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DEVELOPMENT OF EMPTY FRUIT BUNCH FILTER WITH ADDITION OF CHITOSAN FOR PRE-TREATMENT OF PALM OIL MILL EFFLUENT

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ABSTRACT

The separation performance of empty fruit bunch (EFB) filters with addition of chitosan on the pre-treatment of palm oil mill effluent (POME) has been investigated. Chitosan is an adsorbent which has been used widely in the wastewater treatment. A relatively EFB filters with various concentration of chitosan added and different length of fibers were prepared in order to find the most efficient filter. The performance was assessed in terms of chemical oxygen demand (COD), pH and total suspended solids (TSS) reduction. The results obtained showed that the percentage of reduction of the COD, pH and TSS increased as the concentration of chitosan increased and the length of the fibers shorter. The filter made of 6mm fibers and mixed with 4wt% of chitosan yielded the highest percentage of COD, pH and TSS reduction of 25.92%, 26.05 and 49.19% respectively.

Key Words : Chitosan, Empty Fruit Bunches, POME, Wastewater treatment

1.0 INTRODUCTION

The Malaysian palm oil industry is growing rapidly and becomes a very important agriculture-based industry, where the country today is the world's leading producer and exporter of palm oil, replacing Nigeria as the chief producer since 1971 [1]. It contributes about US$7.3b in export earning each year, mostly from the export of palm oil [2]. Aside from being one of Malaysia's highest money earning industry, palm oil production is also one of the major potential, if unabated, organic polluter of the environment producing very high strength wastes effluent. With increased cultivation and production of palm oil in the region, the disposal of the processing waste is becoming a major problem that must be appropriately addressed.

Raw POME is a colloidal suspension containing 95-96% water, 0.6-0.7% oil and 4-5% total solids including 2-4% suspended solids that are mainly consisted of debris from palm fruit mesocarp [3]. This oily waste is produced in large volumes and a number of palm oil mills conveniently discharges their effluents into the river or stream nearby in an untreated or partially treated condition as this was the cheapest method of POME disposal since POME was a non-toxic oily waste [4].

The most common practice for POME treatment nowadays is by biological processes in which based on anaerobic and aerobic ponding system. However, biological treatment systems need proper maintenance and monitoring as the processes rely solely on microorganisms to break down the pollutants. Many palm oil mills which apply the biological treatment system failed to comply with the Department of Environment (DOE)

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standard discharge limits. Therefore, the pre-treatment of POME has become an important feature in order to enhance the removal of residue oil from POME.

Chitosan, poly (D-glucosamine) a natural deacetylated marine polymer has been used in a variety of practical fields including wastewater management, pharmacology, biochemistry, and biomedical [5]. Chitosan is recognized as excellent metal ligands, forming complexes with many metal ions, thus enhance the removal of toxic metals from industrial wastewater. It has been shown to effectively remove metals such as molybdenum, arsenic, gold, cadmium, vanadium, chromium, lead, cobalt, iron, manganese, silver, copper, nickel, mercury, and zinc from aqueous solutions [6]. Apparently, no major studies have been done for pre-treatment of POME using chitosan as an adsorbent medium bind within EFB fibers.

In this study, the separation performance of EFB filters with the addition of chitosan was investigated in order to study the effects of concentration of chitosan and fibers length. A relatively EFB filters were subjected to the pre-treatment of POME and the efficiency of the filters were determined by evaluating the parameter reduction such as COD, pH and TSS.

2.0 EXPERIMENTAL

2.1 Materials

Samples of POME were collected at United Bell Palm Oil Mill, Pekan Nenas, Pontian at a temperature ranging from 70^{o}C-80^{o}C. The samples were then placed in air tight container before being transported to the laboratory. For preservation, samples were refrigerated at about 4°C in order to prevent the wastewater from undergoing biodegradation due to microbial action. A portion of the samples was analyzed for its characteristic.

Commercial chitosan was in the form of a fine off-yellowish powder. For experimental purpose, 1wt% of chitosan solution was prepared as follows: 1.0 g of chitosan powder was dissolved in 99.0 g of 10% acetic acid solution and agitated with a magnetic stirrer for 24 hours duration. Different concentrations of chitosan solution were prepared which are 1wt%, 2wt%, 3wt% and 4wt%.

