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LIGNOCELLULOSIC [illegible]R MEDIA FILTERS AS A POTENTIAL TECHNOLOGY FO[illegible]MARY INDUSTRIAL WASTEWATER [illegible]REATMENT

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Abstrak. By-products fr[illegible]oil mill constitute the most abundant renewable resources available in Malaysia. Amo[illegible]by-products, empty fruit bunches constitutes a significant portion of mill residues. Th[illegible]nce of oil palm empty fruit bunches has created a vital environmental issue. Thus, the use of the lignocellulosic fibers would add its economic value, help reduce the cost of waste disposal, and most importantly, provide a potential inexpensive alternative to existing pre-treatment of palm oil mill effluent. This study was carried out to investigate the potential application of empty fruit bunches as a fiber filter media to remove oil and grease, turbidity and organics in term of Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) from palm oil mill effluent treatment process. Oil palm empty fruit bunch (OPEFB) fibers were modified with chitosan solution before processed into a mat-type filter medium. Microscope images revealed surface morphology changes of the fibers due to the chemical treatment. Bench-scaled experiment results indicated that pre-treatment using the fiber filtration system removed up to 66% of turbidity, 67% of Total Suspended Solid (TSS) and 85% of oil and grease. The results show that the lignocellulosic fiber filter could be a potential technology for primary wastewater treatment.

Keywords: Dempty fruit bunches; chitosan; pre-treatment; palm oil mill effluent

Abstract. Bahan sampingan daripada industri kelapa sawit merupakan sumber terbesar yang boleh diperbaharui di Malaysia. Tandan kosong kelapa sawit merupakan sebahagian besar daripada hasil sampingan industri kelapa sawit. Penghasilan tandan kosong kelapa sawit telah mengakibatkan masalah pelupusan yang rumit. Dengan itu, penggunaan semula gentian liknosellulosik boleh menambah nilai ekonomi, mengurangkan masalah pelupusan serta berkemungkinan mampu bertindak sebagai alternatif baru untuk rawatan kumbahan air kelapa sawit. Kajian ini bertujuan untuk mengkaji penggunaan tandan kosong sebagai penapis gentian untuk rawatan minyak dan gris, kekeruhan serta BOD dan COD bagi kumbahan kelapa sawit. Tandan kosong ditambah dengan larutan chitosan sebelum diproses menjadi penapis dan morfolofi permukaan ditunjukkan dengan menggunakan gambaran mikroskopik. Eksperimen menunjukkan bahawa pra-rawatan dengan menggunakan penapis ini mampu merawat kekeruhan sebanyak 66%, pepejal terampai sebanyak 67% dan minyak dan gris sebanyak 85%. Keputusan menunjukkan bahawa gentian penapis liknosellulosik berpotensi bertindak sebagai pra-rawatan kumbahan air industri.

Kata kunci: Tandan kosong kelapa sawit; chitosan; pra-rawatan; kumbahan kelapa sawit

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1.0 INTRODUCTION

Oil palm is one of the important economic plants of Malaysia and the plantation area has been increased every year. Oil palm empty fruit bunches is one of the biomass materials, which is a by-product from the palm oil industry. Oil palm empty fruit bunches are obtained after the extraction of oil from the seeds. The fiber as available at the palm oil mill is a fibrous material of purely biological origin. It contains neither chemical nor mineral additives, and depending on sensible handling procedures at the palm oil mill, it is available without any foreign elements such as gravel, nails, wood residues, waste, etc. Many million tons of empty fruit bunches are produced annually throughout the world, as an industrial waste by the oil mills, and left unutilized. In Malaysia alone, palm oil mill industry are producing huge quantities of non-oil palm biomass of about 90×10^6 tons of lignocellulosic biomass each year, of which 40×10^6 tons are the form of empty fruit bunches (EFB), oil palm trunks (OPT) and oil palm fronds (OPF) [1]. The EFB represents about 9% of this total solid waste production [2]. This creates a good habitat for insects and pests, thereby causing severe environmental problems.

Until today, a number of utilization techniques have been developed so as to exploit in a rational way these biomass residues. These techniques include the production of fiberboard [3], pulp [4] and composites [5]. EFB also has been utilized for several purposes including agricultural activities [6] and combustible fuel for boiler [7]. However, more than 60% of EFB still remain unused. Thus, finding useful utilization of the EFB will surely alleviate environmental problems related to the disposal of oil palm wastes.

