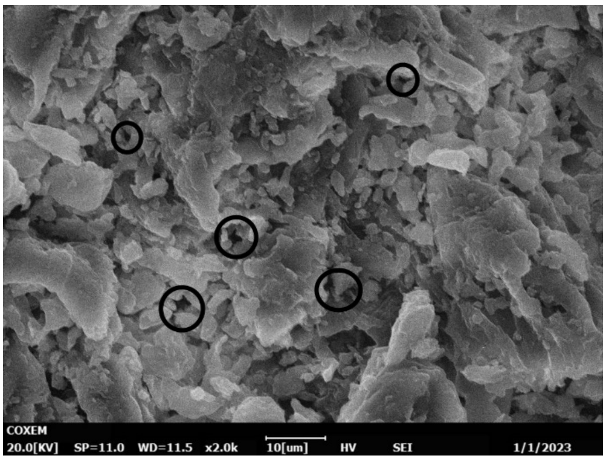

Figure 4.6 SEM Imaging of Orange Peel with x2.0k Magnification Fixed

4.3. Effect of Initial pH of Wastewater

The effect of pH was studied by varying the initial pH between 6.5, 7.5, 8.5, 9.5,10.5 and 11 different with the initial pH, which was 4.5. Ratio for three adsorbents is 1:1:1 equal to 20 grams of each adsorbent. Based on literature, the optimum pH for each adsorbent was at 6.0 for orange peel, 10.5 for sugarcane bagasse and 8.0 for banana stem [19]. At this pH, carboxylate ions were produced from amino acids contained in adsorbent powder [20]. Protons were then released to neutralize the negative charge on the colloids' surfaces. This caused them to coagulate. Based on Figure 4.8, show the effect of pH on turbidity removal.

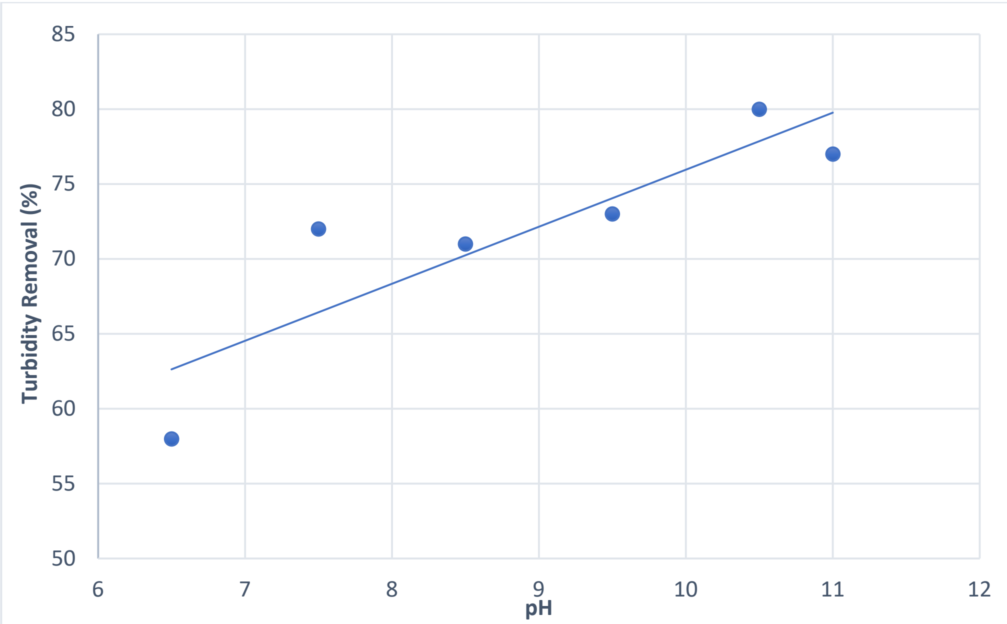

Figure 4.8: Effect of pH on Turbidity Removal.

According to this graph, turbidity removal was greater under alkaline conditions, notably at pH 10.5, whereas pH 6.5 exhibited lower adsorption activities. In the starting turbidity of 214 NTU at pH 10.5, 11, and 9.5, the maximum turbidity reduction was 80.0%, 77.0%, and 73.0%, respectively. The maximum pH for highest removal was 10.5. These findings are consistent with the discovery that higher pH values are best for each natural adsorbent derived from banana stem, sugarcane bagasse, and orange peel. Figure 4.8 also demonstrated that the proportion of turbidity reduction under acidic conditions was lower than at alkaline conditions. Turbidity removal reached 58.0% at pH 6.5, with a starting turbidity of 214 NTU. This finding is consistent with prior studies on the use of adsorbents to extract organic matter from wastewater [21]. The maximum removal of turbidity occurs because sugarcane bagasse has a high protein level of around 38.1% [24]. Protein is made up of three active groups: amino acids, carboxyl groups, and amides. Protein is amphoteric, meaning it contains both acid and basic groups. It is possible that the negatively charged active component of sugarcane bagasse might attract bivalent cations from water, create a net-like structure, and be removed from water by sweep adsorption under alkaline conditions, and vice versa [20]. As a result, organic matter can destabilization by sugarcane bagasse and give low turbidity levels [15].