2.2 Preparation of EFB Filter Media

Initially, 50 grams of grinded EFB was mixed together with 100 ml of 1wt% chitosan solution. The chitosan solution was properly mixed with the grinded EFB to ensure they are well attached. This method was then repeated with 100 ml of 2wt%, 3wt% and 4wt% chitosan solution. Randomly oriented mats were prepared, and the hand lay-up method followed by compression molding was adopted for filter fabrication. Thermal bonding was done using a High Pressure Compression Machine with heated plates. The thermal-bonding temperature was set to 150°C and thickness of the thermal-bonded nonwoven was set to 5.0 mm. The pressure applied was 135 bars. Chitosan was used as an active agent as well as a binder to the fibres. Due to the limitations of the press dimensions, the filter media obtained measured approximately 190 mm X 190 mm. Mats were cut into 90 – by 90 –mm pieces, fitted into stainless steel frames, and installed into filtration system.

2.3 Analytical Methods

The measurement is based on the light-transmitting properties of water. A gravimetric method was used to determine the TSS, with the aid of vacuum filtration apparatus. The weight of solids retained on a filter paper was determined after heating. The COD test was performed by colorimetric method using Spectrophotometer HACH. The pH meter was used for the pH measurements. The measurements of the samples pH were measured instantaneously. The calibration of the pH meter was done for each sample respectively.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of EFB Filter Media

The morphology of the EFB filters were studied using an inverted microscope equipped with a Digital Imager at a magnification level of 100. From Figure 3-A and Figure 3-B we can see that there are some differences in the structure of EFB filter modified with chitosan as compared to the unmodified EFB filter. Both types of EFB filters EFB exhibit a slight different in color; the unmodified EFB filter shows the original brown color, the EFB filter with chitosan having slightly darker brown color. Furthermore, a shining reflects could be seen by for the modified EFB filter which we could not be seen from unmodifed EFB. This phenomenon is clearly due to the addition of chitosan into the structure of the EFB.

Furthermore, Figure 4.1 shows that the structure of filter is slightly loose and having many porous clumps. However, in the Figure 4.3, it shows that the structure of the filter is more compact compared to the unmodified EFB filter which is strongly attached to each other. The addition of chitosan to the EFB filter improves the binding of the EFB fibers resulting in the production of more compact and stronger filter. The strong and compact structures are important for the adsorption process of oily wastewater.

Figure 4.6 shows the picture of EFB filter at the end of the filtration process taken by using the microscope under the magnification level of 100 times. From the figure, we can see that the black colour of oil residue was deposited on the surface of the EFB which was covered initially with chitosan. This phenomenon suggested that chitosan is one of the good natural biopolymers to exhibit a synergistic enhancement of the effective agglomeration, coagulation and adsorption of residue oil. A large amount of water is successfully passed through the chitosan due to its hydrophilic properties while residue oil are coagulated and adsorbed on its surfaces.

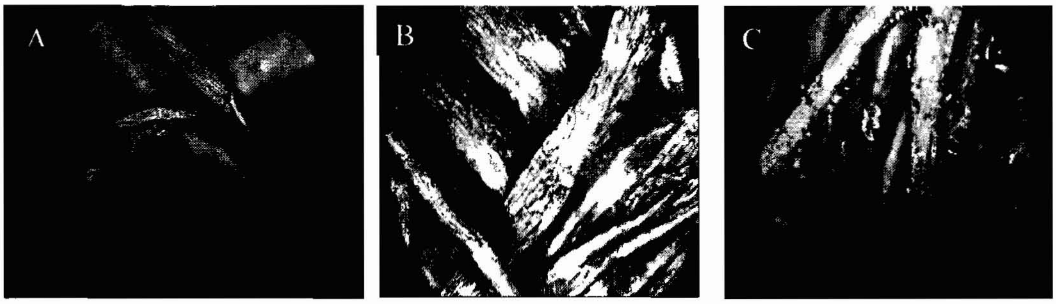

Figure 1 A: Surface of EFB Filter without Chitosan under X100 Magnifications, B: Surface of EFB Filter with Chitosan under X100, C: EFB Filter after Filtration

3.2 COD reduction

Fresh dispensed POME was treated with filters with 4 different concentration of chitosan. The initial content of COD and TSS were about ± 60,000 mg/l and ± 14,000 mg/l respectively while pH of 4.53. Figure 3 shows the effects on COD contents. It was noticed that when the concentration of chitosan increased, the percentage of COD reduction improved as well. The highest percentage of COD reduction was 25.92% with EFB filters of 4% chitosan concentration and made of 6mm fibers.