Filtration is a common process in wastewater treatment. However, the filtration efficiency usually depends on the materials used for filter. Several studies have tried to use low cost, easily available materials for removal of metal [8 – 9], dye [10] and nutrient [11] from domestic and industrial wastewater at different operating condition. Many studies have been conducted on the wastewater treatment or potable water treatment with depth filters, in which the packing material is an ensemble of fibers. Results have demonstrated that these filters are effective in removing nutrient, particulate and heavy metal species. Han *et al.* has evaluated the effectiveness of juniper filter for removing phosphorus from water. Juniper fiber were processed into a mat-type filter medium and used to restore the watershed affected by acid mine drainage. The juniper filter media were installed into a filtration system to remove the dissolved metal ions and suspended solids from water. It was found that juniper fiber has relatively high heavy metal sorption capacity, implying that it can be a natural, inorganic, and hybrid adsorbent [12]. The potential of lignocellulosic fibers to act as filters is related to their sugar, extractives, and lignin contents and physical properties [13].

Lignocellulosic material exhibit interesting capacities as pollutant adsorbents, and chemical modification of lignocellulosic materials has been shown to improve their performance. Recently, new treatment using lignocellulosic filter media and metal membrane filter was investigated for reuse gray water and rainwater in cost effective ways [14]. Chemical modification of the recycled wood fibers filter using aluminum oxide was performed to enhance the removal of phosphate and heavy metals. It appears that the fiber filter media not only reject particulate pollutants but also remove soluble ions. The fiber filter media is known to remove contaminants in rainwater through ion exchange mechanism. Cation exchange reaction occurs for metal removal and anionic exchange occurs for nitrogen and phosphate removal. Two-stage filtration, which consists of precipitation and collection on the fiber, also helps to reduce the contaminants from water.

Empty fruit bunches composed of lignocellulose material consisting of cellulose, hemicelluloses, and lignin, usually account for 65 – 70% of plant dry weight basis, which are major components of plant fibers [15]. These compositions are hydrophilic, namely rich in hydroxyl groups, which are responsible for moisture sorption through hydrogen bonding. The hydrophilic properties must be modified before being utilized for oil removal. Recently, Orawan et. al. had modified oil palm empty fruit bunch fibers by silylation agents to enhance absorbability of oil emulsified in water. Fiber modification was conducted by leaching out surface contaminants resulting in open porous surface. Results shows that the sorption of oil which was emulsified in water on fresh and silylated EFB fibers fit Temkin and Langmuir isotherms, respectively [16]. Therefore, in this context, the empty fruit bunches could be also a potential technology for removing oil and grease from wastewater effluent.

No research to our knowledge has been conducted to investigate the production of filter media from EFB for the adsorption oil and grease from wastewater effluent. The aim of this study was to investigate the possibilities of manufacturing oil-adsorbing filter materials from empty fruit bunches as a porous medium for the primary industrial wastewater treatment.

2.0 EXPERIMENTAL

2.1 Preparation of Filter Media

The lignocelluloses used in the study was empty fruit bunches. The EFB was supplied in bulk with unknown sizes by the supplier. Thus, in this study the Restsch shaker was used to separate the EFB into different sizes. The shaking time and vibration speed were set up at 10 minutes and 60 Hz, respectively. The fiber size used in this study was range of 6 – 12 mm long. The fiber was oven dried at 105 °C for 24 hours until the weight of the fiber was constant. The properties of EFB are presented in Table 1 [17].

Randomly oriented mats were prepared, and the hand lay-up method followed by compression molding was adopted for filter fabrication. The classical 'contact method' involve deposition of the fibers in a rectangular mold and its physical

Table 1 Physical and chemical characteristic of oil palm fiber

Characteristics	Compositions
Lignin	19%
Cellulose	65%
Density	0.7185
Diameter	0.015×10^{-4} – 0.06×10^{-4}
Ash content	2%

impregnation with the liquid resin. 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 × 190 mm. Mats were cut into 90 – by 90 –mm pieces, fitted into stainless steel frames, and installed into filtration system. A bench-scale unit was set up at laboratory as shown in Figure 1.

The unit consists of a feed tank, circulation pump, receiver tank and filter cell. The EFB filter is tightly sandwiched between two stainless plates using nuts and bolts in the filter cell.