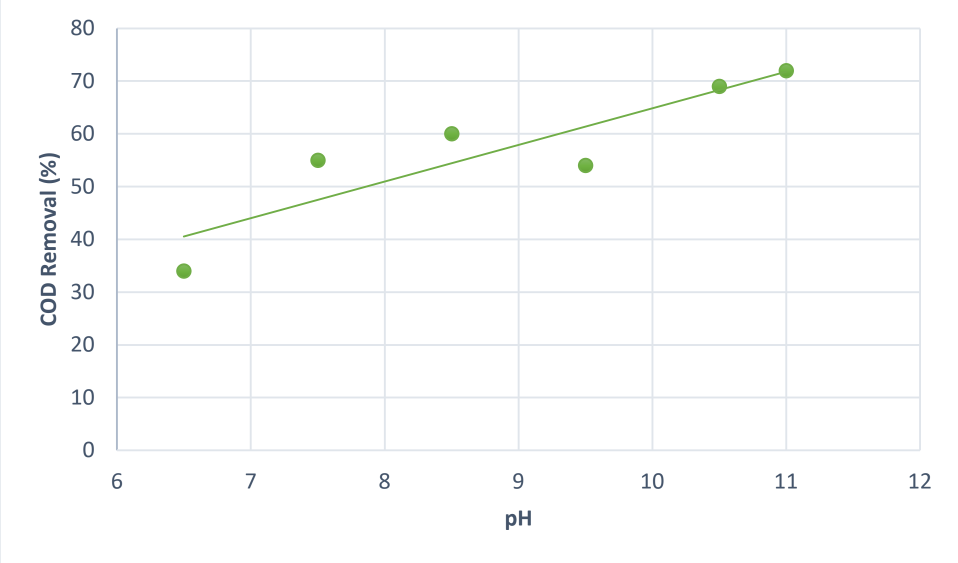

Figure 4.10: Effect of pH on COD Removal.

The influence of pH value on the amount of COD removed by entrapped activated carbon in alginate from the palm oil mill effluent wastewater was estimated by carrying out experiments with different wastewater pH (6.5, 7.5, 8.5, 9.5,10.5 and 11) with same amount of adsorbent (20 gram banana stem, 20 gram sugarcane bagasse and 20 grams orange peel), and plots of the pH against the percentage of COD removal that was removed from the wastewater are shown in Figure 4.10. The conditions used where the initial COD concentration was 1922 mg/L, the adsorbent dosage 20g for each adsorbent and the stirring rate fixed at 100rpm. Subsequently, the COD removal percentage rose steadily with pH and eventually reached maximum adsorption at pH 11. This might be due to lower concentration of hydrogen ions as pH increased. In addition, ample negatively charged ligands of sugarcane bagasse reacting with organic matter also enhanced the organic matter removal [24]. Similar results were reported in the scientific literature for the removal of COD [21]. At higher pH levels which is in alkaline condition, the removal of organic molecules significantly increased due to the electrostatic attraction between the positively charged organic molecules and the negatively charged surface of the adsorbent. On the other hand, at a lower pH level, the reduction in the adsorbent's effectiveness due to the presence of organic ion diffusion hindrances can cause the repulsion of the organic molecules [15]. This is because the plotted graph shown incline in COD removal once the pH adjusted getting higher than initial pH.

4.4 Effects of Adsorbent Dosage

One of the most important factors that can be considered when it comes to the performance of an adsorbent process is the dosage. Overdosing or not being able to properly distribute the adsorbent solution can lead to poor performance. It is also important to consider the optimal amount to minimize the sludge formation and the cost of the treatment.