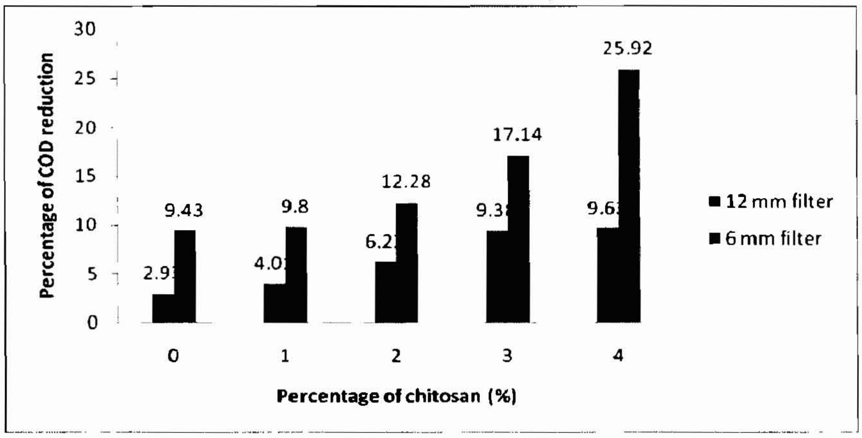

Figure 2 Comparison of COD percentage reduction between 12 mm and 6 mm filter

Chitosan has amine functional group which attracts anionic ions to bind and bridge [7]. Moreover, since the pH of POME is around 4.0-5.0, this acidic condition acts as a catalyst to enhance the reaction between the residue oil molecules and adsorption site of chitosan [3]. In terms of fibres length, 6mm filters yield higher percentage of COD reduction than 12mm filters. This is due to the larger surface area provided by the filters for the adsorption process. Large area covered by chitosan in 6mm filters enhanced the adsorption of residue oil from the POME.

However, the highest percentage of COD reduction is not very encouraging. This is because COD value is associated with the amount or strength of the organic matter in wastewater. Since POME is highly organic and its suspended solids are mainly associated with organic matter, chitosan can effectively remove most of the colloidal and suspended organic matter contents, but is less effective in removing of dissolve organic matter. The behaviour of the functional groups or the small molecular weight fraction of the dissolved organic matter might be the reasons behind the poor COD removal.

3.3 Effect of pH

As for pH, Figure 4 shows the comparison of pH reduction percentage between 12 mm and 6 mm filter. The figure clearly shows a little reduction of pH with unmodified filters. This is clearly due to the absent of chitosan in the filter that acts as not only a binding agent but also as an adsorbent. Filters without chitosan addition reduced the COD by about ±2.5%. On the contrary, filter with chitosan addition reduced the COD up to 26%. There are large different between those modified and unmodified filters. However, between those modified filters, the percentage of COD reduction varies from about ±20-

26%. This small variation may be due to the small different on the concentration of the chitosan which is only 1%.

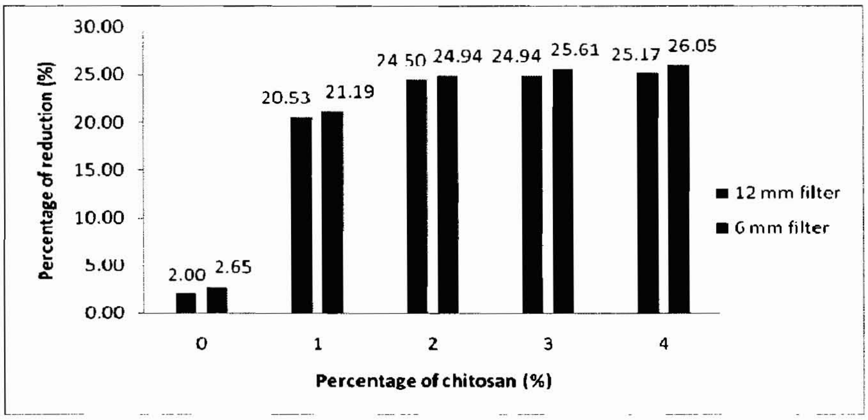

Figure 3 Comparison of pH reduction percentage between 12 mm and 6 mm filter

Anion charges contain in acidic solution react with the positive ions in the chitosan produce a less acidic mixture as both cations and anions create a pH balance in the mixture. In addition, chitosan is an amino-polysaccharide produced by the deacetylation of chitin, one of the most abundant biopolymers. The physico-chemical properties of chitosan related to the presence of amine functions (acid–base properties, solubility, cationicity) make it very efficient for binding metal cations in near neutral solutions, and for interacting with anionic solutes in acidic POME solution. This electrostatic attraction mechanism is responsible for the strong interaction existing of chitosan [8].