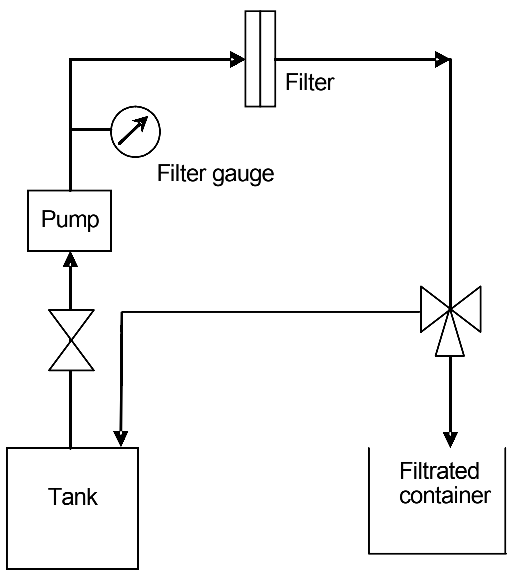

Figure 1 Schematic diagram of the filtration system

2.2 Characterization of Filter Media

In order to observe the changes in microstructure of empty fruit bunch fiber, microscope images of filter media were taken before and after filtration.

2.3 Sorption-filtration Experiment

These studied were done with the objective of evaluating the sorption capacity and the filtration of palm oil mill effluent through a filter composed of the empty fruit bunches. The raw POME samples were collected from the Kilang Sawit United Bell, in Pekan Nenas.

100 ml of raw POME was passed through the filter held in stainless steel plates. After a single pass of the total volume through the filter, an aliquot of the filtrate was taken for determination of its parameters. The tests were performed in batches of 1000 ml. The characteristic of the raw and treated POME, such as pH, color, oil and grease (O&G), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total suspended solid (TSS) and turbidity were determined according to the Standard Methods for the Examination of Water and Wastewater[18] and DR/2100 Spectrophotometer Procedures Manual.

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Lignocellulosic Filter Media

In order to better understand the adsorption and filtration mechanisms of filter media, scanning electron micrographs of the filter used in this study have been taken before and after filtration.

Figure 2(a) shows that EFB filter is randomly laid, forming a 3-dimensional network structure with multilayer perpendicular to the water flow. The fiber has different diameters in the range from 1 to 15 micron and the pore size has a wide range distribution. This kind of structure provides both physical barrier and great adsorbing capacity due to its large surface area, resulting in high capture efficiency for suspended solids. Figure 2(b) shows EFB filter media having slightly shining dark brown color due to the addition of chitosan into the structure of the filter media. 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. Figure 2(c) shows the photograph of the EFB fiber after sorption-filtration process. It can be seen that the large particles are physically blocked by the fibers around the small pores in the fiber network, forming filter cake, and that small particles are attached to the surface of the fiber, being captured inside of the fiber network. Figure 2(d) is the photograph of the chitosan-filled EFB after sorption-filtration process. Compared with the EFB fiber, there are more particles adsorbed on the surface of the chitosan-filled EFB fiber after filtration.

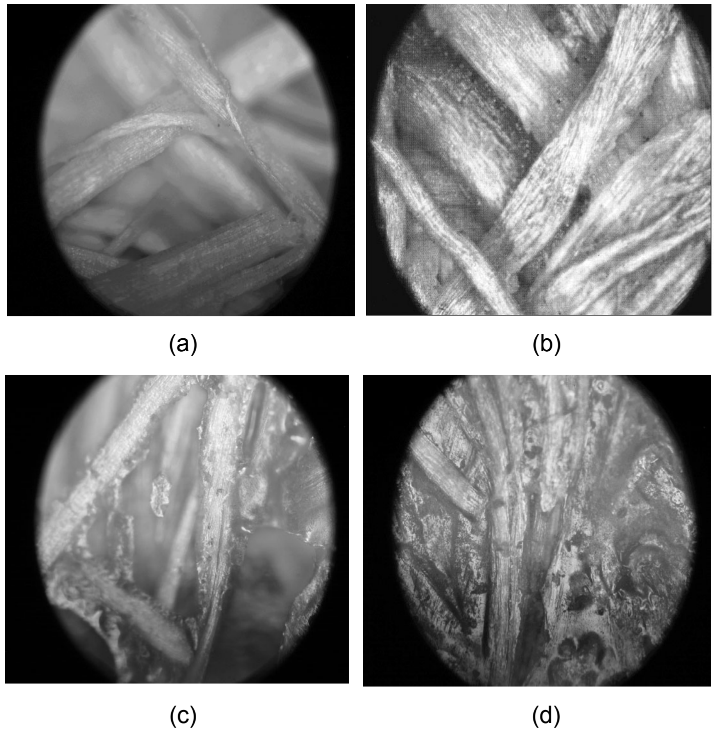

Figure 2 Microscope images of lignocellulosic filter media (a) EFB filter before filtration(100×), (b) Chitosan-filled EFB filter before filtration(×100), (c) EFB filter after filtration (×100), (d) Chitosan-filled EFB filter after filtration (×100)