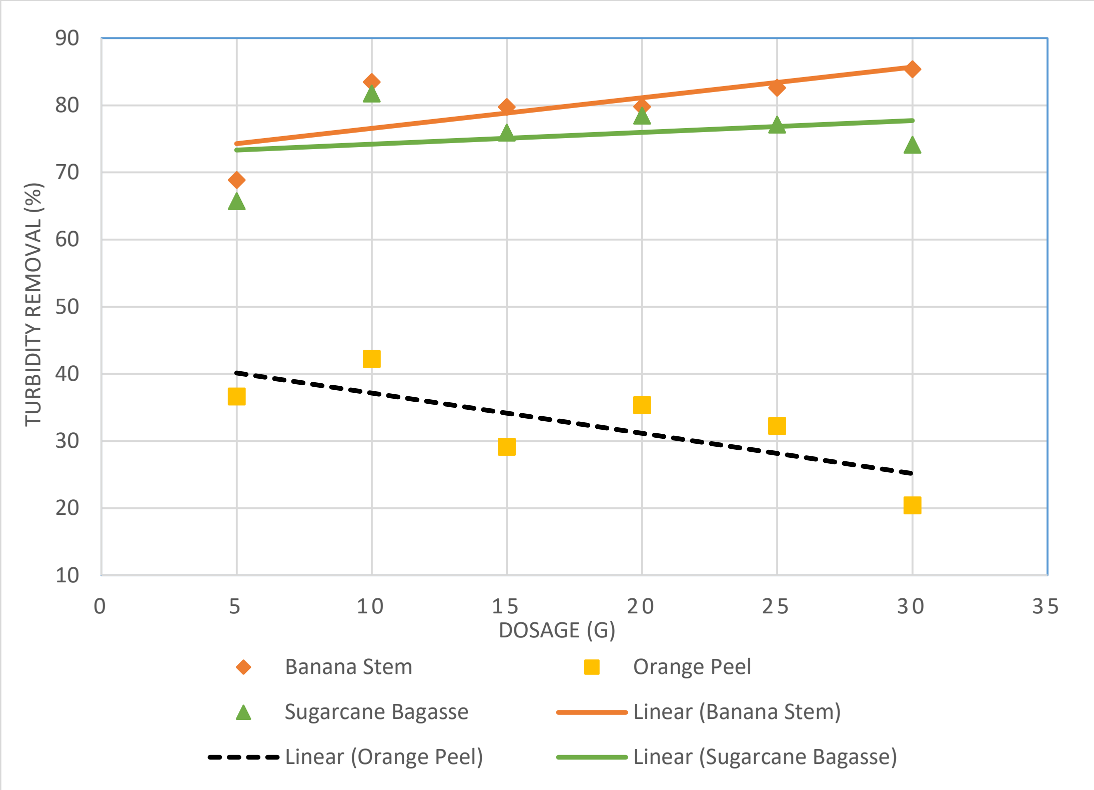

Figure 4.11: Effect of Adsorbent Dosage on Turbidity Removal.

Figure 4.11 depicts the effects of adsorbent dosages (5 - 30 gram) on sustaining pH 10.5 and initial turbidity 214 NTU. Figure 4.14 illustrated the effect of adsorbent dosage on the percentage removal of Turbidity by banana stem powder, sugarcane bagasse powder and orange peel powder. It was found that as the dosage of banana stem powder increased, the percentage removal of turbidity increased. Higher adsorbent dosage indicated higher surface area for adsorption and higher availability of binding sites for organic matter [20].

The maximum dosage adsorption using banana stem powder was 10 g because the percentage removal of turbidity declined, even though higher amount of adsorbent dosage was added. This could be elucidated as the active binding sites on the surface of banana stem powder had been completely occupied with organic matter [12]. Hence, further increasing adsorbent dosage exhibited no significant influence on the adsorption as the equilibrium state of adsorption was reached [19]. The maximum adsorption of turbidity using banana stem powder was 83.47%.

On the other hand, sugarcane bagasse powder and orange peel powder achieved 81.77% and 42.22%r removal of turbidity using 10 g of dosage. From Figure 4.11, inference was made that turbidity removal using sugarcane bagasse powder was almost independent of the adsorbent dosage due to the marginal difference of percentage removal between 74% and 78%. For orange peel powder, when the adsorbent dosage exceeded 10 g, the adsorption became lower. The decrease in adsorption performance could be correlated to the agglomeration of orange peel powder particles [20]. This resulted in lower surface area exposed for adsorption owing to larger adsorbent particle size, resulting in lower percentage removal of turbidity. The maximum percentage removal of 42.22% was achieved with 10 g of orange peel powder.