3.3 Total Suspended Solid Reduction

The addition of chitosan was observed to give the same trend as COD reduction in the reduction of TSS. The percentage of TSS reduction increased as the concentration of chitosan increased. Beside that, 6mm filters exhibited better TSS removal compared to 12mm filters. The highest TSS reduction is 49.19%. Figure 5 shows clearly the trend.

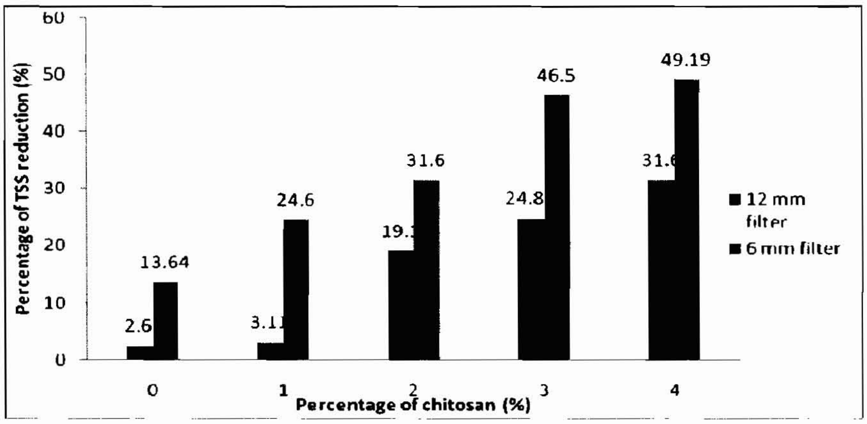

Figure 4 Comparison of TSS reduction percentage between 12 mm and 6 mm filter

The roles of chitosan as an adsorbent really placed an impact in removing the colloidal and suspended form organic matter in POME. According to Hassan et al., 2007, chitosan can effectively remove most of the colloidal and suspended organic matters. This theory supports the result shown in the graph above. The difference in percentage of TSS reduction between 12 mm filter and 6 mm filter could be resulted from the degree of porosity of the filter. Porous structure of the 12 mm filter due to the size of fiber strings which it was made of. The longer the fibers, the harder for the fibers to arrange themselves into available spaces within the matrix. Thus resulting in a filter with a loose structure and large pores size. The larger pores size filter providing wider path for the suspended solid to pass through. Therefore it reduces the efficiency of the filter.

3.2 Turbidity Removal

The effect of different percentage of chitosan in EFB fibres on turbidity removal is shown in Figure 7. The initial turbidity values for raw POME were averaged and are shown in this figure. Based on figure, turbidity value for 6 mm fibres start reduces linearly as the percentage of chitosan increase from 0% to 3%. The turbidity value started constant when the percentages of chitosan increase from 3% to 4%. This result a same 12mm fibre, the turbidity value shows the same result with 6 mm fibres. In figure 3.1 also, it obvious shows the 6 mm fibre has removed more turbidity rather than 12 mm fibres.

Generally, the turbidity decrease as the percentage of chitosan is increased for both 6mm and 12 mm fibres. This designate that the fibres filter made from EFB fibres is able to filter the suspended solid and other particle in POME. Chitosan not only acts as absorbent but also acts as intermediate to join the EFB fibres, these can be prove by seeing the first sample 0% chitosan. When there is no chitosan solution, the structure of fibres is not strong and the fibre not attach to each other. This will straightforward let the suspended solid and other particle to pass through the fibres.

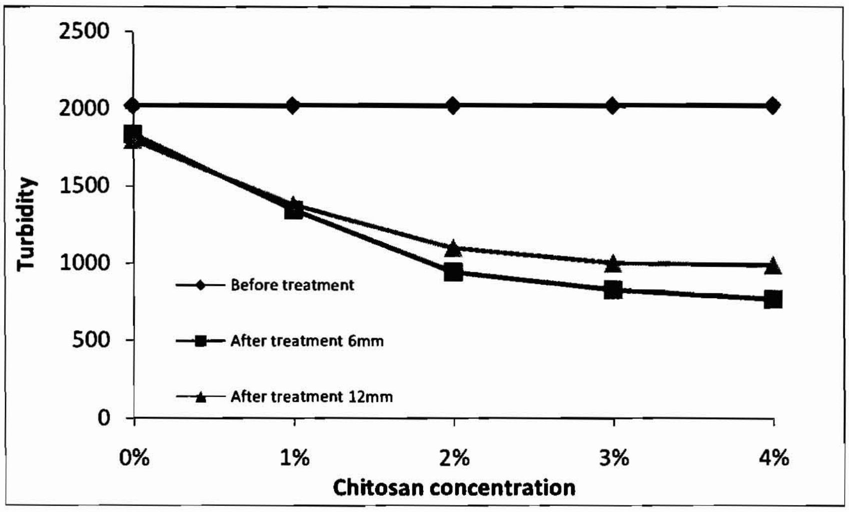

Figure 7 Effect of chitosan concentration for turbidity removal for 6mm and 12 mm fibres