3.2 Sorption-filtration Results

These studies were done with the objective of evaluating the sorption capacity and the filtration of palm oil mill effluent through a filter composed of empty fruit bunch fibres. Table 2 lists the parameters of the samples before and after filtration of 1000 mL palm oil mill effluent. The raw POME sample that collected from Pekan Nenas, Pontian were the mixed effluent from sterilizer condensate, clarification sludge and hydrocyclone discharged. From the range of the data obtained the raw POME samples

Table 2 Comparison of the parameters before and after sorption-filtration

Parameters	Raw POME	EFB Filter	Chitosan-filled EFB Filter
pH	4.5 – 5.2	5.4 – 5.8	6.0 – 6.4
O&G	6000 – 8000	3850	1050
BOD5	10000 – 15000	9960	7560
COD	48000 – 60000	46800	38480
TSS	13000 – 23000	8850	4950
Turbidity	11613	7150	3740

has slightly different compared to the reported typical quality of POME. This POME had higher strength than typical. However, the detected maximum and minimum concentrations do not vary too much.

In Figure 4 the treatment efficiency of two filter media are compared. In comparison to the raw POME, oil and grease, suspended solid and turbidity were reduced by 45%, 47% and 35%, respectively after filtration using EFB filter media. The oil sorption capacity of EFB filter might be due to the presence of waxes on the surface, to a hollowed surface structure, and to its non-collapsed lumen.

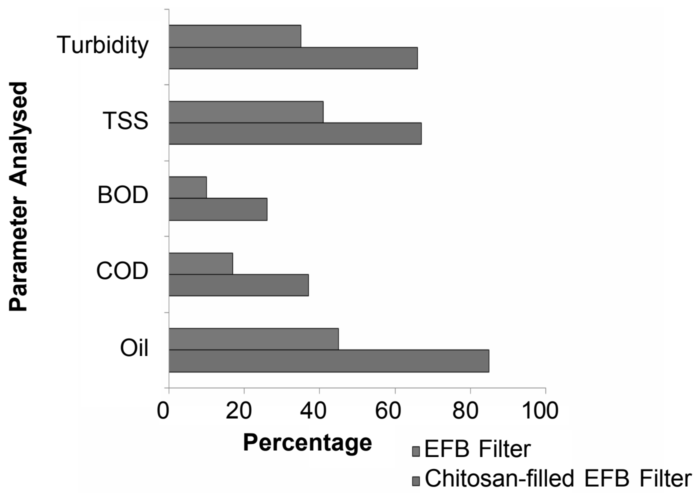

Figure 4 Treatment efficiency of sorption-filtration with EFB filter and chitosan-filled EFB filter media

According to Gregg and Sing (1967), the sorptive capacity in a vast range of solids depends on the surface area and pores [19]. 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 85%, suspended solids to 67% and turbidity to 66%. 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 [20 – 21]

4.0 CONCLUSION

Empty fruit bunches are a natural, inexpensive, and environmental friendly material available in enormous quantities thrown away after palm oil processing in palm oil mill. Due to the 3-dimensional network structure with multilayer, wide ranged pore size distribution, and large specific surface area, empty fruit bunches filter were successfully used as the filter to remove suspended solid and some organics compound from industrial effluent. Filter media produced was able to reduce oil and grease up to 85 percent. The reduction in turbidity and suspended solid were up to 66 percent and 67, respectively. However, BOD and COD of the POME only showed 37 percent and 26 percent reduction, respectively.

The use of natural waste materials for the removal of pollutants from effluents prior to their treatment could decrease the cost of the operation and upgrade the quality of the treated effluents. Because of their low-cost, these materials can be profitably used as alternatives or complements to the more commonly used methods for effluent treatment. Further research is warranted in the application of empty fruit bunches for sorption in order to define the factors contributing to sorption, and to investigate the potential for modification of the surface chemistry to increase sorption capacity.

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REFERENCES

[1] MPOB (Malaysian Palm Oil Board). 2003. Latest Development and Commercialization of Oil Palm Biomass, in *In MPOB-FMM Seminar on Business Opportunity in Oil Palm Biomass*. Selangor: Malaysia.