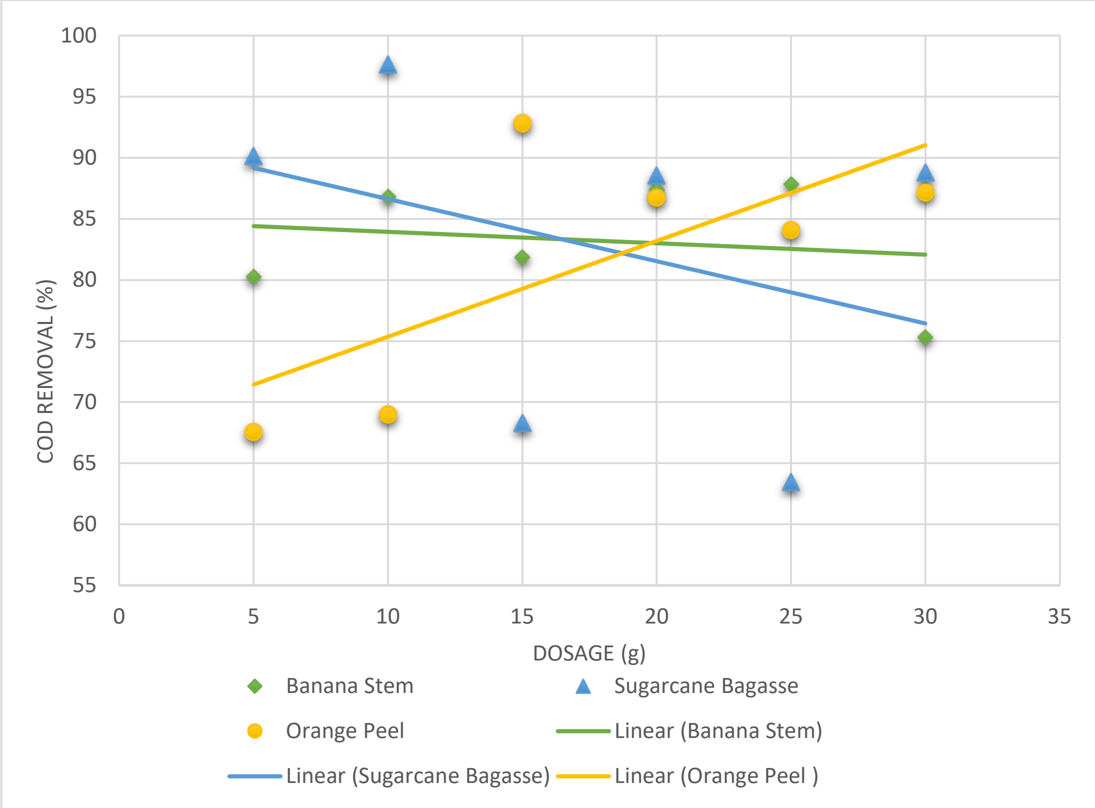

Figure 4.13: Effect of Adsorbent Dosage on COD Removal.

Figure 4.14 depicts COD removal efficiency as a function of adsorbents dosage. The adsorbent dosages ranged from 5 to 30g, while the other operating variables (pH, contact duration, starting COD concentration, and stirring rate) were 10.5, 30min, 1922 mg/L, and 100rpm, respectively. Based on Figures 4.13, it was found that highest percentage removal of COD was achieved by sugarcane bagasse powder at 97.64% and, followed by orange peel at 92.84% and the last was banana stem powder at 87.84% respectively. The increase in the dosage of adsorbent powder has led to an overabundance of active binding sites, which may not be able to adsorb organic matter. In another study, Wanasolo and Bamukyaye (2017) noted that the overlapping and aggregation of the active sites of adsorbent may cause a decline in the capacity of the process. This resulted in a low surface area and high diffusion path length. [20]. Based on Figure 4.13, a decline in adsorption capacity was observed when adsorbent dosage increased from 10 to 35 g for sugarcane bagasse powder. However, it was discovered that the adsorption capacity shown marginal difference when the adsorbent dosage increased from 15 to 35 g for banana stem powder. This showed that the aggregation impact was lower at higher adsorbent dosage as the decrease in adsorption capacity was decelerated [22].

5. Conclusion

To conclude, the potential of recycling banana stem, sugarcane bagasse and orange peel as adsorbents had been explored and they were found to be efficient in turbidity and COD removal from the POME wastewater. The morphology of recycling banana stem, sugarcane bagasse and orange peel had been characterised using SEM and FTIR. The cavities in banana stem, macroporous structure and fiber of sugarcane bagasse waste as well as porous structure of orange peel were observed. The FTIR spectrum demonstrated that carbon dioxide, alkenes and alkyne were present to enhance the adsorption of banana stem. Aromatic compound and alkene were found in sugarcane bagasse, while carboxylic acid and 1,2-disubstituted or 1,2,3-trisubstituted were found in orange peel.

Banana stem, sugarcane bagasse and orange peel had been examined for their adsorption performance under different parameters studies, namely pH and adsorbent dosage. Sugarcane bagasse was proven to be the best agriculture waste adsorbents among three agriculture waste, followed by banana stem and orange peel.

The effect of pH study showed that banana stem, sugarcane bagasse and orange peel presented different maximum removal performance at different dosage. The highest percentage removals achieved by banana stem, sugarcane bagasse and orange peel were 97.66% at dosage 10 g, 92.84% at dosage 15 g and 87.84% at dosage 25 g, respectively. It was also found that higher adsorbent dosage resulted in lower percentage removal of turbidity and COD.

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