3.3 Oil & Grease Removal

Based on Figure 8 the percentage oil and grease removed increase as the increases percentage of chitosan solution. In comparison to the raw POME, oil and grease were reduced by 45% after filtration using EFB filter media without chitosan .The oil sorption capacity of EFB filter without chitosan might be due to the presence of waxes on the surface, to a hollowed surface structure, and to its non-collapsed lumen. According to Gregg and Sing (1967), the sorptive capacity in a vast range of solids depends on the surface area and pores[9]. Lignocellulosic have more surface area than nonporous materials; therefore, they are a good candidates for sorption material. At the initial stage, oil is sorbed by some interaction and van der Waals force between oil and wax in the natural sorbents on the fiber surface. This sorption is due to the fact that both oil and wax are hydrocarbons and there is physical trapping of oil on the fiber surface through its irregular surface morphology. Sorption of oil within the fiber occurs by diffusion through internal capillary movement into sorbent lumens.

However, the pre-treatment of POME with chitosan-filled EFB filter obviously improved the efficiency of the filter to remove oil up to 80%. The 4% chitosan solution show the best result in removing oil and grease. The reason resulting in high removal rate of oil and grease may be governed by oil and grease being adsorbed on the surface of chitosan-filled EFB filter media by chemisorb mechanism. Chitosan a positively charged biopolymer could adsorb residual oil and destabilize the negatively charged colloid of residue oil and emulsion by charge neutralization mechanism. The physico-chemical properties of chitosan related to the presence of amine functions make it very efficient for binding metal cations in near neutral solutions, and for interacting with anionic solutes in acidic POME solution. This electrostatic attraction mechanism is responsible for the strong interaction existing of chitosan. Consequently, the cationic chitosan can easily coagulate with the anionic POME waste. This natural coagulant used has a high molecular weight, high cationic charge and large polymeric molecules. Coagulation is a well-established process in water treatment to remove suspended particles by combining small particles into larger aggregates [10, 11]

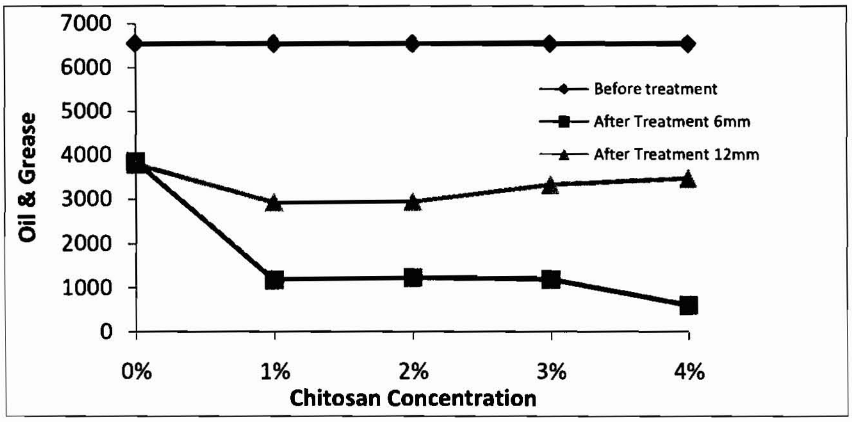

Figure 8 Effect of chitosan concentration for oil and grease removal for 6 mm and 12mm fibres

4.0 CONCLUSION

In conclusion, the addition of chitosan in the EFB filter successfully reduced the parameters which were COD, TSS, oil and grease and turbidity. Addition of chitosan reduced COD as high as 26% while TSS for 49%. From observation, the percentage of reduction become greater as the percentage of chitosan is higher. The reduction in turbidity oil and grease were up to 66 percent and 80, respectively.
The most efficient filter is the filter made of 6mm fibers with the addition of 4wt% of chitosan solution. Beside that, the length of fibres used in developing the filters also significant as the filters that made of shorter fibres show higher reduction in the parameters evaluated. This phenomenon was shown by both the unmodified filters and modified filters. Therefore, this study revealed that EFB filters with addition of chitosan can remove almost half of the colloidal and suspended organic matters in POME, but less effective in removing dissolving organic matter.

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