[2] Alam, M. Z., S. A. Muyibi and N. Kamaldin. 2008. Production of Activated Carbon from Oil Palm Empty Fruit Bunches for Removal of Zinc, in *Twelfth International Water Technology Conference, IWTC12 2008*. Alexandria: Egypt.

[3] Ramli, R., S. Shaler, and M. A. Jamaludin. 2002. Properties of Medium Density Fibreboard from Oil Palm Empty Fruit Bunch Fibre. *Journal of Oil Palm Research*. 14(2): 7.

[4] Chen, S. L., S. Wang and L. A. Lucia. 2004. New Insights into the Fundamental Nature of Lignocellulosic Fiber Surface Charge. *Journal of Colloid and Interface Science*. 275(2): 392-397.

[5] Rozman, H. D., K. R. Ahmadhilmi and A. Abubakar. 2004. Polyurethane (PU) – Oil Palm Empty Fruit Bunch (EFB) Composites: The Effect of EFBG Reinforcement in Mat Form and Isocyanate Treatment on the Mechanical Properties. *Polymer Testing*. 23(5): 559-565.

[6] Chiew, L. K. and Z. A. Rahman. 2002. The Effects Oil Palm Empty Fruit Bunches on Oil Palm Nutrition and Yield, and Soil Chemical Properties. *Journal of Oil Palm Research*. 14(2): 1-9.

[7] Yin, C. Y., *et al*., 2008. An Investigation into Physicochemical Characteristics of Ash Produced from Combustion of Oil Palm Biomass Wastein a Boiler. *Fuel Processing* Technology. 89(7): 693-696.

[8] Abia, A. A., and E. D. Asuquo. 2007. Kinetics of Cd2+ and Cr3+ Sorption from Aqueous Solutions using Mercaptoacetic Acid Modified and Unmodified Oil Palm Fruit Fibre(Elaeis guineensis) Adsorbents. *Tsinghua Science & Technology*. 12(4): 485-492.

[9] Lee, B. G. and R. M. Rowell. 2004. Removal of Heavy Metal Ions from Aqueous Solutions using Lignocellulosic Fibers. *Journal of Natural Fibers*. 1(1).

[10] Shukla, S. R. and R. S. Pai. 2005. Adsorption of Cu(II), Ni(II) and Zn(II) on Modified Jute Fibres. *Bioresource Technology*. 96(13): 1430-1438.

[11] Karageorgiou, K., M. Paschalis and G. N. Anastassakis. 2007. Removal of Phosphate Species from Solution by Adsorption onto Calcite used as Natural Adsorbent. *Journal of Hazardous Materials*. 139(3): 447-452.

[12] Han, J. S., S. H. Min and Y. K. Kim. 2005. Removal of Phosphorus using AMD-treated Lignocellulosic Material. *Forest Products Journal*. 55(11): 48-53.

[13] Han, J. S. 1999. Stormwater Filtration of Toxic Heavy Metal Ions using Lignocellulosic Materials Selection Process, Fiberization, Chemical Modification, and Mat Formation. in *2nd Inter-Regional Conference on Rnvironment-Water 99*.

[14] Kim, R. H., *et al*., 2007. Reuse of Greywater and Rainwater using Fiber Filter Media and Metal Membrane. *Desalination*. 202(1-3): 326-332.

[15] Han, J. S. and J. S. Rowell, Chemical Composition of Fiber. 1997: Lewis Publishers.

[16] Rattanawong, O., *et al*., 2007. Sorption of Oil Emulsified in Water on Oil Palm Fibers. *Korean Journal Chemical Engineering*. 24(1): 67-71.

[17] Sreekala, M. S. and S. Thomas. 2003. Effect of Fibre Surface Modification on Water-sorption Characteristics of Oil Palm Fibres. *Composites Science and Technology*. 63(6): 861-869.

[18] APHA, AWWA, and WPCF, Standard Methods for the Examination of Water and Wastewater 21 ed. 1998.

[19] Gregg, S. J. and K. S. W. Sing. 1967. Adsorption, Surface Area, and Porosity. Academic Press: London.

[20] Ahmad, A. L., S. Sumathi and B. H. Hameed. 2006. Coagulation of Residue Oil and Suspended Solid in Palm Oil Mill Effluent by Chitosan, Alum and PAC. *Chemical Engineering Journal*, 2006. 118(1-2): 99-105.

[21] Ahmad, A. L., S. Sumathi and B. H. Hameed. 2005. Adsorption of Residue Oil from Palm Oil Mill Effluent using Powder and Flake Chitosan: Equilibrium and Kinetic Studies. *Water Research*. 39(12): 2483-2494.